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Dislocation Dynamics During Thin Film Deposition

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Ph.D.

THE HONG KONG
POLYTECHNIC UNIVERSITY
2003
Abstract of thesis entitled:

Dislocation Dynamics During Thin Film Deposition

Submitted by LIU Wing Chung, Averil
For the degree of Doctor of Philosophy
At The Hong Kong Polytechnic University in December 2002

The nucleation of dislocations and their subsequent propagation during thin film deposition are studied. Aiming to reveal the generic mechanisms, the case of tungsten on a substrate of the same material is investigated. Three-dimensional (3D) molecular dynamics (MD) method is used. The substrate is under either uni-axial compression or tension along the [111] direction, with the thermodynamically favoured (011) surface being horizontal. Studies are carried out when the strain (either tensile or compressive) is applied along either [111] or [211] direction.

In this thesis, we first focus on the kinetic processes of newly deposited adatoms on the film substrate. These serve as the guidelines of designing our MD simulations. Then, we focus on the growth mechanisms of deposited film under stressed substrate. In particular, we focus on the mechanisms of dislocation nucleation and propagation. These mechanisms affect or dictate the microstructure evolution processes of thin films, and thereby their performance.

In the first part of my study, diffusion of adatoms on the tungsten (011) surface is investigated using the MD method. The formation energy of each defect cluster, consisting of a few adatoms, is calculated using a combination of annealing and quenching techniques. Diffusion mechanisms of clusters are elucidated by the analysis of atomic trajectories, and are confirmed by calculating energy states along the diffusion path and by fitting the diffusion coefficients to one or more Arrhenius functions. Our dynamic results show that a W adatom diffuses much slower, with diffusion coefficient $1.3 \times 10^{-3} e^{-0.54eV/kT} \text{cm}^2/\text{s}$. The W dimmer and trimmer are probably the critical nucleus in three-dimensional growth.

Then, we simulate the nucleation and propagation of dislocations during deposition of tungsten thin films on an uni-axially and bi-axially stressed tungsten substrate. This mimics the dislocation dynamics processes in a polycrystalline thin film, in which one grain is surrounded and thereby strained by its neighbors. At the
same time, this simulated condition resembles that of heteroepitaxy, except that chemical effects are absent.

Our results show that a dislocation nucleates near a surface step/groove through the ejection/insertion of an atom from a surface layer. Following the ejection / insertion, atoms on the surface layer relax along one of the $<111>$ directions to take up / fill in the extra space of the resulting vacancy. When the relaxed space is small, glissile dislocations are formed. They propagate by gliding along one of the $<111>$ directions and align on the plane with the largest Schmid factor. The obtained Burgers vectors align on the glide plane with the largest shear stress. Therefore, movement of atoms along the slip direction, which results in the nucleation dislocation half loop, is attributed to the large resolved shear stress. However, when the relaxed space is large, a sessile dislocation half loop is formed by climbing. In this case, the Burgers vectors align in one of the $<111>$ directions on the surface $(0\bar{1}1)$ plane. This results in the formation of a sessile dislocation half loop.

Finally, the effect of surface steps on the nucleation of dislocations is investigated. Samples of thin films of critical thickness are annealed under the uniaxial stressing conditions, with surface steps along various directions. The results confirm that the dislocation nucleation during thin film deposition is dictated by the surface steps. Further, propagation is found to be aided by the presence of surface steps, but is possible beyond the stepped region.
ACKNOWLEDGEMENTS

The work described in this thesis was partially supported by a grant from the Research Grants Council of the Hong Kong Special Administrative Region (PolyU 1/99C, 5146/99E), and substantially by grants from the Hong Kong PolyU (G-V698).

The author would like to express her sincere gratitude to her chief supervisor, Professor C.H. Woo, for his invaluable advice, guidance and encouragement throughout this research. Thanks also go to her co-supervisor, Dr. Hanchen Huang, for his effort in introducing me to the field of thin film deposition and molecular dynamics simulation.
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CHAPTER ONE - INTRODUCTION

Thin films are widely used in many modern industries. For example:

- Interconnects in the integrated circuits or electronics industry in general;
- Hard coating for mechanical properties;
- Chemically inert coating for corrosion resistance in power industry.

As a result, the fabrication of thin films has been a focus of study for decades. Initially, films are deposited by trial and error, with a minimum understanding of the physics of the film or the deposition process. This resulted in a slow evolution of the thin-film technology. Throughout the last 20 years, much research has been done to understand the growth and microstructure of thin films, as well as the interplay between microstructure and the deposition process. In selecting an appropriate deposition technology for a specific application, the major consideration is its physical, chemical, and morphological properties. Physical and chemical properties such as electronic, magnetic, mechanical, optical, thermal and chemical reactivity mostly depend on the materials' characteristics, while morphological properties depend on the structural evolution of the film.

One of the challenges of the thin-film technology is the inadequate understanding of the deposition process, to explain how a certain film acquires the properties it has, and, more importantly, to predict how certain aspects of the deposition process would result in certain properties of the film. Efforts to meet the challenge result in the development of a wide range of modeling techniques to describe the film deposition process, based on various mathematical principles and physical laws governing the system.

A modeling exercise can sometimes be described as a ‘virtual experiment’ that is predictive as well as explanatory. Along this direction, new technologies, new sample geometries, and chemical effects can be simulated and predicted, speeding up both the product development cycle, and avoiding the commitment of substantial resources to experimentation.
1.1 Applications of Thin films

Thin films are deposited onto a substrate (by physical vapor or chemical vapor deposition) to achieve one or more of its optical, magnetic, chemical, mechanical and electrical properties \(^1\). There are two key factors for the properties of the finished film: (1) its material characteristics (in terms of physical and chemical parameters given in Table 1-1); and (2) its structure. It is well known that in many instances the characteristics of a thin film can be quite different from its bulk properties, due to the large surface-area to bulk-volume ratio. In addition, physical and chemical characteristics of the thin film can also be quite different from those of bulk material. Thin-film characteristics are dramatically influenced by the structure developed in the proximity of the surface and interface of the substrate, due to surface nucleation effects, surface mobility, surface topography, crystallographic orientation, stress effects due to thermal expansion mismatch, and so on. Details of the film structure developed are given in the following Chapters.

Thin films are used for many different purposes. For optical applications, thin films are used as reflective coatings, interference filters, decoration, memory discs (CDs), wave-guides, and so on. Usually, optical coatings are applied for anti-reflection purposes. These coatings require dielectric materials with precise indices of refraction and absorption coefficients. Laser optics requires metal reflective coatings that can withstand high radiation intensities without degradation. Infrared reflecting coatings are applied to filament lamps for operation under high temperature, to increase the luminous flux intensity. There is also increasing commercial use for optical data storage devices in compact discs and computer memory applications. Processes for the deposition of organic polymer materials as storage media and as protective overcoats are required for this technology.

In magnetic applications, thin films are used for memory discs for data storage. Thin films of magnetic materials have found wide commercial applications for data storage in computers and control systems. Thin films are deposited on the metal, glass or plastic polymeric materials. Processes for the deposition of magnetic materials and for materials with high degree of hardness are required. In such applications, the magnetic, mechanical, and morphological properties of the films should be considered.

For chemical applications, thin films are used as diffusion or alloying barriers, for protection against oxidation or corrosion, and as gas/liquid sensors. Corrosion results from a direct electrical contact between the metal and the electrolyte. The
metal atoms of a component change from the metallic state into an oxidized state. The driving force of this process is the tendency of the system to lower its free energy. To avoid the chemical or electrochemical reaction between a material and its environment that produces a deterioration of the material and its properties, good corrosion protection requires: a coating material with high corrosion resistance, a pore-free structure, good adhesion, and non-conducting. The major consideration in selecting a process is the chemical, electrical, and morphological properties of resulting thin films.

For mechanical applications, thin films are used as tri-biological (wear-resistant) coatings to improve hardness, for adhesion, and in micro-machines. Thin-film coatings of carbides, silicides, nitrides, and borides are finding increased uses for improving the wear characteristics of metal surface, as well as improving its hardness. For example, titanium nitride (TiN) coatings on cuttings tools offer hardness, low friction, and a chemical barrier to alloying of the tool with the workpiece. It achieves surface properties unattainable in a bulk material, since the bulk material must also offer high strength and toughness in the cutting tool application. Diamond-like carbon films are of current interest because of their heat dissipation capability, electrical insulation, hardness, and resistance to high-temperature and high-energy radiation. In selecting an appropriate deposition technology for a specific application, the major consideration is its mechanical and morphological properties. Here again, mechanical properties mostly depend on the materials’ characteristics, while morphological properties depend on the structure developed in the film.

For thermal applications, thin films are used as barrier layers to heat sinks. Thermal barrier coatings are applied to metallic components of advanced heat engines to reduce the metal temperature, and to increase the environmental resistance and service life of the components. In some cases, it reduces noxious exhaust emissions. This thin coating usually consists of a metallic bond coat applied to the metal component, followed by a layer of magnesia-stabilized or yttria-stabilized zirconia. As it is expected to survive the thermal shock of fast cyclic heating and cooling without spoliation (as experienced in gas turbine or diesel engines), thermal, mechanical, and morphological properties are considered in selecting an appropriate deposition technology. Thermal and mechanical properties mostly depend on the materials’ characteristics, while morphological properties depend on the structure developed with the film.
For electrical and electronic applications, thin films are used for insulation and conduction, in semiconductor devices, very large-scale integrated circuits and piezoelectric drivers. The fabrication of electronic components, especially solid-state devices and microelectronic integrated circuits, undoubtedly represents the widest and most demanding range of applications for thin-film depositions. These films typically consist of semiconductor materials, dielectric and insulation materials, and metal or refractory metal silicide conductors. By depositing multiple layers of different materials, additional functionality in thin films can be achieved. Alternating layers are made using nanometer-thick semiconducting materials such as GaAs and (AlGa)As, resulting in a superlattice that has electrical properties governed by the constructed periodicity rather than by the atomic periodicity. Thus, multi-layer thin films can behave as completely new, engineered materials unknown in bulk form. When multiple layering is combined with lithographic patterning in the plane of the films, microstructures of endless variety can be constructed. This becomes the basic structure of the integrated circuit. However, they are also used as electronic displays for interfacing electronic equipment with human operators, such as liquid-crystal displays, light-emitting diodes, electroluminescent displays, plasma and fluorescent displays, and electrochromic displays. The fabrication of these displays requires conductive films, transparent and conductive films, luminescent or fluorescent films as well as dielectric and insulating layers. Appropriate deposition technology for a specific application depends on its specific electrical and morphological properties. Electrical properties mostly depend on the materials' characteristics, and morphological properties depend on the structure developed in the film.

Multi-properties are sometimes needed in thin-film application. For example, Cr coatings used on plastic parts for automobiles impart hardness (mechanical properties requirement), metallic luster and protection against ultraviolet light (optical properties requirement). Obviously, thin-film technology pays an important role in the development of nanotechnology.
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<td></td>
<td>dispersion</td>
</tr>
<tr>
<td>Magnetic</td>
<td>Saturation flux density, coercive force, permeability</td>
</tr>
<tr>
<td>Chemical</td>
<td>Composition, impurities, reactivity with substrate and ambient,</td>
</tr>
<tr>
<td></td>
<td>thermodynamic stability, etch rate, corrosion and erosion resistance,</td>
</tr>
<tr>
<td></td>
<td>toxicity, impurity barrier or gettering effectiveness, stability, and so</td>
</tr>
<tr>
<td></td>
<td>on.</td>
</tr>
<tr>
<td>Mechanical</td>
<td>Stress (intrinsic, residual, composite), anisotropy, adhesion,</td>
</tr>
<tr>
<td></td>
<td>hardness, density, fracture, ductility, hardness, elasticity</td>
</tr>
<tr>
<td>Electrical</td>
<td>Conductivity for conductive films, resistivity for resistive films,</td>
</tr>
<tr>
<td></td>
<td>dielectric constant, dielectric strength, dielectric loss, stability under</td>
</tr>
<tr>
<td></td>
<td>bias, polarization permittivity, electromigration, radiation hardness</td>
</tr>
<tr>
<td>Thermal</td>
<td>Coefficient of expansion, thermal conductivity, temperature variation of</td>
</tr>
<tr>
<td></td>
<td>all properties, stability or drift of characteristics, thermal fusion</td>
</tr>
<tr>
<td></td>
<td>temperature</td>
</tr>
<tr>
<td>Morphology</td>
<td>Crystalline or amorphous, structural defect density, conformality /</td>
</tr>
<tr>
<td></td>
<td>step coverage, planarity, microstructure, surface topography,</td>
</tr>
<tr>
<td></td>
<td>crystallite orientation</td>
</tr>
</tbody>
</table>

Table 1-1 Major physical and chemical parameters of thin film to be considered [2].
1.2 Growth of Thin films and Its Structure

It should be noted in the foregoing section that the structure-dependent film morphology is an important consideration in all applications because of its close relationship to the macroscopic properties of the materials. On the micro-scale, the structure of grain boundaries dictates the strength. On a larger scale extending over many grains, the structure has an effect on more complex phenomena, such as surface contact or optical properties. For coatings, the structure-property relationships are further complicated by the fact that coating microstructures are generally highly anisotropic and contain concentrations of defects that can vary from grain to grain. The characterization of the microstructure is important in understanding the properties and behavior of coatings in many applications.

Good process control during film growth is needed to ensure that films are produced with the correct microstructure and the desired properties for application. Phase composition, size and shape of grains, size and distribution of porosity, defects, presence of cracks and pin holes, anisotropy, stress and strain are all important microstructural factors governing the properties of the film. Thus, microstructural units, such as columnar grains, can be moved away from their equilibrium positions due to the mismatch of properties with the substrate. Stresses can lead to bending of the film, distortion of microstructural units, and generation of defects within microstructural units where they contact. For example, dislocation loops are created by compressive stresses forcing columnar grains together in PVD films. The evolution of microstructure during physical vapor deposition is further discussed in Chapter 1.2.

The structure of a film is determined as much by the nucleation process as by the subsequent growth process. Solid material is distributed in an array of fairly closely packed columns that run perpendicular to the substrate. It is this structural anisotropy that controls many of the properties of the film. The surface structure of the substrate is critically important, including the grain size, defect density, texture, roughness, and surface composition. In order to optimize the structure of the deposited film, careful control of growth at the early stages is important.

In general, films of the same material can be obtained using several different deposition processes. However, the structure of the film produced may be very different, and may have different properties. Considerable attention should be paid to
the microstructure of the film if the difference in performance characteristics is to be understood.

Knowledge of the relationships between the structure and properties of a film has been mostly empirical, and efforts to predict thin-film properties based on microstructure via modeling are still in their infancy. In order to control and optimize the microstructure of the film for a given application, structure characterization is a necessary first step.

In the foregoing, we have seen that the characteristics of thin films of the same materials can be quite different from each other due to the difference in the microstructure. Therefore, attention should be paid to controlling the microstructure of the film during the deposition process. In the case of the physical vapor deposited (PVD) film, this means that both the film formation process and the responsible mechanism should be understood. The factors that directly affect the resulting structure of the film have been reviewed by Donald M. Mattox \[3\], and are briefly described in the following.

Before the production of a film, the material(s) for the substrate and the film should be selected according to the desired properties, as given in section 1.1. Then, the PVD process to be used (e.g. vacuum deposition, sputter deposition, ion plating etc.) and the fabrication parameters for the process should be set. Two main factors determine the final properties of the film, namely, the material of the film and substrate, and the microstructure. The latter involves three processes: (1) the condensation and nucleation of the adatoms on the surfaces, (2) the nucleation of deposited film on the surface, and (3) the growth of deposited film \[4-8\]. In this thesis, we will focus on the control of these three factors.

1.2.1 Condensation of Deposited Adatoms and Film Nucleation

Film growth results from the condensation of atoms on the surface. When an atom reaches the surface of the substrate, it will either be reflected from the surface, re-evaporate, or condense on the surface. Only the condensed atoms will contribute to the film growth. In this section, we consider surface mobility, film nucleation on the substrate surface, and nucleation density.

The mobility of an adatom on a surface depends on a number of factors, including (1) the energy of the adatom, (2) the adatom-surface interaction (crystallography), and (3) the temperature of the surface. To increase the mobility of
adatom on a surface, we can directly increase the energy of the adatom or the surface temperature of the substrate. The adatom-surface interaction depends on the bonding between the surface atoms and the adatoms. Therefore, different crystallographic planes of the surface have different surface free energies corresponding to different surface diffusion behavior of adatoms. For example, for the same face center cubic material, the surface free energy of a (111) surface is smaller than that of the (100) surface. Therefore, the surface mobility of an adatom on the (111) surface is generally higher than that on the (100) surface. An investigation of surface diffusion and the mechanism involved is reported in this thesis (Chapter 4) as part of my study by molecular dynamic simulation of two surfaces with different structures --- the (011) surface of b.c.c. Tungsten, and the (0001) surface of h.c.p. Titanium.

For condensation to occur on a surface, diffusing adatoms have to lose their energies, which can be accomplished via surface reaction, finding preferential nucleation sites, collision, or by being deposited on an unstable surface.

For the surface reaction processes, atom-to-atom chemical bonds, which can be metallic, covalent or van der Waals in nature, are formed when the condensed atoms react with the surface. If the bonding is strong (higher binding energy), the surface mobility is reduced, as energy has to be expended to break the bonds (see Chapter 4).

At preferential sites, generally stronger bonds formed when the diffusing adatoms get there. In general, lattice defects on the surfaces such as point defects or grain boundaries, foreign atoms in the surface, charge sites in insulator surfaces, and surface areas that have a different chemistry or crystallographic orientation provide the conditions for the formation of preferential sites. In particular, morphological surface discontinuities such as steps can act as preferential nucleation sites. Effects of surface steps on the nucleation of dislocations during film growth under stress are investigated in Chapter 5.

Collision of mobile surface adatoms with other adatoms and/or surface clusters generally leads to agglomeration and the loss of mobility of the surface clusters or surface species, which then becomes stable nuclei for condensation. The density of the nuclei (island) depends on the mobility of the adatoms, as well as the deposition rate through the lifetime of the surface adatoms before annihilation at an island.
To summarize this sub-section, when adatoms deposit on an unstable surface, they may interact with the surface lattice resulting in atomic rearrangement \[9\].

1.2.2 \textit{Nucleus Growth and Interface Formation}

Surface energy exists because molecules of a condensed phase are attracted to each other, which is what causes the condensation. A film nucleus is formed by condensation of adatoms on the substrate surface. Three types of nucleation mechanisms have been identified, according to the nature of interaction between the deposited atoms and the substrate materials: (1) the Frank-Van der Merwe mechanism leading to a monolayer-by-monolayer growth; (2) the Volmer-Weber (V-W) mechanism leading to three-dimensional nucleation and growth; and (3) the Stranski-Krastanov (S-K) mechanism leading to an altered surface layer formed due to the reaction with the deposited material \[10\]. These three mechanisms are described in the following paragraphs.

Nucleation behavior is strongly influenced by the surface energy per unit area, $\gamma$. In order to decide which of the three mechanisms are responsible for the nucleation event, we first consider the energies of the film free surface ($\gamma_f$), the substrate free surface ($\gamma_s$), and the substrate-film interface ($\gamma_i$). We assume that nucleation is not kinetically limited, but is reaction-controlled, and can thus approach equilibrium, i.e. there is sufficient time for surface diffusion so that the adatoms can rearrange themselves to minimize the surface energy $\gamma$. Figure 1-1a shows the Frank-Van der Merwe mechanism. In this case, $\gamma_f + \gamma_i < \gamma_s$, the film spreads across or wets the substrate. The total energy is lower for the wetted substrate than for the bare one. A smooth growth, atomic layer by layer occurs. To sustain this mechanism, there must be a sufficiently strong bonding between film and substrate. Otherwise, if the bonding between the film and the substrate is not strong enough, ($\gamma_f + \gamma_i > \gamma_s$), the film does not wet the substrate because the spreading of the film across the substrate would increase total surface energy $\gamma_f$. In this case, three-dimensional (3D) islands form via the Volmer-Weber growth mode (as shown in figure 1-1b). Figure 1-1c shows the Stranski-Krastanov (S-K) growth mode. In this case, the growth mode changes from layer to island after the growth of one or two monolayers. This is due to the change of the surface energy balance condition with the growth of successive monolayers. This mode is associated with epitaxial growth of the film.
By collecting mobile adatoms at the edges of the island, a nucleus grows in size. Following one or more of the three growth modes described in the foregoing, isolated film nuclei can grow laterally or vertically on the surface to form a continuous film\textsuperscript{[11]}. The ‘wetting growth’ is the growth of the nuclei laterally over the substrate surface. And the ‘de-wetting growth’ is the growth of the nuclei vertically over the substrate surface.

![Diagram](image)

Figure 1-1. Film growth modes: (a) Frank-Van der Merwe, (b) Volmer-Weber, and (c) Stranske-Krastanov

A strong interaction between the adatoms and the substrate produces a strong correlation between the crystallographic orientations of the deposited material and the substrate, resulting in a preferential crystallographic orientation in the nuclei when it condenses and grows. This type of growth is called epitaxial growth. Lattice mismatch between the condense nuclei and the substrate at the interface can be accommodated by elastic strain initially when the film is thin. As growth proceeds to beyond a critical thickness, growth will have to be accommodated by the formation of a misfit dislocation network. Thus, a single-crystal epitaxial film can be grown. In this
thesis, epitaxial growth is the main growth mechanism considered. For more results, please refer to Chapter 5.

If the deposited film material is different from the substrate, an interface is formed. Atoms inside the interface diffuse and react with each other. They can be classified into five types (figure 1-2a to 1-2e) [12].

Figure 1-2 Five types of interfaces: (a) abrupt interface, (b) mechanical interface, (c) diffusion interface, (d) compound interface, and (e) pseudo-diffusion interface.
Figure 1-2a shows the formation of an abrupt interface. There is an abrupt change from the film material to the substrate material. The nucleation density is low in this type of interface growth. Formation of interfacial voids along the interface may occur. Usually, an abrupt interface forms at low deposition temperature when there is no bulk diffusion, and chemical reaction between the deposited atoms and the substrate is weak, or solubility between film and substrate materials is low.

Figure 1-2b shows a mechanical interlocking abrupt interface, which is an abrupt interface on a rough surface. The formation mechanism is the same as the abrupt interface, but the deposited material filled in the rough surface and forms mechanical interlocking.

The diffusion interface involves a gradual change or gradation in composition across the interfacial region, without the formation of a compound. When there is a mutual solid solubility between the film material and the substrate material, a high temperature during deposition, and sufficient time for diffusion between deposited atoms and substrate atoms, diffusion interface formed. This type of interface is often found in metallic systems with high solubility materials. Figure 1-2c shows the structure of diffusion interface.

A compound interface forms when a chemical reaction among the diffusing atoms occurs in the interface between the deposited film and the substrate. As new phase(s) form in the interface, the change of volume produces high stress in the interface layers, which can be released by the formation of micro-cracks in the interfacial region, as shown in figure 1-2d. Therefore, the structure formed with compound interface is usually brittle.

By grading the deposition from the substrate to the deposited material, a pseudo-diffusion interface is formed. Its mechanism is similar to diffusion interface, but no compound interface forms between deposited materials and substrate. Pseudo-diffusion usually forms when both the deposited material and substrate are insoluble materials, and deposition proceeds at a low temperature so that the phases do not segregate. Figure 1-2e shows the interface structure of a pseudo-diffusion interface.

The interface formed between the film and the substrate usually influences the performance of the film, such as its strength. To simplify our investigation, atoms are deposited on a substrate of the same element, so as to ensure the absence of chemical reactions between the film and the substrate. We can then concentrate on the microstructure development process of the film.
1.2.3 Structure Formation during Film Growth

After the condensation of the adatoms into nuclei on the surface, film growth proceeds. During this stage, the microstructure, morphology, and properties of the film may be influenced by mass transportation, recrystallization and grain growth. Most of these processes are time and temperature dependent.

At the beginning of deposition, film growth is strongly influenced by the structure of the substrate. The continuous condensation of adatoms on the surface causes the film to thicken, and subsequently a particular growth mode is established. Generally, as the film grows, surface roughness develops due to the difference in growth speeds between certain features or crystallographic planes. The growth processes can be described by the structure zone model (SZM), which directly determines many film properties. A summary of the structure of SZM, based on the published literature of Movchan-Demchishin, Thornton, Messier et. Al, Grovenor et. Al, and Barna-Adamik, is given in the next subsections.

Movchan and Demchishin first applied the SZM on vacuum-deposited coatings in 1969[13]. Then, Thornton extended this model to sputter deposited films in 1977[14]. In 1984, Meissier modified this model again[15]. Grovenor incorporated the specific preparation conditions in the same year[16]. Then, Barna and Adamik studied the effect of impurity content for the structure developed in the four zones[17].

1.2.4 Structure Zone Model and Microstructure Control

SZM is developed by classifying the film morphology. Accordingly, film structure can be divided according to four temperature zones: zone 1 (Z1), zone T (ZT), zone 2 (Z2) and zone 3 (Z3).

In zone 1 (Z1), no bulk diffusion exists and surface diffusion is very limited. It is in the temperature range of less than 0.2 melting point ($T_m$) of the deposited material, which is insufficient for the effect of geometrical shadowing to be overcome by surface features. Columns, typically tens of nm in diameter separated by voids a few nm across, are developed with different shapes. For example, round columns developed for aluminum, and platelets for beryllium. Open boundaries between columns are formed. A film with a high surface area forms with a ‘mossy’ appearance. The columns are not single grains. Sometimes, they can be microns in size, and the grain size can be less than 100 nm. Sometimes, they can be amorphous within a column.
Zone T (ZT) is considered to be a transition from Z1 to Z2. The temperature range for deposition is around $0.2 \ T_m - 0.3 \ T_m$. Surface diffusion increases, but is still too low to be significant. Competitive growth of the primary crystals of random orientation is induced. The competitive growth results in the development of an inhomogeneous morphology and crystals orientation across the film thickness. Small primary crystals of random orientation exist at the substrate surface. When the film thickness increases, crystals with higher growth rate develop into cone-shaped grains as a result of texture competition. ZT is usually associated with energy-enhanced processes.

As deposition temperature increases and is larger than $0.3 \ T_m$, zone 2 (Z2) developed. The growth process is dominated by adatom surface diffusion. The evolution of morphology and texture is controlled by re-structuring. The film is composed of single-crystalline columns with increasing diameter at increasing temperatures. Densification of the inter-columnar boundaries can occur. But the basic columnar morphology remains. The grain size increases and the surface features tend to be faceted.

In zone 3 (Z3), bulk diffusion occurs due to further increases of deposition temperature ($>0.5 \ T_m$). Recrystallization, grain growth and densification are possible. Generally, highly modified columnar morphology can be found with single crystals columns. The film surfaces are often smoother. However, the grain boundaries can develop grooves.

In the above four zones, temperature dominates the structure. At a low deposition temperature, thermal migration of the adsorbed material is negligible. Z1 and ZT films formed as a result of quenched growth processes. When temperature increases so that surface diffusion becomes significant, Z2 and Z3 films form as a result of thermally activated rearrangement on the film. However, the question remains as to how the development of the film structure can be controlled.

From the foregoing, control of the microstructure developed in the film can be accomplished by controlling the deposition temperature, condensation energy release, deposition rate, deposition time, thermal conductivity of the film and substrate materials, heat removal mechanisms, and so on. Some of those factors that directly influence the growth microstructure of the film are given in the following paragraphs.

Increasing deposition temperature increases the surface mobility of the adatom. Therefore, the growth mode of the deposited film is changed, which will directly
change the film morphology. Periodic reaction with ambient species generates a new surface chemistry on the surface of the growing film. Adatoms are forced to re-nucleate on the 'new' surface and the film morphology is changed. For example, the columnar growth morphology can be suppressed by the periodic injection of oxygen during aluminum deposition \[^{18}\]. Angle of incidence of the adatoms is important for texture competition during film growth \[^{19}\]. Periodic mechanical brushing of a surface during deposition can eliminate porosity in film surface, especially when the surface mobility is low. Energy is released by physical collisions when massive energetic particles bombard a surface. These collisions can heat the surface and increase the surface mobility of adatoms. They can also generate point defects that act as nucleation sites for the mobile adatoms. Thus, the columnar morphology of the growing film can be modified.

At this point, we have considered the film formation and growth process and the associated physical mechanisms. We have also considered the growth related factors that affect the film properties. Computer-modeling systems for film growth, as well as theoretical and experimental investigations of epitaxy film will be reviewed in Chapter 2.
1.3 Objectives of the Study

As described in Chapter 1.1, thin films are employed in a wide range of engineering applications. The two governing factors of the properties of the finished film are the material characteristics, and the structure of the finished film. The characteristics of a thin film can be quite different from the bulk material properties. It is because thin films have a large-surface area to bulk-volume ratio. In addition, physical and chemical characteristics of the thin film can also be quite different from those of the bulk materials. As indicated above, thin-film characteristics are dramatically influenced by the structure developed. For example, the density of the film affects its mechanical deformation and electrical resistivity. Porosity of the film effects its corrosion and etch rates. Surface area and morphology of the film influence its contaminant adsorption, optical reflectivity, and electrical resistivity. These are all due to the microstructure developed inside the film.

At the same time during film formation, stresses may develop in response to the changing inter-granular compatibility requirements. The development of such stresses is expected to affect the microstructure development of the film, such as texture formation. There has not been sufficient information on such effects in the literature.

Tungsten is one of those refractory metals that are used in fabricating semiconductor devices, due to its low resistivity and good thermal and electrochemical stability. For example, figure 1-3 shows the structure of an IC chip. Polycrystalline aluminum thin films in the form of metal lines are good interconnections of transistors in integrated circuits, while tungsten thin films are used for plugs.

It is well known that grain boundaries and dislocations are open paths of fast diffusion, which is responsible for the electromigration failure \[20\]. The fast diffusion can be reduced or eliminated if the microstructure, in particular the texture, in the thin films is well controlled. This necessitates the understanding of the evolution of grains and the dynamics of dislocations.

Computer-simulated growth of physical vapor deposited thin films is studied in this thesis. Tungsten film is deposited on its stressed substrate. The applied stresses can be compression or tension in both of uni-axial or bi-axial directions. Two major reasons for studying this system are as follows:
(1) In the electronics industry, grain boundaries and dislocations inside the polycrystalline structure are open paths of fast diffusion, which is responsible for failure due to electromigration. The dangling bonds present at the dislocations and grain boundaries of the polycrystalline material, acting as traps and recombination centers for the charge carriers, degraded the performance of the semiconductor. Therefore, a long-standing goal is the growth of single-crystalline semi-conductors as well as its interconnections on inexpensive substrates. Take MOSFET as an example. At low level of integration, the performance of the MOSFET determines all of the circuit speed, packing density and yield, but at high-level integration, the role played by the distributed wiring becomes dominant. As a side effect, more time is required to charge the inter-connection capacitance, and time delay increases as the circuit density increases. To improve the performance of IC chips, much effort was expended over the last two decades to study the texturing of growth structures of semi-conductors for isolation layers and conduction wire for interconnections (such as Aluminum and Tungsten), both experimentally and theoretically.

(2) During the deposition process of thin films, when film crystals align with the bonds of the substrate surface, epitaxy occurs. Many factors govern the resulting film texture. The interfacial energy that depends on the misfit between the film and the substrate will affect the growth texture of the film, even for the homoeptaxy cases in which surface energy anisotropy or adatom mobility produce some of the thermodynamic forces that drive the orientation of the nuclei into a texture. In most of the cases, the thin film will experience stresses sufficiently large enough to generate dislocations inside the deposited film.

For the above reasons, deposition of tungsten thin films under stresses is investigated by the molecular dynamic method in my study. This necessitates the understanding of the evolution of grains and the dynamics of dislocations.
Figure 1-3 Structure of an IC chips. Polycrystalline aluminum thin films in the form of metal lines are good interconnections of transistors in integrated circuits, while tungsten thin films are used for plugs.
CHAPTER TWO – HISTORY OF INVESTIGATION

In the initial stages of growth of an epitaxial film, the deposited layers are commonly strained according to specific crystallographic relationships with respect to the substrate. When the deposited layers grow on the surface of a substrate with small lattice parameter misfits, the first several atomic layers deposited will be strained to match the substrate to form a coherent interface. Strain energy is stored inside the coherent interface, which increases with film thickness. At some critical thickness, it becomes energetically favorable to relieve this misfit strain by introducing misfit dislocations, when the energy reduction due to the strain energy relaxation is sufficient to balance the energy increase when the coherency of the interface is destroyed by the generation of the dislocations. For half a century, much research effort, both experimental and theoretical, has been expended to understand the growth and microstructure development associated with this phenomenon. They are described in the following paragraphs.

2.1 Theoretical Models of Epitaxial Growth

The main theoretical models for epitaxial growth are still being used today, except in some cases with some modifications. In the following sections, a brief account of the most important ones will be given.

2.1.1 Bragg and Nye’s Dynamic Model

As early as 1947, Bragg and Nye built a dynamic model to study epitaxial growth of metallic crystals [41]. They assumed that the misfit is accommodated by the elastic strain and showed the generation of misfit dislocations in an interface by using soap bubbles. In their experiment, crystal structures such as grain boundaries, dislocations, and other types of fault, slip, recrystallization, annealing, and strains due to foreign atoms were observed. At that time, the real structure of an epitaxial layer had never been seen due to the limitation of the microscope.

2.1.2 Frank and van der Merwe’s Energy Minimization Model

Two years later, Frank and van der Merwe first studied the analytical formulation of dislocations in epitaxial thin films by their energy minimization model
They predicted the dislocation system using isotropic elastic analysis. Using a Lennard-Jones potential, the critical condition of dislocation nucleation and activation energy was calculated. In their theory, a simple model of one-dimensional springs on a periodically modulated substrate was used. The two competing factors were the strain energy of thin films due to the film-substrate mismatching, and the extra energy associated with the strain field of dislocations. A dislocation was nucleated when this leads to the reduction of the total energy. For a given film substrate system, this critical condition translates into a critical thickness of the thin film, at which the strain energy due to film-substrate mismatching was sufficiently large that total energy reduction can be achieved with the generation of a dislocation. The formulation was based on energy minimization among possible configurations of the thin films. However, the equations derived above were for one-dimensional springs model only.

In 1962, Merwe modified their formulations by introducing the concept of ‘critical thickness’ in epitaxy thin film in three-dimensions [24-25]. A more realistic calculation of the interfacial energy between a crystalline film and a crystalline substrate of a different material for the simple case was presented. He considered the minimum energy configuration of a system, in which a flat film was grown on an infinitely thick substrate. Only the lattice parameters which differed in one direction was considered in this calculation.

2.1.3 Matthews’ Studies of Peierls Stress

Almost during the same period, misfit dislocations became observable experimentally for the first time [26-27]. After much experimental work, Matthews and his co-workers showed that the disagreement between experiment and van der Merwe’s theory maybe due to the large Peierls stress [26,28-31]. Matthews started to consider a theory for misfit accommodation including the effect of Peierls stress, which is not considered by earlier theories [32]. It is because in materials with the diamond or sphalerite structures, the Peierls barrier inhibits glide. He was also the first to examine the influence of the dislocation nucleation mechanism on the critical thickness. This equation is reduced to that he derived before, if the Peierls stress is ignored [33-34]. This was the first time the effect of the Peierls stress, temperature and anneal time on the accommodation of misfit between one crystal and another was evaluated.
It was experimentally observed that misfit dislocations in semiconductors glide from a free surface into the interface or junction region \[^{35-38}\]. There are two types of gliding dislocations, namely, those coming from the bowing of threading dislocation, and those from enplaning of half-loop dislocations. The mechanism of bowing of threading dislocations is shown in figure 2-1. Figure 2-1a shows the initial stage of a grown-in dislocation line that extends from crystal B through the interface into crystal A. Figure 2-1b shows the bowing of this dislocation under the influence of the misfit strain. Finally in figure 2-1c, a length of misfit dislocation line formed from the bowing dislocation. The growth of half-loops and generation of misfit dislocation lines are shown in figure 2-2. The difficult part of this process is the nucleation of a half-loop large enough to grow under the influence of the misfit strain. Nucleation of dislocation loops and half-loops has been considered by Frank, Hirth, and Nabarro \[^{39-41}\]. Their results suggested that, in the absence of features that can raise the local stresses above the average value, the nucleation of stable half-loops is difficult, unless the misfit strain is very large. However, in the presence of local stress concentrations, dislocation nucleation can occur even when the misfit strain is small. Dislocation loops or half-loops nucleated in regions of high local stress may then grow under the misfit stress to generate dislocation lines as shown in figure 2-2c \[^{42-43}\].

Figure 2-1 Mechanism for the formation of a misfit dislocation line (threading dislocation) in a deposit of semiconductor (A) on another (B). (a) the initial stage of a grown-in dislocation line that extends from crystal B through the interface into crystal A, (b) the bowing of this dislocation under the influence of the misfit strain, and (c) a length of misfit dislocation line formed from the bowing dislocation.
Figure 2-2 Expansion of a dislocation half-loop to form a length of misfit dislocation line: (a) a subcritical dislocation half-loop (b) a half-loop which is stable under the influence of misfit stress (c) a loop which has grown to generate a length of misfit dislocation line.

Consider the total energy of the system, consisting of the following four components (1) the energy of a semi-circular loop formed by glide, (2) the elastic energy released by the loop formed, (3) the stacking fault inside the loop, if it is imperfect, and (4) the energy of the surface step created by the loop. Since the total energy is zero for a semicircular loop with zero radius, when the loop radius increases from zero, the total energy increases to a maximum value, at $R = R_{crit}$ and then decreases. The conditions that are expected to lead to the nucleation and expansion of half-loops are described by:

$$R_{crit} = \frac{Gb^2}{8} \frac{(2 - \nu)[(\ln \frac{8R}{\epsilon^2b}) + 2] + 2\sigma(1 - \nu)b\sin \alpha}{\pi[2G(1 + \nu)\sigma b \cos \lambda \cos \phi - \gamma(1 - \nu)]}$$

(2-1)

where $G$ is shear modulus, $\nu$ is Poisson’s ratio, $b$ is the Burgers vector of the dislocation, $\epsilon$ is the elastic strain parallel to the film plane, $\lambda$ is the angle between the slip direction and that direction in the interface which is perpendicular to the line of intersection of the slip plane and the interface, $\alpha$ is the angle between the dislocation line and its Burgers vector, $\phi$ is the angle between the specimen surface and the normal to the slip plane, $\sigma$ is the surface tension of the film, $\gamma$ is the stacking fault energy, and $f - \epsilon = \delta$ is accommodated by misfit dislocations.
At that moment, we know that the unexpectedly large values for critical film thickness, which have been found \[^{[32,44]}\], seem to arise from difficulties associated with the formation of dislocations, which include (1) the barrier to dislocation nucleation, (2) the Peierls-Nabarro friction stress \[^{[41]}\], (3) the absence of suitable glide systems \[^{[31]}\], and (4) the interaction between dislocations and other defects \[^{[45-46]}\].

Matthews and Blakeslee were also the first to study the mechanism of dislocation nucleation with critical thickness in epitaxial multilayers in 1974 \[^{[47]}\]. But it is beyond the scope of this thesis.

### 2.1.4 People and Bean's Energy Balance Model

As Matthews' half-loop nucleation theory \[^{[48]}\], Matthews’ and Blakeslee’s mechanical equilibrium theory \[^{[47]}\], and van der Merwe's energy balance calculations \[^{[25]}\] all disagreed with the experimental data measured for the molecular beam epitaxial (MBE) growth of Ge\(_x\)Si\(_{1-x}\) strained-layer on Si substrates; in the range of \(x\) from 0 to 1.0 \[^{[49]}\]. People and Bean \[^{[50]}\] developed an energy balance model that was based on van der Merwe’s \[^{[25]}\] and Nabarro’s \[^{[41]}\] calculations. He assumed that interfacial misfit dislocation would be generated when strain energy density in film is larger than the energy density associated with the formation of a screw dislocation at a distance of \(h_{\text{crit}}\) (the critical thickness) form the free surface of the film to the interface. I.e. screw dislocation will be generated at the film / substrate interface.

He used van der Merwe’s calculation \[^{[25]}\] for strain energy density in the film with thickness \(h\), and Nabarro’s energy density of screw dislocation in the interface \[^{[41]}\]. By the energy balance between strain and dislocation energy density, he got:

\[
h_{\text{crit}} \approx \frac{1-v}{1+v} \frac{b^2}{16\pi \sqrt{2a(x)f^2}} \ln \frac{h_{\text{crit}}}{b} \tag{2-2}
\]

Comparing his calculations with those experimental data measured for growth of Ge\(_x\)Si\(_{1-x}\) strained-layer on Si substrates \[^{[49]}\], he found that his calculation was more consistent compared with the others that have been described in the above paragraphs.
2.1.5 Conclusion of Theoretical Calculations

As a conclusion for the development of the theoretical calculation for epitaxial growth, several models have been proposed in order to determine the critical thickness. Frank and van der Merwe developed the earliest model in 1949. They developed a continuum theory for an array of non-interacting dislocations at the film-substrate interface \[^{[23,51-52]}\]. They concluded that when the film thickness increases, the elastic energy stored within the film increases. At some thickness, it becomes energetically favorable to relieve this misfit strain by the formation of dislocations at or near the substrate/film interface. When the elastic energy relieved by the dislocations balances the increase in interfacial energy associated with their formation it becomes thermodynamically favorable to introduce dislocations at the interface. But this approach did not consider the surface features and dislocation nucleation mechanisms.

Matthews et al. were the first to examine how the dislocation nucleation mechanism influences the critical thickness \[^{[32,48]}\]. In their consideration, the driving force is misfit strain, and the opposing forces are tension in the misfit dislocation line, tension in the surface step, tension in the stacking fault, the interaction between the moving dislocation, and the Peierls stress. It results in a force balance for the threading dislocations. The predicted critical thickness in this mechanical equilibrium approach was very close to the thermodynamic approach of Frank and van der Merwe. It was the first time to explain the effect of Peierls stress, temperature and anneal time by theories for the accommodation of misfit between one crystal and another.

People and Beam \[^{[50]}\] developed an energy balance model base on van der Merwe’s \[^{[25]}\] and Nabarro’s \[^{[41]}\] calculations. He assumed that interfacial misfit dislocation would be generated when the areal strain energy density in film is larger than the energy density associated with the formation of a screw dislocation at a distance of \(h_{\text{cirt}}\). By comparing his calculations with those experimental data measured for growth of Ge\(_x\)Si\(_{1-x}\) strained-layer on Si substrates \[^{[49]}\], he found that his calculations were more consistent compared with the others’.

Although simplistic, the analytical theories above qualitatively predicted the correct critical thickness when dislocations start to be present in thin films. Still, these theories suffer from two intrinsic drawbacks. First, the thermodynamic equilibrium assumption ignores kinetic effects during thin-film deposition. Surfaces of thin films are seldom flat and they are generally rough, and the surface roughness will affect the
nucleation of dislocations. They are also insufficient for the predicting the critical thickness for relaxation. Second, the elastic theory ignores the effects of the crystal structure, the importance of which is well known today \cite{51-53}.

Atomistic simulations do not have these two drawbacks of the continuum theories. In order to consider the effect of crystal structure, as well as the atomic scale phenomena on the role of film growth, and examine the critical thickness of the actual surface morphologies, atomistic molecular dynamics simulation for the deposition of thin films have been studied for around twenty years. A more physical picture can be given through MD simulation.
2.2  

Modeling of Thin-film Growth

Before we go into the MD modeling of thin-film growth, an introduction of modeling is given in the following paragraphs.

The goal of modeling technology is ‘virtual experiment’; modeling is predictive as well as explanatory. The modeling will take the place of physical experiments. Developed in this way, new technologies, new sample geometries, and chemical effects can be simulated and predicted without the need for experimental confirmation. Computer modeling is currently practiced. This approach is used in IC chip design. It is now becoming possible for actual, physical film deposition through the use of modeling approached. Also, computer models can give a cleaner, cheaper and efficient study for film growth.

2.2.1  Classification of Modeling

Modeling of thin-film growth can be classified into two categories: analytical formulations and computer simulations. Burton, Cabrera, and Frank developed an analytical theory of crystal growth, named BCF theory, in 1950\textsuperscript{[54]}. They calculated the rate of advance of monomolecular steps as a function of super-saturation in the vapour and the mean concentration of kinks in the steps. They also found the rate of advance for parallel sequences of steps, and the dependence of the rate of advance upon the curvature of the step. They showed that in most cases of growth from the vapour, the rate of advance of steps would be independent of their crystallographic orientation, so that a growing closed step would be circular. They found the resulting rate of growth and the steepness of the growth pyramids when the persistence of steps was due to the presence of dislocations. The rate of growth of a surface containing dislocations was shown to be proportional to the square of the super-saturation for low values and to the first power for high values of the latter. Development of BCF theory is described in Chapter 2.2.2 in details.

With the advancement of integrated circuits, computer simulations have become feasible since 1970. Many computer simulation methods were developed to study growth of thin films\textsuperscript{[55-56]}. Computer simulations fall into three classifications; solutions of continuum rate equations, Monte Carlo (MC) simulations, and molecular dynamics (MD) simulations.

The continuum approach is capable of simulating growth of thin films of larger dimensions. The film surface is described by an equation, usually in the form of
a sequence of line segments (or a series of nodal points that are advanced according to materials flux in and out of neighboring regions). This equation is modified by various processes such as deposition, diffusion, etc. that occur during deposition. The continuum simulators, such as SPEEDIE [57], EVOLVE [58], SAMPLE [59], and DEPICT [60], have been developed to study topographical evolution of thin films during semiconductor processing, in particular metallization and etching. As an example of the continuum approach, the simulator EVOLVE is described in Chapter 2.2.4. Unfortunately, the continuum approach could not represent the internal information needed to depict microstructure.

To simulate small systems with linear dimensions less than one micron, Monte Carlo method has been widely used. There are two types of MC methods. One is based on a continuum space, and the other is based on a discrete lattice. In the approach based on continuum space, atoms can occupy non-lattice sites. Stacking faults are possible for the simulation. In order to study thin-film growth and etching of semiconductor materials [61], a two-dimensional simulator named SIMBAD has been developed. It is based on the continuum space Monte Carlo method. There are a lot of companies using this simulator in their materials processing. Baumann and Gilmer try to extend the continuum MC method to three-dimensional [62]. But it takes too much computational effort and is constrained by the calculating speed of modern computers. SIMBAD is described in Chapter 2.2.3 as an example of MC simulation. The other approach is based on a discrete lattice. It is capable of simulating thin-film growth under realistic deposition rates in three-dimensions. In this model, atoms are constrained to lattice sites so that it becomes computationally efficient. However, the conventional lattice MC simulations have been conducted to study only epitaxy growth of thin films because of the constraint of discrete lattices [63].

The world is made of atomic and molecular building blocks. Their properties depend on how those atoms are arranged. For example, by rearranging carbon atoms, coal can be converted into diamond. In the molecular dynamics approach, the substrate surface is viewed as an array of distinct points. Typically, these points are representative of a large number of atoms, but are treated physically as a single atom. Physical processes such as adsorption, diffusion, and incorporation are considered on these points. The use of a point to represent a large number of atoms drastically reduces the computational requirements and makes solution more practical. It is now applicable to simulate a system less than a million atoms. Research in molecular
dynamics simulations falls into two areas: development and application. In the development section, some of them are in the area of robust interatomic potentials such as Daw and Baskes investigate the Embedded Atom Method [64-65]. Others are in the area of efficient computational methods, such as Voter studying the hyper molecular dynamics [66] and Vashishta et. al. study parallel computational methods [67]. In the application area, molecular dynamics in the study of thin-film growth has gone through two-dimensional (2-D) and three-dimensional (3-D). These simulations reveal many interesting atomic phenomena. They are described in Chapter 2.3

However, the maximum simulation time using MD simulation method is on the order of nano-seconds. The hyper molecular dynamics method can reach a maximum simulation time on the order of microseconds. But it is still far from reality; industrial and experimental film growth both require durations on the order of hours. Therefore, the deposition rate must be unrealistically high for the simulation of the deposition process during film growth. Many artifacts, such as large roughness, result from the high deposition rate. Details of the setup conditions of the simulation are given in each Chapter in order to give an environment which is close to the reality processes.

As the limitation of MD method, MC method, and the method by continuum method, multi-scale simulation has been developed for a few years. It focused on bridging the MD and MC methods. Johnson and Wadley have incorporated deposition of heat and momentum in their lattice MC method using their molecular dynamics simulation results [68-69]. Huang and co-workers developed a model named ADEPT [70-74] using an imaging method. Multiple lattices are represented by one simple cubic lattice. As a result, texture competition during thin-film growth under realistic deposition rates can be atomistically simulated for the first time. Advancement has been made in simulating growth of polycrystal thin films. The ADEPT simulator is described in Chapter 2.2.5 as an example of multi-scale modeling.

As a summary, the classification of modeling of thin-film growth is given in figure 2-3. BCF theory, EVOLVE, SIMBAD, and ADEPT simulations are given as examples of modeling of the above classification for the branch of analytical formulations, continuum rate equations, MC simulations, and multi-scale simulations respectively in the following sub-chapters.
Figure 2-3 Classification of Modeling of Thin-film Growth
2.2.2 Analytical Formulations - BCF Theory

BCF theory is an important theory in analytical formulations. They calculate the rate of advance of monomolecular steps as a function of supersaturation in the vapour and the mean concentration of kinks in the steps. They also find the rate of advance for parallel sequences of steps, and the dependence of rate of advance upon the curvature of a step. They show that in most cases of growth from the vapour, the rate of advance of steps will be independent of their crystallographic orientation, so that a growing closed step will be circular. They find the resulting rate of growth and the steepness of the growth pyramids when the persistence of steps is due to the presence of dislocations. The rate of growth of a surface containing dislocations is shown to be proportional to the square of the supersaturation for low values and to the first power for high values of the latter. For the growth of perfect crystals, it predicts that when all surfaces of high index (stepped surfaces) have disappeared, the crystal will continue to grow by two-dimensional nucleation of new molecular layers on the surfaces of low index (saturated surfaces). In nucleation processes, the probability for the formation of these two-dimensional nuclei is a very sensitive function of the supersaturation. This probability is quite negligible below a certain critical supersaturation and increases very rapidly above it.

In the year of 1945, Frenkel \cite{frenkel1945} pointed out that the structure of a perfect crystal surface above the absolute zero of temperature would have a certain roughness produced by thermal fluctuations. He discussed the structure of a monomolecular step and proved that it will contain a high concentration of kinks. Then, Frank \cite{frank1958,frank1959} concluded that the growth of crystals under low supersaturations can only be explained by recognizing that the crystals which grow are not perfect, and that their imperfections will provide the steps required for growth, making two-dimensional nucleation unnecessary.

2.2.3 MC Simulations - SIMBAD

Simulation by BAAllistic Deposition \cite{baallistic1,baallistic2} (SIMBAD) simulator has been developed by a group of scientists at the University of Alberta to study thin-film growth and etching of semiconductor materials. The name comes from SIMulation by BAAllistic Deposition. The SIMBAD deposition model is a 2-D simulator based on the continuum MC method. It consists of the core growth algorithm and a number of
extensions specifically focused on different film technologies. Film is represented in two-dimensions by an aggregation of $10^4$ and $10^5$ 2-D disks. Each disk represents the statistical average of a large number of physical atoms with similar trajectories. It tracks the statistical movement and deposition of atoms within the simulation region. The size of the disk is chosen to be much smaller than the microstructural features to be modeled, but large enough that the total film can be represented using the resources of a typical computer workstation. Typical widths of the simulation region are 0.5 to 5 μm. In the modeling process, the substrate is initialized to the device topography by a series of straight-line segments, or a previously deposited film. Disks are launched from just above the film surface with an angular distribution determined by SIMPUD or input by the user from measurements or knowledge of the deposition process. Launch trajectories are determined randomly in a manner consistent with the angular distribution. Because the mean free path for adatoms in the gas phase is very large with respect to the simulation region, these disks move ballistically until they contact the growing film or the initial substrate. The ballistic approach intrinsically incorporates the effects of self-shadowing by the film which gives rise to microstructure evolution, and of shadowing by topography which can create poor coverage over nonplanar features. Disks will be incorporated in the film after undergoing diffusion to minimize the surface chemical potential and reduce local concentration gradients. The surface gradients cause the preferential diffusion of adatoms into areas where the surface is concave. Using this expression, a relative surface potential for each surface disk can be calculated. The surface of the growing film is searched within the specified diffusion length to determine the point of lowest surface energy, where the incident disk will be incorporated into the growing film.

The advantage of microstructure depiction by SIMBAD is the ability to calculate the relative local density of the film. However, the growth model of SIMBAD is 2-D. It is directly comparable only to very long features such as trenches. More recently, it has been rewritten to enable 'quasi-3-D' film growth [61].

2.2.4 Continuum Rate Equations Model - EVOLVE

EVOLVE [80-81] is described as continuum rate equations modeling here. It is a transport and reaction simulator. The topography simulations can be represented in two dimensions: long lines or trenches and features of the circular horizontal cross-
section. Thus, line segments in the plane of the paper represent either infinitely long strips for lines or trenches and sections of cones for circular features. Circular features are inherently symmetric, whereas trenches can either be symmetric or of fairly arbitrary cross-section. More importantly, surface evolution can be done in two dimensions with certain assumptions about the flux distributions. In EVOLVE, the transport is done in 3-D and surface is represented in 2-D, as 3-D/2-D topography simulators.

Topography simulations on completely three-dimensional surfaces require considerably more computational resources, but are being developed to meet the need for realistic simulations of device fabrication in 'virtual'. On the other hand, process understanding has been developed using simulations on 2-D surfaces. This will continue to be the case in general, simply because a method for comparing simulator predictions of surface evolution with experimental surfaces has not been developed for evolving 3-D surfaces.

2.2.5 Multi-Scale Modeling – ADEPT

As described above, the discrete lattice MC approach is capable of simulation thin-film growth under realistic deposition rates in three dimensions. But it has been used to study only epitaxial growth because of the constraint of discrete lattice. MD approach revealed many interesting atomic phenomena, but the maximum reachable time is on the order of tens of nano-seconds. Even using the hyper molecular dynamics method, the maximum reachable time is still on the order of microseconds. Consequently, deposition rate had to be unrealistically high in order to simulate growth of several atomic layers. Many artifacts, such as large surface roughness and formation of voids, result from the high deposition rate.

Some efforts have been focused on bridging the MD and MC methods [82-87]. A major advancement has been made in simulating growth of polycrystalline thin films. ADEPT was developed by the PI in collaboration with Gilmer of Bell Labs and Diaz de la Rubia of Lawrence Livermore National Lab. They used a mapping method so that multiple lattices are represented by one simple cubic lattice. As a result, competition of multiple textures during thin-film growth under realistic deposition rates can be atomistically simulated for the first time. Details of ADEPT are described in the following paragraphs.
ADEPT \cite{70-74,88} is an atomistic simulator for thin-film deposition in three dimensions. It is designed to bridge the atomic and mesoscopic length scales by using efficient algorithms, including an option to speed up surface diffusion using events with multiple diffusion hops. Atoms on the surface of the film execute surface diffusion hops with rates that depend on the local configuration, and are consistent with microscopic reversibility. The potential energies are chosen to match information obtained from a database of first principles and MD calculations. Efficient computation is accomplished by selecting atoms with probabilities that are proportional to their hop rates. A first implementation of grain boundary effects is accomplished by including an orientation variable with each occupied site. Energies and mobilities are assigned to atoms in grain boundaries using values obtained from MD.

The ADEPT model of deposition includes two basic events in the current level of implementation: the deposition event and surface diffusion. In the deposition event, the insertion of a new atom is accomplished by three steps: (1) A launching point is selected in a plane above all occupied sites. This position is chosen with random lateral coordinates. (2) The orientation of the particle trajectory is selected with a random azimuthal angle around the substrate normal. (3) The atom is moved along the selected trajectory until it contacts the substrate. The environment of the atom is searched for an empty site at the nearest neighbour position, and a stable site for the atom, (for example, with three or more nearest neighbours) is chosen at random. Surface diffusion events are chosen in a way that satisfies the condition for microscopic reversibility. As a result, a system evolving under surface diffusion alone will approach the equilibrium structure for the simulated temperature, subject to any constraints imposed on the surface through the boundary conditions. Furthermore, kinetic effects resulting from the deposition process become less pronounced for systems with large surface diffusion mobility. The actual event to be executed by the MC method is chosen by 3 steps: (1) A random number \( \xi_1 \) is selected and compared with the partial sums of probabilities for the selection of a given class \( i \). (2) An atom in class \( i \) is chosen without bias using a second random number \( \xi_2 \). (3) A vacant nearest neighbour site is then chosen using a third random number \( \xi_3 \), with the restriction that the site must have at least three nearest neighbour sites filled. Most of
the simulations are performed using MC events with more than one hop, and the barrier to diffusion across a step can be set to the desired value.

In the ADEPT model, evaporation of film or substrate atoms could be included if conditions required. The model can be applied to any materials which form crystalline deposits, provided atomic level information is available on the energies of atoms in representative surface configurations. As a result, competition of multiple textures during thin-film growth under realistic deposition rates can be atomistically simulated for the first time.

2.2.6 Conclusion of Computer Modeling

With the advancement of integrated circuits, computer simulations have become feasible since 1970. Many computer simulation methods were developed to study growth of thin films \cite{34,68}. Computer simulations can fall into three classifications; solutions of continuum rate equations, Monte Carlo (MC) simulations, and molecular dynamics (MD) simulations.

The continuum approach is capable of simulating growth of thin films of larger dimensions. Unfortunately, it could not represent the internal information needed to depict microstructure. To simulate small systems with linear dimension less than one micron, the Monte Carlo method has been widely used. There are two types of MC methods. One is based on a continuum space, and the other is based on a discrete lattice. However, the simulators based on continuum model are either 2-D simulators or take too much computational effort if modified to 3-D simulators. The other approach is based on a discrete lattice. It is capable of simulating thin-film growth under realistic deposition rates in three-dimensions. However, the conventional lattice MC simulations have been used to study only epitaxial growth of thin films because of the constraint of discrete lattices \cite{90}. Molecular dynamics in the study of thin-film growth has gone through 2-D and 3-D. These simulations reveal many interesting atomic phenomena. However, the maximum reachable time using the MD simulation method is on the order of microseconds. But it is still far away from the reality, where the duration of film growth is on the order of hours.

Due to the limitations of the MD method, the MC method, and the continuum method, multi-scale simulation has been developed for a few years. It focused on bridging the MD and MC methods. As a result, texture competition during thin-film growth under realistic deposition rates can be atomistically simulated for the first time.
2.3 MD Modeling for Film Growth

As described in section 2.2, MD modeling can be classified into 2-D and 3-D. It is due to the limitations of the technology developed so far. In this section, the history of investigation of film growth by modeling is given, especially by MD modeling.

2.3.1 MD Simulation for Unstrained Films

In the last twenty years, the growth of unstrained films has been investigated by MD simulations widely. For example, Muller studied the vapor deposition of energetic-atom film growth by MD simulation in 2-dimensions. He used Lennard-Jones (LJ) potential to study the vapour, sputter, ion-assisted, and cluster beam deposition of films [91-93]. He investigated the dependence of microstructure evolution upon the incident kinetic energy of arriving species. He also simulated the magnetron sputter deposition to elucidate the dependence of internal tensile stress on film growth and microstructure [94]. Effects of energetic incident ions were studied by Brice [95]. They concluded that for the detailed motion of low-energy incident atoms (less than 100eV), molecular dynamics simulations can be examined accurately for the energy regime where the threshold for the surface-atom displacements occurs. Henderson studied thermal deposition with hard-ball potential in which atoms were allowed to relax to the minimum energy positions nearby [96]. Porous columnar structure of film growth was observed. Similar results were obtained by using Lennard-Jones pair potential in 3-D MD simulations [97]. Others like Scheneider also studied this kind of film growth by 3-D molecular simulation. Scheneider studied vapor deposition using LJ atoms [98]. The growth of the thin structure is in well-ordered layers in the range of substrate temperature from 0 to 0.57 Tm with a source temperature of 1.3 Tm. Vacancy clusters near the interface are eventually filled with high-mobility atoms while layers which are far away from the substrate have less atomic density. But almost all of the above atomistic simulations were studied for the unstrained film with varied deposition conditions such as deposition rate, deposition angle, kinetic energy of deposited atoms and substrate temperature.

Gilmore and Sprague simulated the energetic-atom thin-film growth in 500 Ag atoms deposited onto a substrate of 1008 Ag atoms with incident atom energies from 0.1 to 10 eV [99]. Ag-Ag interactions were simulated with the embedded-atom method (EAM) [100] and with Foiles, Baskes, and Daw's potential [101]. For all the range of
energies, epitaxial film growth was found. Three-dimensional islands were found on
the surface in the low incident-atom energy range. The growth changed to layer-by-
layer growth with increasing incident-atom energies (>1.0eV). Dodson studied low
energy atom-beam deposition of Si model with his potential \cite{102-104}. But only 30
atoms were deposited on the (111) orientation substrate of Si.

Srolovitz and co-workers also studied a lot of simulations for film growth. They tested the relationship between deposition parameters on the resultant film
growth \cite{19}. Increasing substrate temperature gives the same effect on voids formation
as increases the deposition kinetic energy. The resultant films have fewer and smaller
voids, smoother surfaces and higher film density. Increased deposition angle will
elongate the voids formed. These void tracks are in the same direction as deposit
angle, and give a highly porous structure. Formation of voids and void tracks are
intimately related to the development of surface roughness \cite{105}. Due to normal atomic
interactions, atoms deposited will be attracted to the sides of the surface easily, due to
the normal atomic interactions. Then, the sides of the surface will develop bumps,
with shadow regions of the surface depression below. These bumps will grow into
bridges over the surface depression; cutting off the underlying atoms from flux and
pinching off voids. Finally, these bridges form below the top edge of the surface
depressions. They also did non-equilibrium MD simulations of vapor deposition to
find the mechanism of texture formation during film growth \cite{106}. But most of the
atomistic simulations have been 2-D or quasi-2D, due to the limitation of
computational capacity.

However, the aforementioned atomistic simulations were for unstrained films
with various deposition conditions such as deposition rate, deposition angle, kinetic
energy of deposited atoms and substrate temperature. There were relatively few
atomistic studies of strained substrate-film systems, which we will describe in the
following paragraphs \cite{107-117}.

2.3.2 MC Simulations for Strained Films

Nandedkar simulated the misfit of f.c.c. Au on Ni substrate in 3-D \cite{118} using
the Lennard-Jones potentials \cite{119} and potentials based on the embedded atom
method\cite{120}. The film was put under compression to simulate the misfit with its
substrate. This produced a high strain energy in the film in the initial state, which was
minimized using the conjugate gradient method, and by Monte Carlo simulations for
about 30 iterations. Misfit dislocations started to nucleate, starting with the formation of vacancies at the film surface, which migrate towards the substrate resulting in a dislocation loop moving to the interface.

Dodson studied the stability of thin, coherently strained layers of mismatched siliconlike semiconductor material \[^{121}\] using the Stillinger-Weber potential. He found that for layers greater than about 20Å, the critical film thickness is accurately described by the continuum theory of Matthews and Blakeslee, as discussed in section 2.4. For thinner layers, however, a smaller than predicted critical thickness was found. The critical mismatch as a function of layer thickness becomes nonmonotonic for the thinnest films considered. However, we note that these results were obtained using MC simulations, and did not take into account the full dynamics of the growth process. Details of MC simulations are given in section 2.2.3.

\subsection*{2.3.3 MD Simulations for Strained Films}

Atomistic simulation is one of the ways to investigate the nucleation, as well as propagation of dislocations during film growth. Ichimur and Narayan \[^{122}\] investigated the misfit dislocations in Ge/(001)Si heterostructures by an atomistic model based on the Stillinger-Weber potential \[^{123}\]. The resultant critical thickness was found to be larger than the continuum analysis reported. They attributed most of the difference to the core energy of the dislocations. The interaction between two 60-degree dislocations, and the formation of a 90-degree dislocation at the interface by a dislocation reaction mechanism were studied. They also calculated the critical thickness in atom cell for Ge/Si (about 4% misfit)\[^{111}\], and studied the role of surface step formation on the nucleation of misfit dislocations.

Molecular dynamics simulation of the relaxation of misfitting films in low-temperature were studied by Liang Dong el al. \[^{113}\]. Lennard-Jones potentials were used in the range of misfit from 5.0 to −5.0. The critical thickness was found to depend not only the lattice mismatch, but it also depends on the sign of the misfit, which was smaller in compression than in tension under the same strain. They compared the mechanisms of dislocation nucleation under compression and tension misfit of the substrate. Dislocations nucleate by squeezing out an atom at the base of surface depressions when its substrate is under compression. While in tension dislocation nucleation involved the concerted motion of a relatively large number of atoms, leading to the insertion of an extra lattice (plane) row into a continuous film.
Under compression, the misfit strain was completely relieved by the dislocation. There was compression below the void and tension above it. This is the pattern of stress expected for an edge dislocation with a Burgers vector parallel to the substrate. Under tension, the misfit strain was only partially relieved by a dislocation. There was tension below the void and compression above it, with Burgers vector opposite as in the case of compression misfit. It is easier to nucleate a dislocation by the compressive misfit, as compared to tensile misfit, and voids can play a significant role in stress relaxation by dislocations.

To extend the foregoing 2-D simulations to 3-D, Grabow and Gilmer used the Lennard-Jones potential to study the limit of the growth of coherent structures \(^{[124]}\). Misfit dislocations parallel to \(<\bar{1}10>\) direction were introduced initially on (001) f.c.c. face. The system was then annealed to minimize the starting energy. The relaxation of the substrate reduced the energy of the misfit dislocations without changing their qualitative features. The dependence of critical thickness on the degree of misfit between the film and substrate interface was then calculated. Defects related to partial misfit dislocations were found to relieve the strain with a lower cost in energy than full dislocations. It was also found that coherent films could often exist in metastable states when it exceeded its critical thickness.

3-D MD simulations on \(\text{LN}_{1-x}\text{Ga}_x\text{As/GaAs(100)}\) systems were performed by Ashu \(^{[112]}\) using Tersoff potential \(^{[125-128]}\). Threading dislocations in the overlayer, and the formation of dislocations at the hetero-junction, were investigated. A 45-degree dislocation strain filed was imposed on the substrate and a 60-degree in the overlayer. The dynamics of threading dislocations and formation of misfit dislocations at the interface are shown. Full relaxation was performed with varied overlayer thickness to obtain the lowest energy configuration of the system for the critical thickness.

Simulations considered in the foregoing were performed using the annealing / relaxation method, and atoms were not deposited one by one. Therefore, surface effects, such as surface step, for the nucleation of dislocations could not be taken into consideration. Effects of surface step were investigated by Ichimura and Narayan \(^{[111]}\), and also Brochard and co-authors \(^{[129-130]}\). Ichimura studied the role of surface step formation on misfit dislocation nucleation by considering a (100) heterostructure composed of 2 diamond cubic or zincblende structure materials \(^{[111]}\). In their model, step formation energy change can be either positive or negative, depending on the
sign of the misfit. It is in contrast to the classical model, in which the step formation energy is independent of the sign of the misfit (the step energy is always positive). They also showed that critical thickness depended on the sign of the misfit. However, there were only a small number of atoms in their model.

Brochard and co-authors, on the other hand\textsuperscript{[131-132]}, used point-force models to study the stress field in the neighborhood of a surface step and a surface groove. 2-D atomistic simulations of aluminum structure (f.c.c.) showed that before dislocations were nucleated, a local shear strain appeared in the glide planes where the nucleation would occur. In the case of the grooves, the stress concentration induced a shear stress in the glide planes, which could directly favor nucleation of dislocations. In the case of the steps, there was no local shear stress in the glide plane. Although the stress concentration did not involve any shear in the glide planes, it produces a variation of the interplanar distance, which can make shear easier. The saddle-point configuration was like a dislocation half-loop emanating locally from the surface step. They also showed that a surface step is a preferred site for dislocation nucleation. Before dislocation nucleation, an elastic shear developed, localized in the plane of the step where nucleation occurred.

However, these are again 2-D MD simulations without thermal activation (at 0K). Atoms are put in their lattice sites and then annealed to satisfy specified conditions as required. The assumed compression and tension have the same magnitude, but opposite signs. Therefore, only tension needs to be done in most cases.

2.3.4 Conclusion of MD Modeling for Film Growth

In the above investigations, computer simulations not only confirmed and improved the growth theory, they also revealed much more detailed information, such as the island shape and surface roughening of a growing thin film. Dislocation nucleation mechanism and/or the non-flat nature of the MD grown film play significant roles in determining the critical thickness. However, the studies of epitaxial growth are either performed using 2-D deposition modeling, which cannot represent the structure of crystals, or using 3-D but annealing method which has not considered the surface effects due to deposition conditions. The difference of dislocation nucleation behaviour under compression and tension misfit of the substrate is a very interesting subject to study and compare using 3-D MD simulation.
CHAPTER THREE - MD METHODOLOGY

Molecular dynamics (MD) simulation is one of the computer modeling techniques described in Chapter 2. It uses time evolution of a many-body system calculated by integrating the equations of motion. The MD simulation methods have been used extensively in condensed matter physics, chemistry, biology, and materials science. In the molecular dynamics approach, the substrate surface is viewed as an array of distinct points. Typically, these points are representative of a large number of atoms, but are treated physically as a single atom. Physical processes such as adsorption, diffusion, and incorporation are considered on these points. The use of a point to represent a large number of atoms drastically reduces the computational requirements and makes solution more practical. It is now applicable to simulate a system with fewer than a million atoms.

The basic algorithms for setup of (1) equations of motion, (2) integration algorithms, (3) periodical boundary conditions, (4) temperature control, and (5) stress/pressure control are given in this chapter.
3.1 Equations of Motion

The simulated atomic molecular system is an assembly of rigid molecules, atoms or ions. The forces of interaction are derived from continuous potential functions acting between sites on each molecule. The Lagrangian equation of motion is used in the simulations. It can be written as:

\[
\frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_k} \right) - \frac{\partial L}{\partial q_k} = 0 \tag{3-1}
\]

And the Lagrangian function

\[
L(q, \dot{q}) = K - V \tag{3-2}
\]

is defined in terms of kinetic energy \((K)\) and the potential energy \((V)\) of the many-body system. It is a function of the generalized coordinates \(\{q_k\}\) and their derivatives \(\{\dot{q}_k\}\). If we consider a system of interacting atoms with Cartesian coordinates \(\{r_i\}\) and usual definitions of \(K\) and \(V\), Lagrangian equations become a Newton-Euler equation of motion. The total force acting on atom \(i\) due to the interactions with other atoms is:

\[
F_i = m_i a_i \tag{3-3}
\]

where \(m_i\) and \(a_i\) are the mass and acceleration of atom \(i\) in a total of \(N\) atoms. The dynamics of the system are governed by the classical Newton-Euler equations of motion.
3.2 Integration Algorithms

Based on time integration algorithms, the equation of motion of the interacting particles in equation 3-2 is integrated. Then, the trajectories of each atom \( i \) are followed. This is the kernel of MD code. Time integration algorithms are based on finite difference methods, where time is discrete on a finite grid. The distance between consecutive points on the grid is the time step, \( \Delta t \). When we get the positions and velocities of each atom \( i \) at time \( t \), by using interatomic potentials, the integration scheme gives the same quantities at a later time \( t+\Delta t \). Time evolution of the system is realized by iterating the procedure. Therefore, we are only required to give the positions (structure of the material) and velocities of each atom in the initial stage of the model block.

The Verlet algorithm \(^{[133]}\) is the commonly used one, due to its accuracy for atomic systems. It assumes that the positions and dynamical properties, such as velocities and accelerations, can be expanded in a Taylor series. It uses the positions and the accelerations of each atom \( i \) at time \( t \), and the positions from the previous time step, \( t-\Delta t \), to calculate the new positions at \( t+\Delta t \). Expanding the position \( r(t) \) to the third order in a Taylor series, we have

\[
    r(t+\Delta t) = r(t) + v(t)\Delta t + (1/2)a(t)\Delta t^2 + (1/6)\dot{a}(t)\Delta t^3 + O(\Delta t^4)
\]

(3-4)

and

\[
    r(t-\Delta t) = r(t) - v(t)\Delta t + (1/2)a(t)\Delta t^2 - (1/6)\dot{a}(t)\Delta t^3 + O(\Delta t^4)
\]

(3-5)

where \( v(t) \) is velocity, \( a(t) \) is acceleration, and \( \dot{a}(t) \) is the third derivative of \( r(t) \) with respect to \( t \). \( O(\Delta t^4) \) is with some coefficient in the fourth order.

Eliminate equations 3.4 and 3.5, we get:

\[
    r(t+\Delta t) = 2r(t) - r(t-\Delta t) + a(t)\Delta t^2 + 2O(\Delta t^4)
\]

(3-6)

And

\[
    v(t) = \frac{[r(t+\Delta t) - r(t-\Delta t) - (1/3)\dot{a}(t)\Delta t^3]}{2\Delta t}.
\]

(3-7)

From the above equations, we find that the accuracy for the calculated atom position calculated is up to the order of \( \Delta t^4 \), but the velocity is only accurate to \( \Delta t^2 \). This is insufficient for an accurate determination of the kinetic energy, pressure and other dynamic quantities. More seriously, it fails badly in the case of polyatomic molecules and for constant-pressure and constant-temperature methods where the velocities themselves enter the dynamical equations. For example, velocity-dependent forces occur in the Parrinello-Rahman constant-pressure equations \(^{[134]}\) and in the Nosé-
Hoover heat bath algorithms. These usually present a problem to the Verlet and its modified algorithms, which are based on the assumption that the forces depend only on the co-ordinates.

Therefore, a correcting subroutine is used in the MD simulator. An integration algorithm with the predictor-corrector algorithms is used in the simulation. A scheme that is correct to a given order can be selected. It has three basic steps: (1) Predictor. New positions, $r(t+\Delta t)$, velocities, $v(t+\Delta t)$, and accelerations, $a(t+\Delta t)$, are predicted according to the Taylor expansions; (2) Force evaluation. The forces are calculated at the new positions to give accelerations $a^{cal}(t+\Delta t)$; and (3) Corrector. The differences between the predicted and the calculated accelerations, $\Delta a(t+\Delta t)=a^{cal}(t+\Delta t)-a(t+\Delta t)$, are used to ‘correct’ the predicted positions, velocities, and accelerations. The predictor-corrector algorithms are used in the simulation in order to improve the poor accuracy of calculated velocities as described in equation 3-7 above. And it is commonly used in other MD programs.
3.3 Periodical Boundary Conditions

Molecular Dynamic methods are typically applied to systems containing a few thousand atoms or less. Surface effects are dominated by such small systems, such as the interactions of the atoms with the container walls. For example, to simulate a bulk material in a cube with a thousand atoms, the edges of the bulk will have a length of about 10 atomic diameters. However, the surfaces interactions will extend 4 to 6 atomic diameters from each edge. Then, the simulation of this system would provide information on the behavior of surface effects, not the information on the bulk material. In simulations in which these surface effects are not of interest, they are removed by using periodic boundary conditions (PBC).

When using PBC, particles are enclosed in a box, and this box is replicated to infinity by rigid translation in all the three Cartesian directions, completely filling the space. In other words, if one of our particles is located at position \( \mathbf{r} \) in the box, we assume that this particle really represents an infinite set of particles located at

\[
\mathbf{r} + l\mathbf{a} + m\mathbf{b} + n\mathbf{c}, \quad (l, m, n = -\infty, \infty)
\]  

(3-8)

where \( l, m, \) and \( n \) are integer numbers, and \( \mathbf{a}, \mathbf{b}, \) and \( \mathbf{c} \) are the vectors corresponding to the edges of the box. All these "image" particles move together, and in fact only one of them is represented in the computer program.

Each particle \( i \) in the box should be thought as interacting not only with other particles \( j \) in the box, but also with their images in nearby boxes. That is, interactions can "go through" box boundaries. In fact, we have virtually eliminated surface effects from our system. And the position of the box boundaries has no effect as the translation of the box with respect to the particles leaves the forces unchanged. As the potentials usually have a short interaction range, the PBC will not increase the number of interacting pairs. Let us use \( S_i \) indicates the set of particle \( i \) and its images, and

\[
S = \sum_{i=1}^{N} S_i \quad \text{where} \quad N \quad \text{is the total particle in the box. The set} \quad S \quad \text{includes all of the particles and their images of the simulated system. The pair summations of interaction should include all of the possible pairs in the set} \quad S. \quad \text{Suppose we are using a potential with a finite range. If the separation between two atoms is equal or larger than the cutoff distance,} \quad R_c, \quad \text{two particles will not interact with each other. If the set up of the bulk materials is larger than} \quad 2R_c \quad \text{along each Cartesian direction, then it is obvious that the distance between any two particles in the subset} \quad S_i \quad \text{is larger than the cutoff, and if the}
\]
distance between \( i \) and \( j \), which belongs to a different subset, is smaller than the cutoff \( R_c \), then the distances between \( i \) and all of the image particles of \( j \) will be larger than the cutoff \( R_c \). Therefore when we calculate the forces acting on particle \( i \), we only need to select the nearest particle \( j \) in each subset to which \( i \) does not belong and ignore all of the images of particle \( j \). As the total number of the subsets is equal to the total number of particles, \( N \), in a periodical box, the possible pairs in the summations are profoundly decreased by this minimum image criterion. These common operating methods greatly simplify the set up of a MD program. And the only requirement is to provide that the box size is larger then \( 2R_c \) along all the directions where PBCs are applied.

The purpose of PBCs is to eliminate surface effects. However, we may also be interested in situations where we want to have surfaces. For example, diffusions of Ti and W clusters on their surfaces are simulated in Chapter 4. For a surface simulation, a slab is usually adopted. This is simply obtained by removing PBCs along one direction (taken to be \( z \) direction in Chapter 4 of my simulation) while retaining them in the orthogonal plane. And PBCs must be applied for the other two directions in order to form an infinity plane. But there is no replication along the slab normal \( z \). If the slab is thick enough, its inner part is expected to be quite similar to the bulk of the material. The top and the bottom surfaces of the slab can then be thought of as two decoupled, independent surfaces. Then, the system behavior would be close to that of an actual single surface at the top of a semi-infinite system.
3.4 Temperature Control

From the equipartition theorem, every degree of freedom in the system has the same kinetic energy, \( \frac{1}{2} k_B T \). The effective temperature of the system is therefore given by the ensemble average of its kinetic energy.

\[
T = \langle T(t) \rangle = \frac{2}{3Nk_B} \langle K \rangle = \frac{2}{3Nk_B} \left( \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 \right)
\]  

(3-9)

where \( N \) is the number of atoms, \( K \) is the instantaneous kinetic energy, and \( T(t) \) is the instantaneous temperature. In a simulation model, it is almost always desirable that temperature is the supplied parameter rather than the kinetic energy. This requires some mechanism to fix the average kinetic energy at thermal equilibrium. The initial kinetic energy is set approximately by choosing random velocities which sample the Maxwell-Boltzmann distribution at the desired temperature. But the initial configuration is usually far from equilibrium, and it will have too much potential energy. As the run progresses, this will be converted into kinetic energy, raising the temperature above the desired value. It is therefore necessary to have some mechanism for removing excess kinetic energy as the run progresses.

Rescaling is a simple method to control the temperature as a run progresses. At periodic intervals, the velocities of atoms in system are multiplied by a factor of

\[
s = \sqrt[3]{\frac{T_0}{T(t)}}
\]

where \( T_0 \) is the desired temperature. By repeatedly setting the "instantaneous" temperature to the correct value while the system approaches its equilibrium state. Then the kinetic energy is made to approach its desired value. Scaling may be performed every time-step, or in a period of simulated time, depending on the simulation conditions required.

However, an MD code run with scaling does not generate a valid statistical ensemble, and scaling must be switched off before any calculation of thermodynamic averages is performed. The common technique of velocity scaling is suitable for use during the equilibration period but does not generate meaningful particle trajectories. For example, if we need to observe the dynamic process of an atom in a time evaluation, such as the surface diffusion during thin film deposition, the rescaling method is not applicable.

A more sophisticated approach is the Nosé-Hoover method \(^{135-137}\). It couples the system to a heat bath using a fictional dynamical variable. In this approach, an
extended-system Hamiltonian is proposed to represent the degrees of freedom of the thermal reservoir. The equations of motion are modified thus:

\[ a_i = \frac{f_i}{m_i} - \zeta v_i \quad (3-10) \]

\[ \dot{\zeta} = \frac{3}{Q} (k_B T(t) - k_B T_0) \quad (3-11) \]

where \( \zeta \) is a new “heat bath” dynamic variable and \( Q \) is the associated fictitious “mass” parameter. With a suitable choice of \( Q \) these equations generate trajectories that sample the canonical ensemble \(^{[3]}\). The coupling to the heat bath introduces nonphysical oscillations of period

\[ t_0 = 2\pi \sqrt{Q^2 / 6k_B T} \quad (3-12) \]

which may be easily detected in the total energy. There are two criteria to be considered when choosing the value of \( Q \). (1) sufficient oscillations must occur during a simulation run. The computed thermodynamic values represent the averages over many periods \( t_0 \). This ensures that the configurations, which are used to calculate the averages of samples of the phase space generated by the fluctuations in \( \zeta \), represent the canonical ensemble. (2) \( Q \) should be chosen so that \( t_0 \) is large compared to the characteristic decay time of dynamical correlation functions. This is to ensure that the fictitious dynamics of the heat bath are decoupled from the real molecular dynamics, and is particularly important in a simulation of dynamic properties \(^{[138]}\) such as velocity correlation functions. Since the first criterion favors a small \( Q \), and the second criterion favors a large one, it may be necessary to increase the total simulation time in order to satisfy both of them.
3.5 Stress / Pressure Control

Simulations are conducted under the conditions of constant pressure or stress, rather than constant volume. This allows the simulation of a solid-state phase transition with a change of symmetry or unit cell size. In a constant-stress simulation the MD cell changes in size and shape in response to the imbalance between the internal and externally applied pressure. In my simulations, the Parrinello-Rahman approach is used to control the stress \(^{134}\). The coordinates of atoms are scaled through the equation

\[ r_i = h s_i \]  \hspace{1cm} (3-13)

where \( r_i \) is the Cartesian coordinate of atom \( i \), \( s_i \) is the scaled coordinate, and \( h \) is a transformation matrix whose columns are the three vectors of the MD unit cell; \( a, b \) and \( c \). In the Parrinello-Rahman method, nine extra ‘degrees of freedom’ are introduced to specify the position and orientation of the MD cell. The ‘potential energy’ associated with the MD box is:

\[ V_r = P V \]  \hspace{1cm} (3-14)

By introducing the extra ‘kinetic energy’ term of the box change, the equations of motion of the constant pressure/stress ensemble are obtained in a usual way from the Lagrangian

\[ m_i \ddot{s}_i = h^{-1} f_i - m_i G^{-1} \dot{G} \dot{s}_i \]  \hspace{1cm} (3-15)

\[ W \ddot{h} = (\pi - P) V (h^T)^{-1} \]  \hspace{1cm} (3-16)

where \( P \) is the external pressure, \( W \) is the box ‘mass’, \( h^T \) is the transpose matrix of \( h \), and \( G = \dot{h} h \). The instantaneous internal stress, \( \pi \) is given by

\[ \pi_{\alpha\beta} = \frac{1}{V} \left( \sum_i m_i (h s_i)_\alpha (h s_i)_\beta + \sum_{ij} \sum_{\alpha} (h s_i)_\alpha (f_{ij})_\beta \right) \]  \hspace{1cm} (3-17)

The choice of fictitious mass, \( W \) is governed by similar considerations to those concerning the heat bath mass, \( Q \) as discussed in sub-section 3.4.
3.6 Interatomic Potentials

In molecular dynamics simulations, we set up a system of N atoms (each of which being a classical point) and allow these atoms to ‘move’ in a computer according to special rulers (the equations of motion in Chapter 3.1) to mimic the behavior of the real atomic system. The essential ingredient for the MD simulations is the interatomic potential to describe the interatomic interactions. For a classic system including many particles, the mechanical behavior and the evolution of the system is solely determined by the Lagrangian function of the system, or the potential energy function, \( V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \) where \( N \) is the number of atoms in the system. In molecular dynamics forces are derived from a potential energy function \( V \), which depends on the particle coordinates:

\[
f_i = -\frac{1}{V_i} V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N)
\]  \hspace{1cm} (3.18)

Therefore, we can model a material by finding a potential function for that material. \( V(\vec{r}_1, \vec{r}_2, ..., \vec{r}_N) \) is rigorously the definition of ‘interatomic potentials’ as a function of atomic positions of a many-atom system. The validity of MD simulation is essentially determined by interatomic potential function.

For a many-atom system in classical MD simulations, the system of interacting atoms is actually made up of nuclei and electrons that interact with each other. The total potential energy should include three parts:

\[
V = V_{nu-nu} + V_{nu-el} + V_{el-el}
\]  \hspace{1cm} (3.19)

where \( V_{nu-nu} \) is the interacting potential between nuclei or ionic cores, \( V_{nu-el} \) is the interacting potential between nuclei and electrons, and \( V_{el-el} \) is the interacting potential between electrons. In the three terms of total potential energy \( V \), the first term is Coulombic or screened-Coulombic interactions between the nuclei, and is in a simple form of pair functions, \( V_{nu-nu} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} V_{nu-nu}(r_{ij}) \). The complexity of interatomic potential comes from two other terms, which are the ground state energy of the Hamiltonian of electrons. If the nuclei are fixed at the coordinators, the ground state energy of the Hamiltonian of electrons can be evaluated from the Schrodinger’s equations of electrons. Born and Oppenheimer approximation assures that the ground state energy of the Hamiltonian of electrons is solely determined by the coordinators of the nuclei even if the atoms in the system are free to move. As nuclei are much
heavier than electrons, and the time scale of nuclei motion is about two or three orders of magnitude larger than that of the electrons, it is reasonable to regard the nuclei as fixed when we evaluate the ground state energy of electrons. Therefore, the potential energy of system including many atoms and electrons can be expressed as the function of coordinates of nuclei (atoms). On the other hand, the electron transfers between atoms are the physical origin of the atomic cohesions and the electrons hoping between two atoms are influenced by other atoms nearby, the many-body effects exist in the interatomic interactions and thus $V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ generally can not be expressed as pair summations of simple functions.

The potential energy function, $V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$, is a very complicated function in a multi-dimensional space. There are two approaches to evaluate the function. The first approach is to solve the Schrodinger’s equations of electrons. We then have first-principles molecular dynamics. However, it requires massive computer resources, and poses severe limitations on the maximum size of the system and on the simulation time.

The second approach is to expand $V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N)$ as:

$$V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \frac{1}{2} \sum_{i \neq j}^{N} \phi_2 (r_{ij}) + \frac{1}{6} \sum_{i \neq j \neq k}^{N} \phi_3 (r_{ij}, r_{jk}, r_{ki}) + \ldots \tag{3.20}$$

where $\phi_2, \phi_3, \ldots$ are pair potential, three-body potential, ..., respectively, or

$$V(\vec{r}_1, \vec{r}_2, \ldots, \vec{r}_N) = \frac{1}{2} \sum_{i \neq j}^{N} \phi_2 (r_{ij}) + \sum_{i}^{N} F_i (\rho_i) \tag{3.21}$$

and

$$\rho_i = \sum_{i \neq j} f_{ij} (r_{ij}) \tag{3.22}$$

where $F_i$ is a functional depending on the surrounding atoms, and covers the many-body effect in the interatomic potentials, $f_{ij} (r)$ is a radical function. The attractive part is in the form of functional $F_i$ of local electron density. The many-body effects between the interatomic interactions are included in this term.

The second approach includes the Finnis-Sinclair potential, which is being used in our simulations.
CHAPTER FOUR - SURFACE DIFFUSION

In this chapter, diffusion of atoms on a surface is presented. As described in Section 1.2, the mechanism of film growth is a result of the condensation of atoms on the surface. When deposited atoms reach the substrate, they will condense on the surface and contribute to the film growth. The mobility of an adatom on a surface depends on many factors such as the kinetic energy of the adatom, adatom-surface interactions (crystallography) and the temperature of the surface. For example, the adatom-surface interactions depend on the bonding between the surface and the atom. Therefore, different crystallographic planes of the surface will have different surface free energy, which will affect the surface diffusion of the adatom. In order to condense on a surface, the diffusing adatoms must lose their energy, which they do by surface reaction, finding preferential nucleation sites, collision, or deposited on an unstable surface.

In this chapter, computer simulation results of diffusion and clustering of Ti atoms on its (0001) surface in an h.c.p. (hexagonal close packed) crystal are reported. We note that the mobility of Ti on its (0001) surface is sufficiently high for the jump mechanism of large clusters to be studied. Then, we shall continue by discussing the simulation results of the diffusion of b.c.c. (body centre cubic) W adatoms on its (011) surface. As the mobility of W on its (011) surface is low compared with Ti adatoms, diffusion of adatoms down a step is studied.

Both molecular dynamic (MD) methods and molecular static (MS) methods are used. The formation energy of each defect cluster is calculated using a combination of annealing and quenching techniques. Diffusion mechanisms of the clusters are elucidated by the analysis of atomic trajectories and are confirmed by calculating energy states along the diffusion path and by fitting the diffusion coefficients to one or more Arrhenius functions. In the study of particle-solid interaction, the molecular dynamics method has been used to calculate formation and migration energies of bulk defects.
4.1 Surface Diffusion and Clustering during Film Growth

The kinetics of diffusion and the stability of various clusters determine the size and shape of the nucleating islands which grow into a film \(^{[139-143]}\). Many recent studies investigate the microscopic mechanisms of crystal growth. The growth kinetics encompass all atomic processes taking place during growth. They are determining the growth mode of a given system. In metal-on-metal systems, recent studies have shown that even very large clusters can have significant mobility at moderate temperatures \(^{[144-146]}\). Smaller clusters are expected to move even faster. It is intuitively obvious that cluster mobility should play an important role in the growth characteristics of such systems. In order to investigate the diffusion of islands on surfaces, surface imaging techniques such as field ion microscopy (FIM), scanning tunnelling microscopy (STM), and low energy electron microscopy (LEEM) have been used to image the changes in position or shape of islands at intervals. It is, however, difficult to image transition states, because they are short-lived. Therefore, the mechanism of island diffusion is typically inferred from indirect evidence. On the other hand, the short-lived transition states may be studied in a more direct way for clusters diffusion using MD calculations.

Two issues are important for the migration mechanisms of clusters on the surface. One is the ability to migrate over solid surfaces. The observation of this mobility generates immediate speculation about the atomic mechanisms responsible. Motion of the cluster as a whole, gliding over a surface with which it is not in perfect registry, has sometimes been proposed \(^{[147-148]}\). Another possibility for cluster motion is the transfer of individual atoms, diffusing along the rim of the cluster, from one side of the particle to the other, thereby shifting its center of mass \(^{[149-156]}\). They are described as follows.

Current models of the migration and dissociation of relatively small metal clusters on metal surfaces are based on the basic assumption that cluster dynamics result from sequential motion of individual adatoms. Shi uses bond-counting arguments and embedded-atom calculations to establish the crucial importance of dimer shearing in metal (100) sub-monolayer epitaxy \(^{[157]}\). It provides the easiest pathway for diffusion of compact clusters of sizes 4, 6, and 8. A combination of the dimer shear motion and the traditional mechanism of sequential motion of individual atoms provide a better interpretation of the oscillatory behaviour of cluster mobility.
with cluster size. This combination also defines a new set of critical cluster sizes that are likely to be selected in epitaxial growth.

The quantitative study of cluster behaviour shows that in some systems, small clusters such as dimers and trimers can move by a series of individual atomic jumps; example, rhenium atoms on W (211) \textsuperscript{158} surface and platinum on W (110) surface \textsuperscript{159}. Wang has investigated diffusion of large clusters \textsuperscript{160}. He examined iridium clusters containing from 2 to 13 atoms held on the close-packed iridium (111) plane using the field ion microscope. He found that the binding energy increases sharply from dimers to trimers, drops for tetramers, and then rises again. For clusters containing 5 or more atoms, the binding energy is relatively insensitive to size. The diffusion characteristics for dimers through pentamers again reveal an abnormally low activation energy for tetramers. And the pre-factor is insensitive to cluster size, which indicates that the mechanism of diffusion is the same independent of the number of cluster atoms. A detailed observation of cluster motion at low temperatures has been made to identify the individual atomic events in diffusion. It appears that diffusion occurs by a series of single atom jumps.

The field ion microscope clearly reveals the overall shape of clusters \textsuperscript{161}. However, more recent studies of cluster diffusion are rather limited, and there have not been enough studies to establish a dominant model. The atomic arrangement of clusters on surfaces is largely unexplored. As described in Chapter 1, during the film growth processing, clusters of atoms coalesce with each other on the surface. This plays an important part for the properties of thin film. Despite that, there is little information available concerning the properties of such clusters self-adsorbed on a crystal made up of the same atoms \textsuperscript{160}. In this chapter, we have therefore studied the diffusion of adatom/clusters on its own surface in order to give a full picture of the film growth processing. Two materials have been studied: diffusion of Ti clusters on its (0001) surface, a h.c.p. metal with high diffusivity of clusters, and diffusion of W adatom on its (0\bar{1}1) surface, a b.c.c. metal with relative low diffusivity of clusters.
4.2 Simulation Method and Formulations

In this section, we report our work on the MD and MS simulations to study the diffusion and clustering of (1) Ti particle on its (0001) surface; and (2) W particle on its (0\overline{1}1) surface. Here, a particle can be either an adatom or a cluster of atoms.

In the first case, diffusion and clustering of Ti particles are investigated. To minimize the computational demand and ensure convergence of the simulation results, we use a computational cell that is 32Å, 30Å, and 33Å along the \(\langle 11\overline{2}0 \rangle\), \(\langle 1\overline{1}00 \rangle\), \(\langle 0001 \rangle\) directions, respectively. In our simulations, the periodic boundary condition is applied along the \(\langle 11\overline{2}0 \rangle\) and \(\langle 1\overline{1}00 \rangle\) directions, leaving two free surfaces along the \(\langle 0001 \rangle\) direction. The set up coordinates are shown in figure 4-1a.

In the second case, diffusion of W on its surface is investigated. Similarly, an effective computational cell with 33Å x 31Å x 20Å along the \(\langle 111 \rangle\), \(\langle 2\overline{1}1 \rangle\), and \(\langle 0\overline{1}1 \rangle\) directions, respectively, is used for the simulations. For both cases, the atoms within 10 Å (1.5 times the cut-off distance of the interatomic potential) from one of the free surfaces are fixed to their lattice sites, so as to simulate an infinitely large bulk crystal under only one free surface. The set up coordinates are shown in figure 4-1b.
Figure 4-1 Set up coordinates and conditions of the simulation cells. Atoms of the lower layers are fixed to their lattice sites, and other layers are served as a thermal bath. (a) (0001) Ti surface. (b) (011) W surface.

Based on the configuration of the free surface, an adatom is formed by adding an extra atom to one lattice site right above the free surface. Similarly, adding multiple atoms at the lattice sites above the free surface forms a dimer or a larger cluster. These atoms are placed close to each other to minimize the formation energy. In general, a cluster consisting of a large number of atoms can take many different shapes. In this study, we consider only the thermodynamically most favorable configuration of each cluster. It is worthwhile to mention that the extra atoms are assumed to be from kink sites; removal of an atom from the kink site increases the potential energy by an amount equal to the sublimation energy.

In calculating the potential energy of each configuration, we use a combination of annealing and quenching. During this process, the lowest energy state of each configuration will be obtained. A thermal bath surrounding the computational cell is simulated using the Langevin force\textsuperscript{[162]}. A friction coefficient is chosen so that change from one temperature to another takes 25 pico-seconds; this choice is made to maximize computational efficiency and minimize artifacts of the strong random force. The temperature history of annealing and quenching in calculating the formation energy of an adatom is shown in figure 4-2. To ensure that the Langevin force\textsuperscript{[162]} has not artificially affected the calculated formation energy, the process of figure 4-2 is
repeated with a doubled frictional coefficient. The formation energy is found to be unaffected. This confirms that the chosen Langevin force \textsuperscript{162} does not cause artifacts in our calculations. For each defect cluster consisting of \( n \)-atoms above the surface, its formation energy \( F_j \) is defined as:

\[
F_j = E_{(m+n)} - E_{(m)} - nE_{\text{sub}}
\]

(4-1)

where \( E_{(m+n)} \) is the potential energy of the simulation cell containing the defect cluster, \( E_{(m)} \) is the potential energy of the simulation cell without the defect cluster, and \( E_{\text{sub}} \) is the sublimation energy of the simulated material.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4-2.png}
\caption{Annealing and quenching history to bring the system to the state of minimum free energy}
\end{figure}

Similar to the calculations of the formation energy, the diffusion mechanisms are studied by a combination of MD and MS methods. In order to carry out the dynamic simulations under constant volume, we first determine the lattice constant of the Ti as a function of temperature. A computational cell consisting of 1980 Ti atoms with periodic boundary conditions is used to calculate the lattice constant at finite temperatures. The Parrinello-Rahman \textsuperscript{134} algorithm is employed to keep the simulated system stress-free at finite temperatures. The perfect crystal is brought to a finite temperature using the Langevin force \textsuperscript{162}, once the temperature reached the
desired value, the Langevin force is removed. Under thermal equilibration, the lattice constant varies around its mean, which is taken to be the average over a period more than 50 ps. As shown in figure 4-3, the thermal expansions of Ti along the three axes, \( <1120> \), \( <1100> \), and \( <0001> \) directions, are plotted. Figure 4-3a and 4-3b show that the lattice constant at 900K can be 0.6% larger than its nominal value at 0K along its basal plane; i.e. along \( <1120> \), \( <1100> \) directions. The calculated thermal expansion is 7 \( \mu\text{m/m-K} \) for these two directions. And it can expand up to 2.4% larger than its nominal value along the \( <0001> \) direction, which is perpendicular to its basal plane as shown in figure 4-3c. The thermal expansion is 30\( \mu\text{m/m-K} \) along the \( <0001> \) direction. Compared with experimental data of 6.5 to 12.8\( \mu\text{m/m-K} \) \cite{163-166} around room temperature, our results are in the acceptable range and give much detail about the crystal directions. Similarly, the thermal expansions for W along the three axes, \( [111] \), \( [\bar{2}11] \), and \( [0\bar{1}1] \) directions, are shown in figure 4-4. Figure 4-4a, b and c show that the lattice constant at 2500K is on the average 1.9% larger than its nominal value at 0K along each of the three axes. In our calculation, the thermal expansion is in a range of 3.4 \( \mu\text{m/m-K} \) to about 8 \( \mu\text{m/m-K} \), with temperature 0K to 2500K. For comparison, the experimental values of the thermal expansion coefficient is 4.4 to 4.6\( \mu\text{m/m-K} \) \cite{165-166} for W at 20°C, and our simulated one is 3.4\( \mu\text{m/m-K} \) for the temperature in the range between 0K to 500K. The variation is acceptable because, experimentally, no real crystals are perfect. Usually, a smaller value of thermal expansion is measured due to the defects inside the sample, such as voids that will act as buffers for expansion. Also, we cannot measure the thermal expansion along an identical crystal direction by experiments. We may therefore conclude that their temperature dependencies are similar, in that the thermal expansion is non-linear with temperature. Its slope increases as temperature increases, which can confirm the reliability of the interatomic potential.
Figure 4-3  Lattice constant at finite temperatures for Ti on the basal plane (a) along the \( <1\bar{1}20> \) direction, (b) along the \( <\bar{1}00> \) direction, and perpendicular to the basal plane (c) along the \( <0001> \) direction.
Figure 4-4  Lattice constant at finite temperatures for W along the three axes (a) [111], (b) [211], and (c) [011] direction.
In the following, we use the case of a diffusing adatom as an example to describe the calculation details. The same principle applies to a defect cluster, when the position of the adatom is replaced by the position of the center of mass of the cluster. In a dynamic simulation of diffusion at a finite temperature, the trajectory of the adatom is recorded as a function of time. To take into account the stochastic nature of the diffusion process, we follow Soneda et al.\textsuperscript{167} and divide the simulated diffusion process into \( N \) sub-processes, so that each sub-process on the average contains one or several fundamental jumps. Considering that sometimes only several hundred sub-processes are used, visual inspection may help eliminate the contribution from rare sub-processes corresponding to drastically different diffusion coefficients. We then calculate the total squared displacement of a diffusing particle as a function of time according to:

\[
R^2 = \sum_j (r_j - r_{(j-1)})^2
\]  \hspace{1cm} (4-2)

where \( r_j \) is position of the adatom at the end of the \( j^{\text{th}} \) sub-process, and the summation runs over all sub-processes. For the simulation of the adatom at 900\textdegree K, the total squared displacement as a function of time is shown for various numbers of sub-processes in figure 4-5. Once the duration of each sub-process is long enough, the jumps in neighbouring sub-processes are uncorrelated, and therefore the diffusion coefficient is not affected by further increasing the duration. The calculated diffusion coefficients are found to converge when each sub-process on the average contains more than one fundamental jump. For comparison, the total squared displacement calculated by counting the number of fundamental jumps is also shown in the figure.
Figure 4-5  The total squared displacement calculated by counting the number of fundamental jumps (solid line) and those by dividing the simulated process into 2300 (dotted line) and 1400 sub-processes (broken line) for Ti. The overlap of the dotted and broken lines indicates the convergence of the calculations.

The diffusion coefficient of the adatom at 900°K is derived from the total squared displacement of figure 4-4, according to:

\[ D = \frac{R^2}{4t} \]  

(4-3)

where \( t \) is the simulated diffusion time. If no correlation exists, the diffusion coefficient depends on the number \( M \), and distance \( a \) of the fundamental jumps according to \( D_o = Ma^2/4t \). For correlated diffusion, this diffusion coefficient, \( D_o \), is a reference value, and the ratio of \( D \) and \( D_o \) is the correlation factor. In the case of the adatom diffusion at 900K, the correlation factor is 1.06 indicating that the adatom diffusion is forward correlated. Repeating the simulation of figure 4-5 at other temperatures, we obtain the converged diffusion coefficients of the adatom at five finite temperatures. These values can be used to obtain the temperature dependence of the diffusion coefficient. However, the number of Arrhenius functions to be fitted depends on the number of operating diffusion mechanisms. For the adatom, it diffuses
by a single mechanism. Therefore, the diffusion coefficient as a function of temperature is fitted to a single Arrhenius function for the adatom. When multiple diffusion mechanisms operate, several Arrhenius functions must be fitted, as is the case in diffusion of the defect clusters.

To confirm that migration energies derived from the dynamics calculations, we also calculate these energies using the MS method for the identified diffusion mechanisms. For an adatom, a series of nodal points are generated between two nearby positions that are the most stable. At each nodal point, the potential energy of the simulated system is calculated; the adatom is allowed to move on the plane perpendicular to the straight line connecting the two stable positions. For the diffusion of a cluster, the atom that jumps first is placed at various nodal points as the adatom is, leaving other atoms to relax accordingly. In general, the migration barrier derived from the MS calculations is equal to or higher than that obtained from the MD simulations, because the MS calculations may be based on a diffusion bath that is not optimal. The migration energies derived from the MS calculations can nevertheless provide guidance to the fitting of the diffusion coefficients.

To simulate the mechanisms of an adatom diffusing down a step, a compact hexagonal island is placed on the simulated cell described above in figure 4-1. The hexagonal island is formed by an extra monolayer of atoms limited by the six edges of 
\([111]/(\bar{1}0\bar{1})\), \([\bar{1}1\bar{1}]/(10\bar{1})\), \([\bar{1}00]/(01\bar{1})\), \([1\bar{1}1]/(10\bar{1})\), \([\bar{1}1\bar{1}]/(110)\) and \([\bar{1}00]/(011)\) -faceted steps right above the flat surface. The geometry of the hexagonal island with the surface is given in figure 4-6a and the six steps described above are indicated by 1, 2, 3, 4, 5 and 6 in figure 4-6b respectively. In our setup coordinate, the \([111]/(\bar{1}0\bar{1})\) and \([1\bar{1}1]/(10\bar{1})\) steps, the \([\bar{1}1\bar{1}]/(10\bar{1})\) and \([\bar{1}1\bar{1}]/(110)\) steps, and the \([\bar{1}00]/(011)\) steps are symmetric. Therefore, there are only 3 types of steps formed on the island. The three sets of steps with 9, 7 and 9 atoms along the edges of \([111]\), \([\bar{1}1\bar{1}]\) and \([\bar{1}00]\) are chosen, which are equal to about 3 cut-off energy. An adatom is introduced on the island to study its diffusion mechanism down an island. A finite temperature, 1500K is chosen so that edge evaporation, corner break and surface melting are absent during the dynamic simulation. Figure 4-6b shows the surface of the simulated cell. The dark atom represents the adatom on the surface of the island.
while the hexagonal island on the surface is represented by those gray atoms. The light atoms are the surface of the bulk. In figure 4-6b, only the top surface layer with the hexagonal island is shown. They are not in scale.
Figure 4-6  (a) The set up coordinates of the simulated cell with an island on the top surface. The dark atom represents the adatom on the surface of the island, while the hexagonal island on the surface is represents by those gray atoms. The light atoms are the surface of the bulk. (b) The surface coordinates of the island. The open circles represent those atoms of the island, and the grey circles represent those atoms on the top surface of the simulated cell.

Once the mechanisms for the adatom diffusing down a step are identified, MS method as described in the above paragraph is used to find the energy barrier for the observed mechanisms. To investigate the effect of stresses on the mechanism of an adatom diffusing down the island, similar MS calculations are repeated with the set-up atoms under uni-axial stresses of 10 GPa along the [111] direction, in both tension and compression. The calculation results are given at the end of section 4.4.
4.3 *Simulation Results on Surface Diffusion of Ti*

We start with the calculation of defect formation energy, and consider defect clusters of up to eight atoms. The formation energies of these defects are listed in table 4-1. Also listed is energy reduction when one or more atoms are added to form each of the clusters. Effectively, the magnitude of this energy decrease is equal to the binding energy if the cluster with \(n+m\) atoms breaks up into an \(n\)-atom and an \(m\)-atom cluster. The listed binding energies show that when a cluster breaks up into two parts, it is most desirable to have one of the parts an adatom, as compared with breaking into two larger clusters. The energy change clearly indicates that a cluster of three or more atoms is more stable than other clusters of comparable size. The stability is a direct result of the underlying crystal structure; i.e., atoms of the substrate are on a hexagonal lattice. Because of the stability, a trimer and a heptamer are likely the critical nuclei of three-dimensional growth of films on the (0001) surface. The condition under which they act as the nuclei depends on their mobility, as in the following paragraphs.
<table>
<thead>
<tr>
<th>Cluster Description</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formation Energy $E_f$ (eV)</td>
<td>1.16</td>
<td>1.76</td>
<td>1.95</td>
<td>2.23</td>
<td>2.60</td>
<td>2.83</td>
<td>2.76</td>
<td>3.07</td>
</tr>
</tbody>
</table>

Binding Energy for Cluster, $E_b$ (eV)

<table>
<thead>
<tr>
<th>Cluster</th>
<th>$E_b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 adatom + (N-1) cluster</td>
<td>N/A, 0.56, 0.97, 0.88, 0.79, 0.93, 1.23, 0.85</td>
</tr>
<tr>
<td>1 dimer + (N-2) cluster</td>
<td>N/A, N/A, 0.97, 1.29, 1.11, 1.16, 1.60, 1.52</td>
</tr>
<tr>
<td>1 trimer + (N-3) cluster</td>
<td>N/A, N/A, N/A, 0.88, 1.11, 1.07, 1.42, 1.48</td>
</tr>
<tr>
<td>1 tetramer + (N-4) cluster</td>
<td>N/A, N/A, N/A, N/A, 0.79, 1.16, 1.42, 1.39</td>
</tr>
</tbody>
</table>

Table 4-1  Formation and binding energies of Ti defect clusters (eV)

In the diffusion studies, the total square displacement as a function of temperature for Ti on its (0001) surface is shown in figure 4-7a - h. Its diffusion coefficient as a function of temperature is calculated and shown in figure 4-8.
Figure 4-7  The total squared displacement of adatom/cluster as a function of temperature for Ti (a) adatom, (b) dimer, (c) trimer, and (d) heptamer.
Figure 4-8  Diffusion coefficients of the adatom, dimer, trimer, and heptamer. The lines represent the fitted Arrhenius function.

We start with an adatom. The migration barrier of the adatom is fairly small, similar to that of an adatom on the (111) surface of aluminum. On the (0001) surface of Ti, an adatom has only three nearest neighbors in the substrate. Figure 4-9 shows the HCP sites (by symbol “H”) and the FCC sites (by symbol “F”) of the (0001) surface. It also shows the movement of an adatom from a HCP site to a FCC site. The energy of the adatom along the first half of its diffusion path, i.e. from a HCP site to the next FCC site, is calculated by the MS method. The other half of the trajectory from the FCC site to the next HCP site is symmetrical but reversed. We find that the adatom has two nearest neighbors from the substrate even at the saddle point. The small change in the number of nearest neighbors maybe the reason for the small migration energy barrier. Our MS calculations show that the migration barrier is 0.04 eV, slightly lower than the 0.06 eV derived from the dynamic calculations; fitting of the dynamics results to an Arrhenius plot gives the temperature dependence of the adatom diffusion coefficient: \( 4.1 \times 10^{-4} e^{-0.06eV/kT} \text{ cm}^2/\text{s} \). The difference of 0.02 eV is attributed to the uncertainty of the calculations. Although the MS calculations are less important for the adatom diffusion, they prove to be informative for the cluster diffusion, the mechanisms of which are more complex.
Figure 4-9 The trajectory of the adatom (open circle and solid line) moving from an HCP site to an FCC site on the (0001) surface (solid circle). The path from the FCC site to the next HCP is symmetrical but reversed.

In the following, we consider the surface diffusion of a dimer. The dynamic simulations indicate that the dimer diffuses by two mechanisms, as shown in figure 4-10. In the first step, one of the two atoms jumps to a nearby lattice site, and the other one follows; this mechanism is labeled A in figure 4-10. As a result, both atoms of the dimer jump by one nearest neighbor distance. In the second mechanism, labeled as B in the figure, one of the two atoms jumps to a nearby lattice site while the other stays at its original lattice site. This process leads to a rotation of one atom around the other; a substrate atom (labeled C) always stays in between the two atoms during the rotation. Although the two atoms start as a dimer and end up being another dimer in both mechanisms, the migration barriers of these two processes can be entirely different. Wang proposes similar behavior of the Ir dimer: a dimer motion occurs either by jumps of the individual cluster atoms, or localized rotation of cluster atoms \[160\]. Our MS calculations show that the barrier is 0.02 eV when one atom rotates around the other, and 0.14 eV when both atoms jump. As a result of the small barrier of the rotation, the two atoms rotate around each other more often than jump together. The rotation eliminates possible forward correlation of diffusion but does not contribute to diffusion. In the process of diffusion according to mechanism A, one atom jumps to a nearby HCP site through an FCC site. Once the first atom arrives near the FCC site, the other atom follows to its nearby FCC site, maintaining the dimer structure. In the second half of the process, once the first atom arrives at the final HCP site, the other
atom also follows to its nearby HCP site. At the end of the diffusion process, the dimer keeps the orientation of its bond. However, due to the much more frequent rotations, the diffusion is made up of uncorrelated random jumps. Because only one mechanism contributes to the total squared displacement, we can use a single Arrhenius function to fit the temperature dependence of the diffusion coefficients. As shown in figure 4-8, the diffusion coefficient of the dimer can be obtained as $2.9 \times 10^{-4} \ e^{-0.12 \text{eV}/kT} \ \text{cm}^2/\text{s}$. As expected, the migration barrier of 0.12 eV is close to the corresponding results derived from the MS calculations (0.14 eV).

From our simulation results for the surface diffusion of an adatom and dimer, we find that a dimer has a lower energy barrier following path B in figure 4-10. However, from our simulation results of figure 4-8, the diffusion constant of a dimer has a lower diffusion constant. This is because the rotation mechanism (path B of figure 4-10) does not contribute to diffusion. And the surface diffusion is contributed by the jumping mechanism (path A in figure 4-10). And the process of diffusion according to jumping mechanism has a higher energy barrier (0.14 eV), compared to that of a single adatom (0.04 eV).

![Diagram](image)

Figure 4-10  The trajectory of the leading atom (open circle and solid line) and that of the other atom (solid line only) of the dimer during a diffusion jump. The two mechanisms are shown in regions labeled A and B. According to mechanism A, both atoms jump, as indicated by the two solid lines. According to mechanism B, the second atom does not jump, and one of the solid lines is reduced to a solid circle representing the vibration of the atom. Because of symmetry, only half of the path is studied (open circle), but the entire path is shown with a solid line for clarity.
Diffusion of the trimer is much more complex. The atomic trajectories from dynamic simulations indicate that possibly three mechanisms operate during the diffusion, as shown in figure 4-11. According to mechanisms A and B, one of the three atoms is leading and jumps first, while the other two follow in sequence. According to mechanism A, the leading atom drags the other two with it during a diffusion jump. In mechanism B, the leading atom pushes the other two forward during a diffusion jump, and in mechanism C, the three atoms rotated around their center of mass, with a substrate atom staying near the center. Wang\textsuperscript{[160]} shows that there is only one way for the Ir trimer on its (111) surface. The trimer motion of Ir occurs by jumps of individual atoms. Our MS calculations show that the migration energies are 0.19 and 0.22 eV according to mechanisms A and B, respectively. The energy barrier of the rotation is only 0.14 eV, and the rotation will therefore be more frequent and will reduce possible correlation effects. Because the two barriers of diffusion are close, we may use one Arrhenius function to fit the diffusion coefficients of the dynamic simulation results. The use of one Arrhenius function also leads to a smaller error between the fitted function and the simulation results than using two Arrhenius functions. The fitting leads to an expression: \( 2.1 \times 10^{-4} e^{-0.12/kT} \text{ cm}^2/\text{s} \). Based on both fitting and MS calculations, we can draw the conclusion that the diffusion coefficient of the trimer is well represented by a single Arrhenius function. It is worthwhile to point out that the diffusion of trimer is uncorrelated. The lack of correlation may be a result of both fast rotation and large inertia.
Figure 4-11  The trajectory of the leading atom (open circle and solid line) and those of the other atoms (solid line only) of the trimer during a half diffusion jump. The three mechanisms are shown in regions labeled by A, B, and C. Because of symmetry, only half of the path is studied (open circle).

Since the trimer is still very mobile, and experimental results\textsuperscript{[168]} indicate that large clusters are mobile on low index surfaces of metals, the next cluster of study is the heptamer because of its stability. Dynamic simulations show that this large cluster diffuses very fast. To understand the mechanisms of the fast diffusion, we analyze trajectories of the diffusing atoms in detail. Our analyses indicate that the mechanism is surprisingly simple. All the diffusion events start with one of the seven atoms moving to a nearby FCC site. The rest of the atoms follow the first and push it to an HCP site. The others then follow the first atom to an HCP site immediately. Three mechanisms, labeled as A, B, and C in figure 4-12, are possible for the diffusion. Because of the large number of atoms involved, the analysis of the atomic trajectories does not clearly reveal which of the three mechanisms is operative. Using the MS method, we calculate the three possible migration barriers of A, B, C as 0.42eV, 0.50eV, and 0.50eV, respectively. Although there are two different migration barriers according to the static calculation, fitting of the dynamic results gives it a single Arrhenius function: $2.1 \times 10^{-3} e^{-0.39eV/kT} \text{cm}^2/\text{s}$, as shown in figure 4-8. Since the dynamic simulations are carried out at high temperatures, they should include all
operative mechanisms. Combing the static calculations and the fitting, we believe that mechanism A is the only one that is operative. For evidence, Wang observes similar mechanisms for the movement of Ir heptamer \cite{160}. An atom in the outer shell of the heptamer jumps from a bulk site into a surface site adjacent to it. Once this step, which involves breaking three nearest-neighbor contacts, has taken place, other atoms follow until the heptamer center has moved to an adjacent surface site. Due to this motion, no change in the shape of the cluster is observed. Further, the analyses of atomic trajectories indicate that the diffusion of the heptamer is uncorrelated. After each diffusion jump, the seven atoms oscillate around their equilibrium positions for a substantial period of time, eliminating any memory of the linear momentum. The lack of correlation may be a result of the large inertia of the cluster.

![Diagram](image)

**Figure 4-12** The trajectory of the leading atom (open circle and solid line) and those of the other atoms (solid line only) of the heptamer during a diffusion jump. The three mechanisms are shown in regions labeled by A, B, and C. Because of symmetry, only half of the path is studied (open circle), about the entire path is shown with a solid line for clarity.
Using the diffusion coefficients and binding energies, we next estimate the efficiency of the largest cluster, the heptamer, as a critical nucleus during three-dimensional growth of thin films. The diffusion distance \( R \) of the cluster in the duration \( \Delta t \) is:

\[
R = \sqrt{4D\Delta t}
\]  

(4-4)

where \( D \) is the diffusion coefficient of the cluster. Using the diffusion coefficient derived in the last paragraph, we estimate that the heptamer diffuses 60 nm at room temperature in 0.014s, which is the time of growth of one monolayer under typical deposition conditions; the typical deposition rate is taken to be 1 \( \mu \)m/min. For any facets of smaller diameter, the heptamer is therefore ineffective as a critical nucleus in three-dimensional growth on the (0001) surface of Ti films. Previous studies show that most facets are of this dimension; that is, 60 nm. Since the heptamer diffuses even faster at higher temperatures, it is essentially ineffective as the critical nucleus, at room temperature and above.

The effective distances for diffusion of cluster (adatom, dimer, trimer, and heptamer) under typical deposition rate at room temperature are given in table 4.2.

<table>
<thead>
<tr>
<th></th>
<th>adatom</th>
<th>dimer</th>
<th>trimer</th>
<th>heptamer</th>
</tr>
</thead>
<tbody>
<tr>
<td>diffuse distance (( \mu )m)</td>
<td>15</td>
<td>4</td>
<td>3</td>
<td>0.06</td>
</tr>
</tbody>
</table>

Table 4-2 The effective distances for surface diffusion of Ti clusters under typical deposition rate at room temperature.
4.4 Simulation Results on Surface Diffusion of $W$

We start with the calculation of defect formation energy and consider defect clusters of up to eight atoms. The formation energies of these defects are listed in table 4-3. Also listed is the energy reduction when some atoms are added to form each of the clusters. Effectively, the magnitude of this energy decrease is the binding energy, if the cluster with $n+m$ atoms breaks up into two parts with one being an $n$-atoms cluster and another being an $m$-atoms cluster. Similar to the case of Ti, the listed binding energy shows that a cluster breaking up into two parts with one being an adatom is most favored compared with breaking into two larger clusters. The energy change clearly indicates that a cluster consisting of three, four or seven atoms is more stable than consisting two, five, six and eight atoms. The stability is a direct result of the underlying crystal structure; atoms of the substrate are on a parallelogram lattice. Because of the stability, a dimer and a trimer are likely the critical nuclei of three-dimensional growth of thin films on the (011) surface, as the binding energy for a dimer is more than 1eV. Whether it does act as the nucleus depends on its mobility, to be presented in the following paragraphs. The formation energy of the W adatom on (011) surface (2.37eV) is much higher than the Ti adatom on its (0001) surface (1.16eV). It is due to the atomic bonding between the adatom and the surface. A Ti adatom has only three nearest neighbors in the substrate, while a W adatom has four nearest neighbors in the substrate.
<table>
<thead>
<tr>
<th>$N$, number of atoms in cluster</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
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<tbody>
<tr>
<td>Formation Energy $E_f$(eV)</td>
<td>2.37</td>
<td>3.67</td>
<td>4.16</td>
<td>4.73</td>
<td>5.37</td>
<td>6.06</td>
<td>5.95</td>
<td>6.57</td>
</tr>
<tr>
<td><strong>Binding Energy for Cluster, $E_b$ (eV)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 adatom + (N-1) cluster, $E_b$ (eV)</td>
<td>N/A</td>
<td>1.07</td>
<td>1.88</td>
<td>1.80</td>
<td>1.73</td>
<td>1.67</td>
<td>2.48</td>
<td>1.75</td>
</tr>
<tr>
<td>1 dimer + (N-2) cluster, $E_b$ (eV)</td>
<td>N/A</td>
<td>N/A</td>
<td>2.61</td>
<td>2.46</td>
<td>1.77</td>
<td>3.09</td>
<td>3.16</td>
<td></td>
</tr>
<tr>
<td>1 trimer + (N-3) cluster, $E_b$ (eV)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>1.80</td>
<td>2.46</td>
<td>2.26</td>
<td>2.94</td>
<td>2.96</td>
</tr>
<tr>
<td>1 tetramer + (N-4) cluster, $E_b$ (eV)</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>1.73</td>
<td>1.77</td>
<td>2.94</td>
<td>2.89</td>
</tr>
</tbody>
</table>

Table 4-3 Formation and binding energies of W defect clusters (eV)

This time, we only consider surface diffusion of an adatom. It is because the diffusion of W adatom on its ($\bar{0}$I$|$I) surface is much slower, compared with Ti. The diffusion of W adatom is to be presented in the following paragraphs.

In the diffusion studies, the total square displacement as a function of temperature for W on its ($\bar{0}$I$|$I) surface is shown in figure 4-13. Its diffusion coefficient as a function of temperature is calculated and shown in figure 4-14. We observed that by fitting of the dynamics results to a single Arrhenius function: $1.3 \times 10^{-3} e^{-0.34eV/kT} \text{cm}^2/\text{s}$, which indicates that the activation barriers of the operating mechanisms are almost the same. To prove this point, the activation barriers for migration of an adatom on the surface with difference mechanisms are calculated by the MS method. The results are given in the following paragraphs.
Figure 4-13  The total squared displacement of cluster as a function of temperature for W adatom.

Figure 4-14  Diffusion coefficients of a W adatom. The lines represent the fitted Arrhenius function
The dynamic simulations indicate that the adatom diffuses by two paths with mechanisms labeled A and B, as shown in figure 4-15a. In our observation, the probability of mechanisms A and B are almost the same. Figure 4-15b refers to the reference energy when an adatom moves from a kink site to another one near it along path A. Similarly, figure 4-15c refers to the reference energy when adatom moves from a kink site to another one on the right hand side along path B. Similarly, our MS calculations show that the activation barriers of mechanisms A and B are the same; 0.46eV. It is because the two mechanisms, A and B, are symmetrical. Both of the two movements are along the <111> direction. The movement of A is along the $[\bar{1}11]$ direction, while the movement of B is along the [111] direction. As the observed two migration barriers are the same (A and B), fitting of the dynamics results to a single Arrhenius function as shown in figure 4-14. The results of the MS simulation are slightly lower than the 0.54eV derived from the dynamic simulations. The small difference is attributed to the uncertainty of the calculations. Despite being less important for the adatom diffusion, the MS calculations prove to be informative for the adatom diffusion. The migration barrier of the W adatom on its (011) surface is large, compared with the Ti adatom on its (0001) surface. Again, it is because a Ti adatom on its (0001) surface has only three nearest neighbors in the substrate, while a W adatom has four.
Figure 4-15 (a) The trajectories of the W adatom (open circle and solid line) moving from a kink site to another kink site on the surface (solid circle). (b) calculate potential energy of adatom move along path A, (c) calculated potential energy of adatom move along path B. The x axis are the reference displacement of the mechanism, with initial configuration with the adatom on the starting kink site (x coordinate =0) to the final configuration with the adatom moved to another close kink site (x coordinate =1).
Using the diffusion coefficients and binding energies again, we estimate the efficiency of the adatom as a critical nucleus during three-dimensional growth of thin films. The diffusion distance $R = \sqrt{4D \Delta t}$ of equation 4-4 for the adatom in the duration $\Delta t$ is obtained. Using the diffusion coefficient derived above, we estimate that W adatom diffuses 70 nm at room temperature in 0.014s, the same time for the growth of one monolayer under typical deposition conditions (deposition rate is taken to be 1 \( \mu \)m/min) in section 4.3. As dimer diffuses much slower than adatom; for example, Ti dimer diffuses 4\( \mu \)m while Ti adatom diffuses 15\( \mu \)m on its (0001) surface at room temperature under typical deposition conditions. Therefore, we may estimate that a W dimer diffuses several times slower than its adatom. A W dimer is therefore effective as a critical nucleus in three-dimensional growth on its (0\( \bar{1} \)\( \bar{1} \)) surface.

The diffusion of vacancy on the surface is not active during our simulation. To identify our observation, migration barrier of vacancy on its (0\( \bar{1} \)\( \bar{1} \)) surface are calculated by MS method. All the three possible migration paths labeled C, D, and E, which are shown in figure 4-16, are being simulated. Our simulation results show that the activation barriers of mechanisms C and D are the same. Again, it is because they are both along the [111] direction on the surface. The movement of C is along the [\( \bar{1} \)1\( \bar{1} \)] direction, while the movement of D is along the [111] direction. Their activation barriers are 1.15eV and 1.14eV for mechanism C and D respectively. They are shown in figure 4-16a and 4-16b. The 0.01eV difference is attributed to the uncertainty of the calculations. On the other hand, the activation barrier for mechanism C involves a path along the [\( \bar{1} \)00] direction, which is about 4eV in a rough simulation and plotted in figure 4-16c. It is because in B.C.C. structure, the shortest atomic distance is aligned along the <111> direction. Activation energy for mechanism E is much larger than the first two mechanisms, C and D. Therefore, even at high temperature, only the vacancy diffusion mechanisms A and B are considered to be operative. However, compared to the activation barrier of an adatom, 0.46eV or 0.54eV calculated above, the diffusion of vacancy is not favored.
Figure 4-16  Activation energy of vacancy on the surface. (a) Trajectories of possible moving paths; A, B, and C with an neighbour atom moving form a kink site to another close kink site are indicate. Open circles indicate the neighbour atom trajectories while the solid line indicate the moving trajectories of vacancy. The close circles indicate those atoms on the surface. (b) calculate potential energy of vacancy move along path C, (c) calculated potential energy of vacancy move along path D, (d) calculated potential energy of vacancy move along path E. The x axis are the reference displacement of the mechanism, with initial configuration with the adatom on the starting kink site (x coordinate =0) to the final configuration with the adatom moved to another close kink site (x coordinate =1).
To simulate the mechanisms of an adatom diffusing down a step, the geometry of the hexagonal island described in section 4.2 is used. In the dynamic simulations of ten trials with an adatom initially placed on the center of the island, two representative mechanisms are observed for the adatom diffusing down the island. It diffuses down either through the [111] or [I11] steps. All of them involve an exchange mechanism with an atom at the edge when diffusing down the step. In this chapter, we investigate the mechanism of diffusion down of an adatom through the [I11] steps. Figure 4-17a-c is the corresponding mechanism when an adatom diffuse down on one of the [I11] step. The upper figure indicate the surface condition with the step atoms, while the lower figure indicate the “vertical level” of the adatom corresponds to “dropping” down the island. The dark atom represents the adatom on the edge, while the gray atoms represent those atoms of the island, and the light atoms represent those atoms of the surface. In figure 4-17a, adatom diffuse to the edge and stay on the kink site near the step. As shown in figure 4-17b, when the adatom approaches the [I11] edge, the adatom has to push the step-atom further away along the [100] direction. Finally, the adatom will replace the original atom as indicated in figure 4-17c and becomes a step-atom. And the original step-atom is being pushed away and diffuses around the step edges.
Figure 4-17  The corresponding mechanism when an adatom diffuses down the step. The upper figure indicates the surface condition with the step atoms, while the lower figure indicates the “vertical level” of the adatom corresponds to “dropping” down into the island. The dark atom represents the adatom on the edge, while the gray atoms represent those atoms of the island. And the light atoms represent those atoms of the surface. (a) the adatom approaches the $\langle \bar{1}11 \rangle$ edge, (b) the adatom is pushing the step-atom further away along the $\langle 100 \rangle$ direction, (c) finally, the adatom replaced the original step-atom and the original step-atom is being pushed away and diffuses around the step edges.
Its Schwoebed barrier for the above process is calculated by the MS method. In figure 4-18, the calculated potential energy of the system is plotted varies the reference displacement of the adatom diffusing down the step. The initial configuration (coordinate=0.0) corresponds to the adatom at the kink site near the edge of the island, and the final configuration (coordinate=1) corresponds to the adatom replacing the original edge atoms. The calculated Schwoebed barrier of the diffusion jump is 0.6eV (for breaking the old bonds), and after passing through the energy barrier, a total energy of 2.1eV will be released (formation of new bonds). A total energy of 1.5eV is released when an adatom moves down from the $[\bar{1}11]$ step. It is because two [111] bonds and two [110] bonds will be formed when the adatom is placed on the surface. However, three [111] bonds and three [110] bonds will be formed when the adatom is placed on the edge down in the island.

To investigate the effect of applied stress for the mechanism, uni-axial stresses of both tension and compression are applied along the [111] direction. Our simulations show that under compression, similar results are obtained. The Schwoebed barrier of the diffusion jump is 0.6eV, with a total energy of 1.5eV released for the adatom moving down the step. However, the calculated Schwoebed barrier is 0.7eV under tension, and 1.4eV is released for the adatom moving down the step. The shift of energy barrier in figure 4-18 is due to the shift of the energy equilibrium under stress. As the non-symmetric properties of lattice distance varies the direction of stress, a tensile stress should give a more significant shift compared with the same compression. For the small difference (0.1eV) of the activation energy for the diffusion of adatom down the $[111]$ step, we conclude that there are small effects on the above mechanism under the applied stresses.
Figure 4-18  Calculated potential energy of the adatom diffusing down the [111] step. The initial configuration (coordinate=0.0) corresponds to the adatom at the kink site near the edge of the island, and the final configuration (coordinate=1) corresponds to the adatom replacing the original edge atoms. The open circles represent the calculated results without applied stress. The open triangles and diamonds represent the results under uniaxial compression and tension along the [111] direction.
Unlike from the adatom diffusing down a \([\bar{1}11]\) step under uni-axial stresses, we cannot make a conclusion for the adatom diffusing down the other \([111]\) step. It is because the applied uni-axial stress results in a large shear stress along the \([\bar{1}11]\) direction (slip direction) on the \((101)\) plane (slip plane), with Schmid factor of 0.27. However, the Schmid factor is 0 for the \([111]\) slip direction on the \((\bar{1}00)\) plane. Investigation for the other step is required in order to complete the study.
4.5 \textit{Conclusion}

Condensation of the deposited atoms on the surface contributes to the film growth. In this chapter, we consider the mobility of clusters on a surface for two structures, h.c.p. Ti on its (0001) surface and b.c.c. W on its (0\overline{1}1) surface. Comparing the results of the two cases, we investigate the effect of atom-surface interactions (crystallography) and surface temperature on surface mobility. Using the molecular dynamics and the molecular static methods, we investigate the mechanisms of diffusion and clustering on the Ti (0001) surface, and that of an adatom on W (0\overline{1}1) surface. Our studies show:

1. The Ti adatom diffuses very fast, similar to that of an Al adatom on the aluminium (111) surface. The diffusion is also forward-correlated and it may be due to the high frequency of the jumps. However, the diffusivity of W adatom is much slower. We cannot conclude any forward correlation in this case.

2. The Ti trimer and heptamer are more stable than other clusters of comparable size, in accordance with the atomic structure of the underlying substrate. Similarly, the W trimer, tetramer and heptamer are more stable than the other cluster with two, five, six and eight atoms.

3. Diffusion of the Ti clusters is uncorrelated. The lack of correlation is a result of frequent rotation for small clusters, and also may be a result of large inertia of the large clusters.

4. All the Ti clusters investigated, as large as heptamer, are highly mobile. Even the heptamer diffuses 60 nm at room temperature during the time period of growing one monolayer. Therefore, Ti clusters as large as a heptamer are not effective nuclei in the three-dimensional growth of thin films. However, the mobility of W clusters is not as high as Ti. The W dimer or trimer are probably the critical nucleus in three-dimensional growth.

5. Two representative paths are observed for the W adatom diffusing down the island on its [0\overline{1}1] surface. It diffuses down either through the [111] or [\overline{1}11] steps. All of them involve an exchange mechanism with
an atom at the edge when diffusing down the step. The Schwoebel
barrier of the adatom diffusing down the [\(\overline{1}11\)] step is 0.6eV.

6. Although varied in details, diffusion of all the clusters investigated
starts with the jump of one atom. Therefore, in the mobility of clusters,
not all the atoms in a cluster diffuse simultaneously; this is true at least
for the clusters investigated in this chapter.

The formation and migration energies of the adatom and clusters provide the
input to Monte Carlo simulations of thin-film growth. At the same time, diffusion of a
dimer can be simply represented by a random walk of its centre of mass, because the
diffusion is uncorrelated. Further, the orientation of the dimer bond can be randomly
assigned after each diffusion jump, because of the small barrier of rotation.

Knowing the diffusion coefficient of an adatom on the surface, the movement
of adatoms at a finite temperature can be calculated. Therefore, we can estimate the
simulation temperature and deposition rate for film growth to obtain results
comparable to experimental processing. For example, in the simulation of deposition
of W thin film in Chapter 5, the deposition rate is 1 meter per second, in contrast to
the typical value of 1 micron per minute. This high deposition rate is a result of the
limitation of molecular dynamics simulations. The most serious consequence of this
high deposition rate is the lack of diffusion during film deposition. To compensate,
the substrate is kept at a very high temperature, say, 2500K. As a result, the amount of
atomic diffusion during the simulations is equivalent to that during an experiment at
340K at a deposition rate of 1 micron per minute.
CHAPTER FIVE - DISLOCATION NUCLEATION AND PROPAGATION DURING THIN-FILM DEPOSITION UNDER STRESS

In this chapter, we study the nucleation of dislocations and their subsequent propagation during thin-film deposition, using the three-dimensional molecular dynamics method. Aiming to reveal the generic mechanisms, tungsten, an almost elastically isotropic metal is considered. Four cases of tungsten on a stressed substrate of the same material are investigated. In the first two cases, the substrates are under uni-axial compression and tension, respectively, along the [111] direction, with the thermodynamically favored (0\overline{1}1) surface being horizontal. In the last two cases, the substrates are respectively under bi-axial compression and tension along the [111] and [\overline{2}11] directions, with the same thermodynamically favored surface. Half-loop dislocations are observed near the surface.

The simulation method is described in section 5.2, and results are presented with discussions in 5.3 for the substrate under uni-axial compression, in 5.4 under uni-axial tension, 5.5 under bi-axial compressions, 5.6 under bi-axial tensions, and 5.7 describes the verification of the results by annealing. Then, we discuss the results in 5.8. Finally, a summary of this chapter is given in 5.9. Inside this chapter, the method involved for lattice disregistry, stress calculations and critical thickness calculations are given in Appendix I, II and III respectively.
5.1 Introduction

Thin films are employed in a wide range of engineering applications, especially in a form with low defect concentration. For example, tungsten is one of those refractory metals that are often used in the fabrication of semiconductor devices due to its low resistivity and good thermal and electrochemical stability. Polycrystalline aluminum thin films in the form of metal lines are also used to provide good interconnection to transistors in integrated circuits.

It is well known that grain boundaries and dislocations are open paths of fast diffusion, which is responsible for the electromigration failure \(^{[169]}\). Fast diffusion can be reduced or eliminated if the microstructure, in particular the texture and the dislocation density, can be well controlled. This necessitates the understanding of the evolution of grains and the dynamics of dislocations \(^{[70-74,88]}\). However, the effects of dislocation in polycrystalline thin films have not been well understood, particularly at the atomistic level.

The nucleation of dislocations at surfaces and their subsequent propagation into the polycrystalline thin films bears some similarities to the case of epitaxial thin films. For the polycrystalline thin films, dislocations nucleate during film growth, as if the films are deposited on a stressed substrate made of the same materials. During epitaxy, on the other hand, dislocations nucleate when films are deposited on a substrate of different materials; mismatch strain exists in hetero-epitaxy. In view of the common features between the dislocation dynamics in the two types of thin films, it is worthwhile reviewing the studies of epitaxial thin films also.

The theoretical investigation of dislocation dynamics in epitaxial thin films has gone through two stages: analytical formulation and atomistic simulation. The analytical formulation of dislocations in thin films started with Frank and van der Merwe \(^{[22]}\). In this theory, a simple model of one-dimensional springs on a periodically modulated substrate was used. The two competing factors are the strain energy of thin films due to the film-substrate mismatching, and the extra energy associated with the strain field of dislocations. A dislocation is nucleated when its presence leads to the reduction of the total energy. For a given film-substrate system, this critical condition translates into a critical thickness of the thin film, at which the strain energy due to film-substrate mismatching is so large that the total energy decreases with the generation of a dislocation. The formulation is based on energy minimization among possible configurations of thin films. However, it is not clear
how the dislocations nucleate and how they propagate. In an attempt to address the issue of dislocation nucleation and propagation, Matthews and Blakeslee\cite{47} assumed a semi-circular loop on the film surface as the nucleus of a dislocation. They derived a critical radius of the loop, beyond which the dislocation will propagate into the film, while below which the dislocation will be absorbed by the surface. Based on this nucleation mechanism and extension of threading dislocations, they considered more factors in later calculation\cite{48}.

Although simplistic, the analytical theory of Frank and van de Merwe\cite{22} qualitatively predicted the presence of the critical thickness when dislocations start to be present in thin films. Efforts were made to achieve more quantitative predictions by considering some characteristics of the dislocations (such as screw or edge nature of the dislocations)\cite{50}. Still, these theories suffer from two intrinsic drawbacks. First, the thermodynamic equilibrium assumption ignores kinetic effects during thin film deposition. Surfaces of thin films are seldom flat and they are generally rough, and the surface roughness will affect the nucleation of dislocations. Second, the elastic theory ignores the effects of the crystal structure, the importance of which is well known today\cite{52,170}. Comparing the above theoretical calculation with experimental results, only some systems agree with the predicted critical thickness\cite{28-30}. However, in other experiment results, the critical thickness is much greater than the predicted values\cite{32,44}.

Atomistic simulations do not suffer from the same problems as the continuum theories. However, most of the atomistic simulations have been two-dimensional (2D) or quasi two-dimensional, because of the limited computational capacity. In a 2D molecular dynamics study, Smith et al\cite{105} showed that dislocations lie within the voids under unstrained substrate during film growth. When a void is closed on the top during deposition, it can happen that one fewer atom is incorporated, leading to the nucleation of a dislocation in the 2D simulations. Nucleation mechanisms are due to bridging of two outgrowths joined together on a rough surface. Dong et al\cite{113} found that the critical thickness of dislocation nucleation depends not only on the magnitude, but also the sign of the mismatching. According to these authors, dislocations nucleate by squeezing out an atom at the base of the surface depressions when the substrate is under compression, while dislocation nucleation involves concerted motion of a relatively large number of atoms under tension. In another 2D molecular dynamics study, Ichimura and Narayan\cite{122} investigated the nucleation of
misfit dislocations in Ge/(001)Si hetero-structures. An activation energy associated with the propagation of a dislocation loop from the surface towards the interface was calculated. The critical thickness of the dislocation nucleation is larger than those predicted by classical continuum theories. In addition, they also addressed the effects of surface steps. The step formation energy on a surface was found to be negative for compressive misfit stress in the heterolayer, and positive for tensile misfit stress. The step formation energy affects the critical thickness and the energy barrier for dislocation nucleation. Unfortunately, the above atomistic simulations are either two-dimensional or quasi two-dimensional. A three-dimensional molecular dynamics study, which is feasible now, is capable of revealing the nucleation mechanisms more reliably.
5.2 Simulation Method

In this paper, we use the classical molecular dynamics (MD) method to investigate the nucleation and propagation of dislocations during thin film growth. Tungsten is chosen as a representative metal, because (1) it is almost elastically isotropic, and (2) it does not have Shockley partial dislocations. These two features enable a simpler analysis at the start. In the present simulation, interatomic interactions among the BCC tungsten atoms are defined according to the Ackland’s potential in the Finnis-Sinclair form. The tungsten atoms are deposited on a stressed tungsten substrate, with the (0 \bar{1} 1) surface horizontal. This surface orientation is thermodynamically the most preferred. The two horizontal directions are [111] and [\bar{2}11]; the first direction is along one of the Burgers vectors. Sketch of figure 5-1 shows the set up coordinates and growth process for the rough surface of the film.

![Diagram of deposited atoms and layers](image)

**Figure 5-1** Set up coordinates and conditions of the thin film. Atoms of the lower layers (substrate) are fixed to their lattice sites, and other layers are serve as a thermal bath. The deposited atoms result in the growth of the film with a rough surface, as shown.
To minimize the computational effort, dimensions of the initial substrate for the four deposition cases are set as the follows:

Case (1): The dimensions of the initial substrate are set to be 43Å, 130Å and 14Å along the [111], [\( \overline{2}11 \)] and [0\( \overline{1}1 \)] directions respectively, in our simulations. Relaxation of a lattice block under an uni-axial compressive stress of 16 GPa along the [111] direction, with the other two perpendicular directions [\( \overline{2}11 \)] and [0\( \overline{1}1 \)], produces a strain of -0.04 (compression) in the substrate along the [111] direction, and 0.01 (tension) along the [\( \overline{2}11 \)] direction approximately on the substrate. Sketch of the above mentioned set up is shown in figure 5-2a.

Case (2): The dimensions of the initial substrate are set to be the same as in case (1); 43Å, 130Å and 14Å along the [111], [\( \overline{2}11 \)] and [0\( \overline{1}1 \)] directions respectively, in our simulations. A strain, which is obtained from the relaxation of a lattice block under an uni-axial tensile stress of 13Gpa along the [111] direction, with the other two perpendicular directions along [\( \overline{2}11 \)] and [0\( \overline{1}1 \)], is applied to the substrate. The above condition gives a strain of 0.05 (compression) along the [111] direction, and -0.01 (tension) along the [\( \overline{2}11 \)] direction approximately on the substrate. Sketch of the above-mentioned set up is shown in figure 5-2b.

Case (3): The dimensions of the initial substrate are set to be 66Å, 62Å and 14Å along the [111], [\( \overline{2}11 \)] and [0\( \overline{1}1 \)] directions, respectively, in our simulations. A bi-axial compressive strain of -0.02 is applied to the substrate along the [111] and [\( \overline{2}11 \)] direction, respectively. Sketch of the above mentioned set up is shown in figure 5-2c.

Case (4): The dimensions of the initial substrate are set to be similar to case (3); 70Å, 66Å and 14Å along the [111], [\( \overline{2}11 \)] and [0\( \overline{1}1 \)] directions, respectively, in our simulations. A bi-axial tensile strain of 0.04 is applied to the substrate along the [111] and [\( \overline{2}11 \)] direction, respectively. Sketch of the above-mentioned set up is shown in figure 5-2d.
Figure 5-2  Set up coordinates and conditions of the substrate for the simulation of thin film growth by physical vapor deposition. (a) under uni-axial compressive stress, (b) under uni-axial tensile stress, (c) under bi-axial compressive stress, and (d) under bi-axial tensile stress.
The periodic boundary condition is applied along the two horizontal directions, leaving two free surfaces along the $[0\overline{1}1]$ direction. Atoms within the bottom 7 Å (that is 1.5 times the cutoff distance of the interatomic potential) of the substrate are fixed to their BCC lattice positions, to mimic the bulk of one grain in polycrystalline thin films. Atoms within the top 7 Å of the substrate are subjected to random frictional forces, and effectively serve as a cooling layer $^{[162]}$. This stress is represented by applied strain, and the two are related by using the Parrinello-Rahman algorithm $^{[134]}$.

The stressed substrate is bombarded by tungsten atoms, which carry 0.01 eV of kinetic energy and are directed toward the substrate vertically. This particle source essentially simulates a 100% collimated physical vapor deposition process. The small kinetic energy is chosen to minimize the surface over-heating. The simulation cell for case (1), after deposition of nine atomic layers, is shown in figure 5-3. The gray scale is an indication of shear stress on each atom, with the lighter color corresponding to higher stress.

![Deposited atom (0.01eV)](image)

**Figure 5-3** A typical simulation cell, with directions of trajectory of deposited atoms and applied stress indicated. The gray scale represents the von Mises shear stress — the lighter scale corresponds to higher stress.
It is worth mentioning that the film in figure 5-3 is deposited at the rate of 1 meter per second, seven orders of magnitude faster than the typical deposition rate of 1 micron per minute. This high deposition rate is a result of the short time scale in molecular dynamics simulations. The most serious consequence of this short time scale and high deposition rate is the lack of diffusion during film deposition. To balance this artifact, we keep the substrate at a very high temperature, 2500K (about 0.7 $T_m$). As the results in Chapter 4 indicate, the amount of atomic diffusion in the simulations is equivalent to the condition under 1 micron per minute during an experiment at about 340K.

During each simulation, the positions of deposited atoms are recorded periodically for analysis. In order to facilitate the visualization, the thermal fluctuation of the positions is eliminated by quenching each set of the recorded atomic positions to about 0.1 K. An “atomic movie” is prepared, using a sequence of the atomic positions under the condition of lattice disregistry (refer to appendix I), to identify dislocations. Potential energy, the von Mises $^{[173]}$ atomic shear stress, and lattice disregistry methods are used to differentiate atoms near a dislocation from the rest. Because high potential energy and shear stress might exist on atoms that are far away from any dislocations, we take the above conditions for guidance only. The dislocation position and configuration are uniquely defined using atomic positions. The dislocation Burgers vector is defined by SF/RH Burgers circuits $^{[174]}$.

We use relaxation method (please refer to Chapter 2.3 for the backgrounds of MD modeling) to verify the above simulation results. The dimensions of the initial substrate are set to be the same as before, 43Å and 130Å along the [111] and $\bar{[211]}$ directions respectively. However the dimension along the $[0\bar{1}1]$ direction is set to be 50Å, i.e., about 22 atomic layers. A cluster step with edges in the $[\bar{1}11]$, [111], and [100] directions is put on the top of the $[0\bar{1}1]$ surface. They are the three close-packed directions on the $[0\bar{1}1]$ surface to form a polygon. In our simulation work, the strain obtained from the relaxation of a lattice block, under the application of an uni-axial compressive/tensile stress along the $[111]$ direction, is applied to the whole simulation cell. Similar to the 4 cases in the foregoing, atoms within the bottom 7 Å (that is 1.5 times the cutoff distance of the interatomic potential) of the substrate are fixed to their BCC lattice positions, to mimic the bulk of a grain in polycrystalline
thin films. Atoms within the top of the substrate are subjected to Langevin forces to mimic the required temperature of 2500K for the entire relaxation process \cite{162}. The periodic boundary condition is applied along the two horizontal directions, leaving two free surfaces along the \([0\bar{1}1]\) direction. The simulation results are given in section 5.7.

Before presenting the results of dislocation dynamics, we describe the calculation of the lattice constant under applied stress and at finite temperatures in the following. The stress on the substrate is applied via the elastic strain, which is derived according to the Parrinello-Rahman algorithm \cite{134}. Using a perfect crystal cell, which is 40 \(\text{Å} \times 39 \text{Å} \times 45 \text{Å}\) along the \([111]\), \([2\bar{1}1]\) and \([0\bar{1}1]\) directions, respectively, we have calculated the lattice constants along the three directions. In the first two cases, only an uni-axial stress along the \([111]\) direction is applied. The temperature is first brought to 2500K using Langevin forces \cite{162}, which is then removed to keep the simulation cell a micro-canonical system. The calculated lattice constants are plotted as a function of temperature in figure 4-4a-c in Chapter 4, section 4.2. The thermal expansion coefficient is consistent with those obtained by experiment. For more details of the lattice constant determination, the readers are referred to Chapter 4.2. The change of the lattice constants due to stresses are analyzed in figure 5-4. The calculated lattice constants are plotted as a function of the applied uni-axial stress and bi-axial stresses in figure 5-4a and figure 5-4b respectively. The elastic modulus given by experiments are observed under tension and small stresses (provided that the test sample are in the elastic region). Therefore, we compare the slope under bi-axial compressive stress of 1GPa and 3GPa in figure 5-4b. The elastic modulus is 430GPa and 390GPa under compression of 1GPa and 3GPa, respectively. Compared with the experiment results of elastic modulus of 400GPa \cite{175}, our MD results are consistent with the experimental ones. The change of the lattice constants consists of two parts: that due to the stress, and that due to the thermal expansion at 2500K. In the simulations of thin film deposition, the lattice constants of the substrate are fixed according to the applied stress and the substrate temperature.
Figure 5-4  The calculated lattice constants as a function of (a) applied uni-axial stresses, and (b) applied bi-axial stresses. The open circles indicate the lattice constant along [111] direction (x-axis), while the open triangles and crosses indicate the lattice constants along [211] (y-axis) and [011] (z-axis) direction, respectively.
To proceed with the simulation of the deposition process, we need information on the diffusion of an adatom on the \((0\bar{1}\ 1)\) flat surface. This we have accomplished in Chapter 4. Following Soneda et al. \(^{[176]}\), we divide the simulated diffusion process into \(N\) sub-processes and the calculated diffusion coefficients are found to converge when each sub-process on average contains more than one or two fundamental jumps. At each temperature, the diffusion coefficient is calculated according to \(D = \frac{R^2}{4t}\) where \(R^2/t\) is the slope of the total squared displacement as a function of time. Repeating the simulation at several finite temperatures, we can fit the diffusion data to an Arrhenius function, assuming that a single diffusion mechanism operates. According to the calculated diffusion coefficient, the mean distance that a deposited atom migrates before burial is estimated to be \(\sqrt{4DAt} = 29\text{Å}\), under a deposition rate of 1 meter per second at 2500K as used in our simulation; the burial time is taken to be that of growing one monolayer. This diffusion distance corresponds to that under a deposition rate of 1 micron/minute at about 340K, according to the adatom diffusion coefficient. Details of the surface diffusion of tungsten are given in Chapter 4. To obtain an estimated measure of the rate of diffusion, we checked the surface roughness during deposition. Prior to the dislocation nucleation, the height variation of the surface roughness is less than three atomic layers. No voids are observed during the deposition process. We noticed that the surface roughness increases as dislocations are nucleated. Some studies have shown that stresses may affect the surface instability and result in an increase of surface roughness.\(^{[177-178]}\) It is worth mentioning that an equivalent amount of surface diffusion, although not sufficient to guarantee the equivalence of low and high temperature simulations, does minimize the risk of artificial roughness.
5.3 Simulation Results of Case 1: substrate under uni-axial compression

Using the substrate with the stress condition i.e., an uni-axial compression of 16 GPa, and temperature, setup as aforementioned, a dislocation is nucleated when the film grows to 6-8 atomic layers. Along the direction of compression, the magnitude of the strain is about 4% and 1% along [111] and [211] directions respectively. The nucleation of dislocation is first identified using the "atomic movie" under lattice disregistry, which have been described in Appendix I, and then confirmed by configuration analyses. Under the setup conditions, two types of nucleation have been observed. When the allowed space is less than one Burgers vector along the principal stress axis, a dislocation is nucleated with Burgers vector $\frac{1}{2}[1\overline{1}\overline{1}]$. However, when there is sufficient space (more than one Burgers vector along the principal stress axis), a sessile dislocation half-loop (sessile type) is nucleated on the \{110\} plane with Burgers vector $\frac{1}{2}[\overline{1}\overline{1}\overline{1}]$. The two types of dislocations are described in the following paragraphs.

We repeat the simulation, with dimensions along [111] and [211] increased by a factor of 1.5, keeping all other conditions the same. It is interesting that both cases discussed above are observed during the same simulation when the larger simulation cell is used.
5.3.1 Dislocation Nucleation on the (101) Plane

![Diagram of dislocation nucleation](image)

Figure 5-5 Sketch of the simulation block with indicates two symmetric (110) and (101) planes are shown. The dash-line indicates the thickness of the film deposit. The thick curve indicates the dislocation half-loop. The solid thick line then becomes the bottom of the dislocation half-loop. The ‘eye’ indicates the direction of the plane that shows in figure 5-6 and 5-7, as reference coordinates.

For the first event, a dislocation is nucleated on a non-flat surface on the (101) plane, and propagates into the film for two or three atomic layers. A sketch of the simulation block with indicated planes and coordinates is given in figure 5-5. Under the compressive stress, an atom (circled in figure 5-6b) near a step is ejected from a \(\{0 \bar{1} 1\}\) surface layer, leaving a vacant site behind. Atoms along the \([1 \bar{1} \bar{1}]\) direction in this layer relax to share the extra space left. Then, atoms along the relaxed direction form a twin structure on the \(\{0 \bar{1} 1\}\) layer, contained by dislocation lines created along the two ends, 3 atomic layers into the substrate (figure 5-7). Since a dislocation line
must not end in the bulk, a dislocation line is anticipated to connect the two ends of the dislocation lines forming a dislocation half-loop. With reference (101) plane in figure 5-5, atoms in the five (101) layers neighboring the dislocations are projected along the [111] direction in figure 5-7. The relative shift of the atomic positions indicates the area contained by the dislocation, and the absence of vertical shift indicates that the Burgers vector is on a horizontal plane (011). It extends quickly by gliding in the [111] direction. Note that the small vertical shift near the surface is the result of surface relaxation, and should not be confused with the atomic shift near the core of a dislocation.

Figure 5-6 One of the (101) atomic layers containing the dislocation, (a)481ps, (b)482ps, and (c)483ps after the deposition starts. The snapshot in (b) corresponds to the moment when an atom is being ejected. The circle with a dot indicates the direction pointing out of the paper. The grey scale in represents the von Mises shear stress – the lighter scale corresponds to higher stress.
Figure 5-7  Projection of atoms in five (101) layers neighboring the dislocations, along the [111] direction. The snapshot is taken 485ps after the deposition starts. The circle with a dot indicates the direction pointing out of the paper. The grey scale represents the von Mises shear stress – the lighter scale corresponds to higher stress.

In order to identify the Burgers vector, atomic arrangements in a horizontal (011) layer near the surface are shown in figure 5-8. From the sketched Burgers circuit, it is clear that the Burgers vector is \( \frac{1}{2}[1\bar{T}1] \). The dislocation propagates toward the substrate for two to three atomic layers along the (101) plane. The later stage of the propagation is not investigated in detail, because the periodic boundary condition may have introduced artifacts due to the interaction of the dislocation with an infinite number of its own image. To understand why the dislocation is nucleated on this (101) plane, we have calculated the Schmid factor on all possible \{110\} planes with the shortest Burgers vector in one of the \(<111>\) directions, and found that the largest Schmid factor occurs on (101), (110) and (011) planes. They are the (101) plane with either [\bar{T}11] or [1\bar{T}1] slip direction; the (110) plane with either [1\bar{T}1] or [1\bar{T}1] slip direction; and the (011) plane with either [1\bar{T}1] or [1\bar{T}1] slip direction (refer to figure 5-3 for the coordinate of the planes). Calculations of all the possible planes with slip directions are given in Appendix II. As (101) and (110) planes are symmetric planes under our set-up coordinate, a dislocation can also be nucleated on the (110) plane consistent with the analyses of the Schmid factors.
However, the (011) plan is the only one of the planes with the same Schmid factor on which dislocation nucleation is not seen.

Figure 5-8  Atoms in a (0\bar{1}1) horizontal layer near the surface, 500ps after the deposition starts. The solid line is a sketch of Burgers circuit around the core of the dislocation, and the arrow represents the Burgers vector. The circle with a dot indicates the direction pointing out of the paper. The grey scale is represents the von Mises shear stress – the lighter scale corresponds to higher stress.
5.3.2 Sessile Dislocation Half-loop on (011) Plane

Figure 5-9 An "atomic movie" of nucleation of sessile dislocation half-loop at the simulation time of (a) 1300ps, (b) 1400ps, (c) 1500ps, and (d) 1900ps under uni-axial compression.
For the second type of events, a dislocation is nucleated also on a non-flat surface, but on the (011) plane, and the dislocation is sessile. Figure 5-9a-d shows, through lattice disregistry, successive snapshots of the nucleation and propagation of a sessile half-loop. Here only atoms of the substrate and surface, as well as those atoms indicated by lattice disregistry for the dislocation loop (dark color) are shown. Dislocation nucleation starts at the simulation time step of 1300ps in figure 5-9a. In the initial stage, it moves into the substrate slowly by climbing two atomic layers. Due to its slow propagation by continuance of the climbing mechanism, we call it a sessile dislocation loop. Then, as the simulation continues, the bottom of the sessile dislocation half-loop forms.

![Diagram](image)

**Figure 5-10** Growth and propagation of sessile dislocation half-loop on (011) plane, with a reference close-packed (110) plane that cut the half-loop. The dash-line indicates the thickness of the film deposit. The thick curve indicates the dislocation half-loop. The solid thick line then becomes the bottom of the dislocation half-loop, and the thick dotted line indicates the propagation direction of the dislocation half-loop for the further growth of the film.
Figure 5-10 indicates the plane where the dislocation half-loop is situated and propagates. The dash-line indicates the thickness of the films. The thick curve indicates the dislocation half-loop. The solid thick line then becomes the bottom of the dislocation half-loop, and the thick dotted line indicates the propagation direction of the dislocation half-loop for further growth of the film. The dislocation nucleates and propagates on the (011) layer with Burgers vector in the [111] direction. With reference planes in figure 5-10, the nucleation process in our simulation is given in the following paragraphs.

Atomic arrangements in the $\{1\bar{1}0\}$ layer are shown in figure 5-11, which shows a horizontal cut of the half-loop with Burgers vector in the plane. Near a surface step, two atoms (as circled in figures 5-11a and 5-11b) are ejected, one after another, from a surface layer. Following the ejection, the atoms in this layer relax along the [111] direction to take up the extra space of the vacancy, as shown in figure 5-11c. In figure 5-12, atoms in seven (011) layers neighboring the dislocations are projected along the [0$\bar{1}1$] direction. The relative shift of atoms indicates the location of the dislocation half-loop. Also the lack of a vertical shift indicates that the Burgers vector is along the horizontal $(0\bar{1}1)$ plane, similar to the first case.
Figure 5-11  Atoms in one \(\{1\overline{1}0\}\) layer. (a)970ps, (b)976ps, (c)978ps, (d)1830ps after the deposition starts. Atoms to be ejected are indicated by circles. The circle with a dot indicates the direction pointing out of the paper. The grey scale is represents the von Mises shear stress – the lighter scale corresponds to higher stress.
Figure 5-12  Projection of atoms in seven (011) layers neighboring the dislocations, along the [011]; this snapshot is taken 980ps after the deposition starts. The grey scale of atoms indicates the positions along the [011] direction. The circle with a dot indicates the direction pointing out of the paper.

To identify the Burgers vector, atoms in a horizontal (011) plane are shown in figure 5-13. The sketched Burgers circuit clearly shows that the Burgers vector is \( \frac{1}{2}[111] \). Since this Burgers vector is not in the plane (011), the dislocation does not propagate into the film. Rather, it extends upwards as the film is grown (figure 5-11d) – if any climb occurs, it is too slow to be visible.
Figure 5-13  Atoms in a horizontal layer near the surface, 1830ps after the deposition starts. The solid line is a sketch of Burgers circuit around the core of the dislocation, and the arrow represents the Burgers vector. The circle with a dot inside indicated the direction point out of the paper. The grey scale is represents the von Mises shear stress – the lighter scale corresponds to higher stress.
Comparing the figures 5-9 and 5-12, we observe that the dislocation core obtained by the lattice disregistry method (figure 5-9) and projection method (figure 5-12) are different even though they are taken from the same set of data. By the calculation base on lattice disregistry, there are no atoms selected by lattice disregistry near the center of the dislocation half-loop (figure 5-9c and d). Only those atoms around the dislocation core are selected. Therefore, we can get the dislocation loop clearly with the plot atoms that indicate the core of the dislocation line. However, by the projection method, the area of the dislocation half-loop involved is observed (figure 5-12). The dislocation line cannot be observed directly. This can be explained in the following paragraphs.

Take a sketch dislocation half-loop in figure 5-14a-b. Figure 5-14a is the defined of ½ dislocation half-loop with a whole Burgers vectors. Figure 5-14b is the projection of two dislocation planes, one is above the dislocation loop and one is under the dislocation loop. Open circles indicate those atoms on the upper layer, and dark circles indicate those atoms on the lower layer. As only ½ half loop (1/4 circle) are drawn, b=1/2 whole Burgers vectors. Therefore, all the atoms in the center of the half loop (around location B) will shift for ½ b, not a whole b, while atoms around the dislocation loop (curve of A to C) will shift in a factor of b. The other half-loop of b will be in the end of another mirror of the ¼ circle (which are not drawn in the figure). Therefore by projection, we cannot see the overlap of the atoms in the two layers (as shown in figure 5-14b). But is the shift is two whole Burgers vectors for the half-loop, then we see the total overlap of the atoms around the center of the dislocation half-loop.

In reality, the shift between the two atomic layers is smoothly transmitted with ‘effective stressed regions’ in some atomic layers. Therefore, when atoms are indicated by lattice disregistry and suitable criteria are set, only those atoms around the core of the dislocation line of the half-loop will be selected. But for the projection method, it is IMPOSSIBLE to get the overlap of those atoms in the center of the half-loop with the ‘effective stressed regions’ in this case.

Therefore, we conclude that: (1) By projection method, for some kinds of dislocation half-loop we cannot see the overlap of atoms in the center of the loop. It depends on the direction and magnitude of the Burgers vectors. (2) By using lattice disregistry, only those atoms around the curve of the dislocation line will be selected as the shift is smoothly formed in two or three atomic layers.
Figure 5-14 Sketch of dislocation half-loop. (a) is the defined of \( \frac{1}{2} \) dislocation half-loop with a whole Burgers vector. (b) projection of two dislocation planes, one (open circles) is above the dislocation loop and one (dark circles) is under the dislocation loop.
5.3.3 Effects of Surface Steps for Dislocation Nucleation

In comparing the cases of the two types of dislocations, we note that the dislocation lines in both cases extend in a direction parallel to a surface step, and this direction determines the residential plane of the dislocation. The correlation between the direction of extension and the surface step will be elaborated in the next paragraph with reference to figure 5-15. It is possible that the availability of a surface step dictates which of the two types of dislocations nucleates.

It is important that the results are independent of the size of the simulation cell, in particular when the dislocations are involved. This is because dislocations interact with each other even at large separations. We repeat the simulation, increasing the dimensions along $[111]$ and $[\overline{2}11]$ by a factor of 1.5, keeping all other conditions the same. It is interesting that both cases discussed above are observed during the same simulation when the larger simulation cell is used. The atomic arrangement on a horizontal $(0\overline{1}1)$ plane near the surface is shown in figure 5-15a. The aforementioned two types of dislocations are indicated by the two Burgers circuits “I” and “II”, respectively. Two other dislocations are about to nucleate on the right side of figure 5-15a, as indicated by the high von Mises shear stress. The dislocation encircled by “I” is equivalent to that observed in the smaller simulation cell, although it is on the $(110)$ plane, in contrast to the one in the smaller simulation cell, which is on the $(011)$ plane. Under the uni-axial compression, the two planes, $(110)$ and $(011)$, are equivalent in BCC tungsten – having the same Schmid factors. In other words, the mechanisms of dislocation nucleation and propagation are independent of the simulation cell dimensions used. The surface structure corresponding to the dislocation structure in figure 5-15a is shown in figure 5-15b. For clear visualization, atoms in complete layers – except for a few vacancies – are not shown. Comparing figures 5-15a and 5-15b, one can see that the dislocations have extended along the directions of surface steps; the complete layers between surface steps indicate the step directions.

The identified dislocation nucleation mechanism confirms the 2D molecular dynamic simulation results$^{[113]}$ that ejection of one surface atom is the starting point of the formation of an edge dislocation with a Burgers vector parallel to the substrate. The nucleated dislocation climbs downward into the substrate, relieving the applied stress. The 2D simulations show that the nucleated dislocation is free to glide parallel
to its Burgers vector. Apart from the consistency with the 2D atomistic simulations, our 3D studies provide a direct observation of the dislocation geometry, and the formation process of a half-loop during the nucleation stage. The 3D observation of the formation of the half-loops confirms the continuum assumption of half-loop formation at nucleation\textsuperscript{[47]}. Furthermore, some of the half-loops have been observed to shrink back at the film surfaces right after their nucleation, under the line tension of the loop line. As is well known, the nucleation mechanism also depends on the tensile or compressive nature of the applied stress.
Figure 5-15  (a) Atoms in one \((0 \bar{1} 1)\) horizontal layer near the surface in a simulation using larger dimensions, and (b) top view of atoms in the top two incomplete surface layers without showing atoms in the complete layers; both snapshots are taken 400 ps after the deposition starts. The solid line is a sketch of Burgers circuit around the core of the dislocation, and the arrow represents the Burgers vector. The circle with a dot indicates the direction pointing out of the paper. The grey scale in (a) represents the von Mises shear stress – the lighter scale corresponds to higher stress, and the grey scale in (b) represents the height of the incomplete layers – the lighter scale corresponds to smaller height.
5.4 Simulation Results of Case2: substrate under uni-axial tension.

With the substrate under an uni-axial tension of 13 GPa, and temperature at 2500K, setup as aforementioned, a dislocation is nucleated when the film grows to 11-13 atomic layers. In the direction of the tension, the magnitude of the strain is 0.055. Again, two types of dislocations are nucleated according to the available space for relaxation. When the available space is less than one Burgers vector, a glissile half-loop is nucleated, which grows by gliding on two of the \{112\} planes. When the available space is much larger, a sessile dislocation is nucleated. This simulation result is obtained when the dimensions of the initial substrate is increased to 1.5 times the original ones, i.e., 65Å, 195Å and 14Å along the \([111]\), \([\bar{2}11]\) and \([0\bar{1}\bar{1}]\) directions respectively. The sessile dislocation and the Burgers vector are not on the interstitial plane. However, the nucleation mechanisms of both types of loops are very similar. Both are produced by the insertion of atoms from the surface to release the applied stresses, by adjusting the space with those atoms aligned in one of the \{111\} directions. They are described in the following sub-sections in details.

5.4.1 Nucleation of Glissile Dislocation Half-loop on \{112\} Plane by Gliding

For the glissile type of dislocation half loops, the nucleation event is first identified by lattice disregistry in the successive snapshots of figure 5-16a-d, which is subsequently confirmed by configuration analyses. A dislocation starts to nucleate in figure 5-16b. Then, the loop grows in the glide plane in figures 5-16c and 5-16d.

Figure 5-17 indicates the alignment of the dislocation half-loop and its propagation. The thick solid line (small half-circle) is the initial stage of the dislocation half-loop, and the thick dotted line indicates the further growth of the dislocation half-loop with the propagation direction (with arrows). The dislocation nucleates and propagates on the \((112)\) layer with Burgers vector in the \([1\bar{1}1]\) direction. With the reference planes in figure 5-17, the nucleation process in our simulation is given in the following figures. The sketch of figure 5-18 indicates the atomic alignment on the top surface, with the atoms involved in the propagation (dark atoms) mechanism. A dislocation nucleates near a step, and propagates into the film as a half-loop, on the two neighboring \((112)\) planes.
Figure 5-16 An “atomic movie” of nucleation of sessile dislocation half-loop at the simulation time of (a) 1300ps, (b) 1330ps, (c) 1340ps, and (d) 1390ps under uni-axial tension. Results are obtained form another set of simulation starts with a thicker thermo static layers.
Figure 5-17  Growth and propagation of glissile dislocation half-loop on (112) plane, with a reference close-packed (110) plane that cut the half-loop and its symmetric (121) plane. The thick dotted curve with arrows indicates the dislocation half-loop and its propagation direction during film growth under uni-axial tension.
Figure 5-18  Atoms on the $(0\bar{1}1)$ horizontal surface – only part of the simulation cell is shown for clarity. The dark color indicates atoms squeezed into the film along the $[11\bar{1}]$ direction. The two dotted lines indicate directions of dislocation extension, and the extension follows a zig-zag path between the two parallel lines. The circle with a solid dot indicates the direction pointing out of the paper.
By another set of simulation results, one of the \((1 \bar{1} 0)\) layers (refer to figure 5-17), which shows a horizontal cut of the half-loop with Burgers vector in the plane, is shown in figure 5-19a-c; the nucleation starts at the encircled atom. First a step is formed on the surface, as is shown in figure 5-19a; the step would also show up in parallel \((1 \bar{1} 0)\) layers. The atom near the step, as indicated by the circle, inserts into the film along the \([11 \bar{1}]\) direction, as shown in figure 5-19b. Afterwards, the atom at the upper edge of the step relaxes down to eliminate the sharp step, as shown in figure 5-19c; the energy is likely minimized by the elimination of the step. This nucleus of dislocation propagates along the \([\bar{3}11]\) line, which is in close proximity of the surface step. This process generates a dislocation, and the corresponding Burgers vector has a component of \([\bar{1}11]\) in the \((1 \bar{1} 0)\) plane; as will be seen later, this component is also the whole Burgers vector.

To identify the geometry of this dislocation, atoms in seven \((112)\) layers (refer to figure 5-17 for the plane) neighboring the dislocations are projected along the \([111]\) direction, as shown in figure 5-20. A small half-loop is nucleated in figure 5-20a, and it extends by propagation to a near circular half-loop in figure 5-20b. Theoretically, there should be only a shift of atoms along the Burgers vector’s direction around the dislocation core. In reality, the elimination of the surface step is not so prefect. Taking the projection along the same \([111]\) direction for the dislocation half-loop in figure 5-19c, we find that we can see a shift of atoms in this projection until the dislocation half-loop totally propagates into the substrate. They are not shown in the following figures because the artifacts, such as the periodic boundary, in this stage are too large. The shift in level of the surface step in figure 5-19c results in the shift of atoms not only in the dislocation core, but also in the center of the dislocation half-loop.
Figure 5-19 Atomic positions in one of the \( \{1\bar{1}0\} \) atomic layers containing the dislocation nucleus at, (a)1873ps, (b)1883ps, and (c)1893ps after the deposition starts. The circle with a solid dot indicates the direction pointing out of the paper.
Figure 5-20  Projection of atomic positions in seven (112) layers neighboring the dislocation, along the [111] direction – only part of the simulation cell is shown for clarity. The snapshot is taken at (a) 1883ps and (b) 1889ps after the deposition starts. The grey scale of atoms indicates the depth of various (112) layers. The normal vector of the (112) plane is also indicated by an arrow in (a).
In another simulation, similar phenomena are observed. In this case, the step is reversed, favoring nucleation of a dislocation on the \((\{121\})\) plane. The nucleation starts by inserting one atom along the \([\bar{1}1\bar{1}]\) direction. Both the \((121)\) plane and the \([\bar{1}1\bar{1}]\) direction are symmetrical images of the \((112)\) plane and the \([11\bar{1}]\) direction when the step is reversed (refer to figure 5-17). It is worth mentioning, the two glide planes, \((112)\) and \((121)\), also have the largest Schmid factor in the simulated stress condition. The \((211)\) plane is the other one that has the largest Schmid factor. Calculations for all the possible planes with Schmid factor are given in Appendix II. However, the corresponding \((111)\) direction is the \([\bar{1}11]\), which is in the horizontal \((0\bar{1}1)\). If an atom was to squeeze in along the \([\bar{1}11]\) direction, the tensile stress under the surface is not released. As a result, nucleation of the corresponding dislocation does not minimize the total energy. This scenario is consistent with the fact that no dislocation on the \((211)\) plane has been observed; validation of the hypothesis using energy calculation is under way.
5.4.2 Nucleation of Sessile Dislocation Half-loop by Interstitial Plane

The second event for the sessile type is the generation of an extra layer, which extends to several atomic layers along the [111] direction. A dislocation nucleates on a non-flat surface, and propagates into the film for two to three atomic levels. Then, it becomes the bottom of a sessile dislocation half-loop. Figure 5-21 indicates the two symmetric planes where the dislocation half-loop may align and propagate. The thick curve indicates the bottom of the dislocation half-loop with direction of Burgers vector.

Figure 5-21 Growth and propagation of sessile dislocation half-loop on one of the \{110\} planes, with a reference close-packed \{1\bar{1}0\} plane that cut the half-loop. The bottom of the sessile dislocation half-loop with the two symmetric \{110\} and \{101\} planes are shown. The dash-line indicates the thickness of the film deposit. The thick curve indicates the dislocation half-loop. The solid thick line then becomes the bottom of the dislocation half-loop.
With reference planes in figure 5-21, the mechanisms for the movement of those interstitial atoms are shown in the following figures. Atomic arrangements in the (1\overline{1}0) layer are shown in figure 5-22a-c. Initially one atom on surface is inserted into the top layer (figure 5-22a). The extra atom takes the space shared by those atoms along the [111] directions. Then, the point defect made by the interstitial atom extends along the surface. However, it extends into the interface for only a few atomic layers. Figures 5-22b and 5-22c show the extension of the defect into the interface. The original atom under the top layer inserted into the next lower layer under the top one, while a diffuse adatom inserted into the top surface again. The same mechanism repeats again until the interstitial of the third layer is below the top surface. This defect cannot propagate into the interface anymore as the Burgers vectors are not aligned on the dislocation plane. The movement of insertion of extra atoms inside the film also extends along the [\overline{1}11] direction on the surface. The extension of the interstitial atoms results in the insertion of an extra layer on the top of the film.
Figure 5.22 One of the $\{1\bar{1}0\}$ atomic layers containing the dislocation, (a) 1192ps, (b) 1202ps and (c) 1204ps after the deposition starts. The snapshot corresponds to the moment when an extra atom (circled in (a)) is being inserted. The dark atoms are chose out by lattice disregistry. The circle with a dot indicates the direction point out of the paper.
Figure 5-23 is the snapshot of atoms projected along the [100] direction. A dislocation half-loop is observed by the interstitial plane (refer to figure 5-21). As the relative shift of the atoms are all in horizontal direction, we conclude that the atoms only move on the (0 1 1) horizontal plane to adjust their position, and the Burgers vector is aligned on the (0 1 1) plane.

Figure 5-23  Projection of atoms in six (110) alternative layers neighboring the dislocations, along the [100] direction. The snapshot is taken at 1192ps after the deposition starts.

Considering the projection snapshot of figure 5-24a along the (0 1 1) direction, we find that all those extra atoms take up the space freed by those atoms along the [111] directions. Figure 5-25 is the complete surface (0 1 1) plane, which indicates the Burgers vector. From the sketched Burgers circuit on the surface plane, it is clear that the Burgers vector is \( \frac{1}{2}[1 1 1] \). The extra layer extends to about eight atomic layers along the [111] direction. The sessile dislocation propagates along the [\(\bar{1} 1 1\)] direction on the surface, having a Burgers vector aligned in the same direction as the applied stresses. Similar as case (1), dislocation nucleates in the groove (figure 5-24b). As the depth of the dislocation loop only extends to a maximum of three atomic layers inside the film, it is difficult to decide the plane which dislocation loop lies in.
Figure 5-24  
(a) is the projection snapshot of the (0\bar{1}1) planes. The snapshot is taken at 1192ps after deposition starts. The circle with a dot indicates the direction point out of the paper.  
(b) is the top view of atoms in the top two incomplete surface layers without showing atoms in the complete layers at the same moment for simulation. The grey scale represents the height of the incomplete layers – the dark atoms represent the highest incomplete layer, while the light atoms correspond to the layer below the top one.
Figure 5-25 Atoms in the (011) horizontal layer near the surface, 1192ps after the deposition starts. The solid line is a sketch of Burgers circuit around the core of the dislocation, and the arrow represents the Burgers vector. The circle with a dot indicates the direction pointing out of the paper.
5.5 *Simulation Results of Case3: substrate under bi-axial compressive strain.*

In this case we set up, as aforementioned, a simulation model in which the substrate has a temperature of 2500K, and is under a bi-axial compression causing an elastic strain of 2% along the $[111]$ and $\{211\}$ directions. The equivalent tensile stresses, applied along the two directions $[111]$ and $\{211\}$, are -9.4GPa and -6.0GPa, respectively, with a shear stress $\tau_{xy}$ of -0.09GPa on the $(111)$ surface along $\{211\}$ direction. Details of the calculation are given in Appendix II.

![Diagram](image)

**Figure 5-26** The formation of the bottom of a dislocation half-loop with reference coordinates of our setup. The dash-line indicates the thickness of the film deposit. The thick curve indicates the dislocation half-loop. The solid thick line then becomes the bottom of the dislocation half-loop.

A dislocation can be seen to nucleate on a groove of the surface after 7-9 atomic layers are deposited. Figure 5-26 is the sketch of the setup coordinates and reference planes for further analysis in the following paragraphs. In this case, only
one type of dislocation has been observed. The nucleating event starts with an atom (circled in figure 5-27b and figure 5-27c) near a step being ejected from a \((0\bar{1}1)\) surface layer, leaving a vacant site behind. Atoms along the \([1\bar{1}1]\) direction in this layer then relax to share the extra space of this vacancy.

Figure 5-27d shows the \((110)\) plane at 1000ps after the nucleation of the first dislocation. The encircled area indicates the removal of a layer near the surface. Going through the snapshots from figures 5-27a-d, the location of the dislocation is only one atomic layer lower than the original position, showing that the dislocation has not propagated into the interface. It grows to three or four atomic layers along the \((100)\) direction on the \((0\bar{1}1)\) surface layer (figure 5.28c), in a way very similar to the type 1 dislocation in case (1) (section 5.3.1), except that the dislocation loop grows much faster on the surface in the initial moment. Further growth after the stage represented by figure 5-27d can only give us information of its sessile growth. The later stage of the propagation cannot be investigated in detail, because the periodic boundary condition may have introduced artifacts when a dislocation extends close to the boundary and interacts with an infinite number of its own image. Due to the limited model size of the present work, we cannot get the dislocation plane in this case, as the dislocation extends to the boundary before any further growth of the film.

![Diagram showing dislocation and [111] direction](a) 2190ps
Figure 5-27  Atomic positions in one of the (110) atomic layers containing the jump out of an atom, (a)2190ps, (b)2200ps, (c)2204, and (d)3200ps after the deposition starts. The gray dotted circle represents the removal of one layer.
In order to identify the Burgers vector, atomic arrangements in a horizontal \((0\bar{1}1)\) layer near the surface are shown in figure 5-28a-c. From the sketched Burgers circuit, it is clear that the Burgers vector is \(\frac{1}{2}[1\bar{1}\bar{1}]\). In figure 5-28a, the first atom jumps out from the horizontal \((0\bar{1}1)\) layer and results in a vacancy around there (encircled area). Then, it extends on the surface and more atoms are jump out from the horizontal layer in figure 5-28b (encircled area). Then, atoms along the direction relaxed (figure 5-28b) to form dislocation lines at the two ends of the encircled area for a few atomic layers into the substrate. To fulfill the condition that 'a dislocation line must not end in the bulk, i.e., complete, there must be another dislocation line that connects the two ends of the dislocation lines, and form a dislocation half-loop. In figure 5-28c, another group of similar dislocations starts to nucleate at the bottom (area labeled B). Figure 5-28d is the top layers of the horizontal \((0\bar{1}1)\) plane. Comparing the locations of the two dislocations with the top two incomplete horizontal \((0\bar{1}1)\) planes in figure 5-28c, we observed that dislocation nucleates in a groove.
Figure 5-28 Atomic positions in one $[0\bar{1}1]$ horizontal layer near the surface, with dislocation nucleus at (a)1335ps, (b)1350ps, and (c)2210ps. Figure (d) is the surface layer at 1350ps. Burgers vector is $\frac{1}{2}[1\bar{1}\bar{1}]$, as indicated in figure (b). The circle with a solid dot indicates the direction pointing out of the paper.
5.6 Simulation Results of Case4: substrate under bi-axial tensile strain

In this case we set up, as aforementioned, a simulation model in which the substrate has a temperature of 2500K, and is under a bi-axial tension causing an elastic strain of 4% along the [111] and [211] directions. The equivalent tensile stresses, applied along the directions [111] and [211], are 10.1GPa and 12.1GPa, respectively, with a shear stress \( \tau_{xy} \) of -1.82GPa on the (111) surface along the [211] direction. The calculation of this part is given in Appendix II. The dislocation nucleation event is first identified using the consecutive snapshots and then confirmed by configuration analyses.

In this case, a dislocation is observed to nucleate after 16-18 atomic layers of film are deposited. Figure 5-29a-e are consecutive snapshots showing the nucleation and propagation of a glissile dislocation half-loop (indicated by solid circles), as well as that of another sessile dislocation (indicated by an arrow in figure 5-29a). Similar to the first two cases, two types of nucleation events have been observed in this case. When the relaxation space is less than one Burgers vector, a glissile dislocation half-loop is formed, which extends by gliding on two of the \{112\} planes (indicated by dotted-circle and solid-circle in figure 5-29). The encircled areas in figure 5-29 indicate the competition for the nucleation of glissile dislocation on the two \{112\} planes. In the initial stage, they are easily absorbed by the surface. However, when one of them successfully propagates into the film, a stable dislocation half-loop nucleates. The further propagation of this dislocation half-loop will dominate the dislocation mechanism (figure 5.29e). A sessile dislocation is nucleated when the relaxation space is much larger. Here the Burgers vector is not on the interstitial plane. The glissile type is nucleated as a half-loop by gliding, as indicated in the dotted-circled area in figure 5-29. The sessile type is nucleated as an interstitial plane, which is indicated by the high-atomic density area (indicated by an arrow in figure 5-29a) on the right hand side under the surface. Details are given in the following subsections.
Figure 5-29: Consecutive snapshots showing the nucleation and propagation of a glissile dislocation half-loop (indicated by solid circles), as well as that of another sessile dislocation (indicated by an arrow) in the same simulation time. Competition of the glissile dislocations nucleation are visible in the consecutive snapshots. The solid-circle indicates those disregistered atoms with glissile dislocation half-loop on the (2\text{I}1) plane. The dotted-circle indicate those disregistered atoms with glissile dislocation half-loop on the on (2\text{I}1) the plane. (a)-(c) In the initial stage, those two dislocations are easily absorbed by the surface. (d) One of them successfully propagates into the film, a stable dislocation half-loop nucleates. (e) The further propagation of this dislocation half-loop will dominate the dislocation mechanism (e).
5.6.1 Nucleation of Glissile Dislocation Half-loop on \((2\bar{1}1)\) Planes

The glissile type of dislocations nucleate near a step, and propagate into the film as a half-loop on the \((2\bar{1}1)\) planes. Figure 5-30 indicates the two symmetric \((2\bar{1}1)\) and \((2\bar{1}1)\) planes where the dislocation half-loop is aligned and propagates. The thick curve indicates the bottom of the dislocation half-loop in \((2\bar{1}1)\) planes with the direction of the Burgers vector as shown. With the reference planes in figure 5-30, the mechanisms for the movement of those interstitial atoms are shown in the following figures.

![Diagram of dislocation half-loop](image)

Figure 5-30  Growth and propagation of a glissile dislocation half-loop on \((2\bar{1}1)\) plane, with a reference close-packed \((011)\) plane that cuts the half-loop. Two symmetric planes, \((2\bar{1}1)\) and \((2\bar{1}1)\), are shown with a dislocation half-loop propagating in one of the planes. A \((011)\) plane is also drawn for further reference. The thick dotted curve with arrows indicates the dislocation half-loop and its propagation direction during film growth under bi-axial tension.
To visualize the atomic configuration of this dislocation, atoms are projected along the [111] direction, as shown in figure 5-31. A small half-loop is nucleated in figure 5-31a, and it extends by propagation to a near-circular half-loop in figure 5-31b. The circled area on the right hand side of figure 5-31a is another dislocation (sessile type), which will be described in later paragraphs. The relative shift of the atomic positions along one direction indicates the area contained by the dislocation and the absence of the shift on the direction that is perpendicular to it indicates that the Burgers vector is located on that plane; (011) plane.

Figure 5-31 Projection of atomic positions along the [111] direction. The snapshot is taken at (a)1503ps, and (b)1517ps after the deposition starts. The dark atoms indicate the condition under lattice disregistry. Encircled area is the nucleation of another type of sessile dislocation that will be described in the sub-section 5.6.2. The circle with a solid dot indicates the direction point out of the paper.
One of the \((011)\) layers is shown in figure 5-32a-b, which cuts the dislocation loop and contains the direction of the Burgers vector; the nucleation starts at the encircled atom (solid line). Atoms shown with darker color are chosen by the condition of lattice disregistry. For comparison of the vertical layer, another atom next to it in the same horizontal level is circled by dotted line. In the beginning, a rough surface with steps is first formed by deposition. An atom near one of the steps, as indicated by the solid-circle in figure 5-32a, inserts into the film along an atomic row along the \([11\bar{1}]\) direction. Afterwards, this encircled atom (solid-line) at the upper edge of the step moves down one atomic layer to eliminate the step, as shown in figure 5-32b. A dislocation half-loop is already formed with one more atomic layer on the right hand side. The formation process is similar as the glissile type in case(2) in section 5.4.1. A whole Burgers vector \(\frac{1}{2}[\bar{1}1\bar{1}]\) is found for this loop in figure 5-32b. The energy is likely minimized by the elimination of the step. The dislocation nucleus thus formed propagates along the \([100]\) line on the surface (refer to figure 5-30).

Similar to the case under uni-axial tension, symmetric phenomena should be observed in further simulations. If the step were reversed, nucleation of a dislocation on the \((2\bar{1}1)\) plane with Burgers vector \(\frac{1}{2}[\bar{1}1\bar{1}]\) would be favored. This is because both the \((2\bar{1}1)\) plane and the \([\bar{1}1\bar{1}]\) direction are symmetry images of the \((21\bar{1})\) plane and the \([\bar{1}1\bar{1}]\) direction when the step is reversed. The geometry of the described symmetrical planes can be seen in figure 5-30. As they are symmetric, the competition between the above-mentioned phenomena between the two planes can be observed and described in the above paragraphs with figure 5-29. Again, it is worth mentioning, the two glide planes, \((2\bar{1}1)\) and \((21\bar{1})\), have the largest Schmid factor. Details of the calculations are given in Appendix II.
Figure 5-32  Atomic positions in one of the (011) atomic layers containing the dislocation nucleus at (a)1499ps and (b)1510ps after the deposition starts. The circle with a solid dot indicates the direction pointing out of the paper.
5.6.2 Nucleation of Sessile Dislocation Half-loop by an Interstitial Atomic (121) Plane

In the second event (by another simulation), a dislocation is nucleated roughly in the same atomic layers after 13–14 atomic layers of film have been deposited. Figure 5-33 shows the geometry of the dislocation loop, as well as the reference planes that will be described for the analysis in the following paragraphs.

Figure 5-33 Growth and propagation of sessile dislocation half-loop on (121) plane, with a reference close-packed (110) plane that cuts the half-loop. The bottom of the sessile dislocation half-loop formed by interstitial (121) planes is shown. The dash-line indicates the thickness of the film deposit. The thick curve indicates the dislocation half-loop. The solid thick line then becomes the bottom of the dislocation half-loop.
Figure 5-34 Formation of an interstitial (121) plane. Dislocation loop is shown by lattice disregistry. Atoms inside the dotted circle are competing for the formation of the type 1 dislocation loop on one of the two \{112\} planes, which has been described in Chapter 5.6.1.
Similarly, the nucleation of dislocation is first found in the consecutive snapshots figure 5-34a-f, where atoms are identified by lattice disregistry, with subsequent confirmation using configuration analyses. In the same figure, we can see the competition between the nucleation the two types of dislocations: the first event (encircled area) and the second event (indicated by an arrow). The nucleation of the first event (glissile dislocation half-loop) has been described in sub-section 5.6.1. As a result of the competition, the encircled atoms finally disappear (in figure 5-34e and 5-34f), resulting in the nucleation of the second event, i.e., an interstitial plane shown in figure 5-34f.

In figure 5-33, one of the (110) layers is shown in figure 5-35. Atoms on the surface, circled in figure 5-35a and 5-35b, are inserted into the top layer of (011) surface, at an interstitial defect. Atoms along the [111] direction share their space to this interstitial atom. At the same time, each additional atom distorts the lattice configuration around itself. The uneven spaces make it easier for other additional atoms in the neighborhoods to drop inside. This results in a steady increase in the number of interstitial atoms on the horizontal plane along the [100] direction. (Refer to figure 5-36b for the [100] direction on the surface plane) At the same time, the interstitial atoms extend into the film along the [111] direction for three atomic layers. The extension of interstitial atoms along the two directions results in an interstitial (121) plane. In this event, the dislocation does not expand by a gliding mechanism, but by the formation of an interstitial plane.
Figure 5-35  Atomic positions in one of the (110) atomic layers containing the interstitial atoms, (a)1334ps, (b)1337ps, and (c)1346ps after the deposition starts.
Figure 5-36 shows the horizontal layer near the surface. We can observe the sharing of space with atoms along the $[\bar{1}11]$ in figure (b) when a dislocation nucleates with Burgers vector $\frac{1}{2}[\bar{1}11]$. Figure 5-36c is the top layer at the simulation time step when the dislocation starts to nucleate. Comparing figure (c) with (b), we observe the correlation between the dislocation nucleation site and the groove.

As in the case of the glissile dislocation, symmetric phenomena should be observed in further simulations. In this case, the interstitial atoms extend along the same $[\bar{1}00]$ direction on the surface, but form an interstitial (112) plane with the same Burgers vector $\frac{1}{2}[\bar{1}11]$. 

(a) 1335ps
Figure 5-36  Atoms in one (011) horizontal layer near the surface with a dislocation nucleus at (a) 1335ps and (b) 1350ps. Figure (c) is the surface layer at 1350ps. Burgers vector is $\frac{1}{2}[\bar{1}11]$, as indicated in figure (b). The circle with a solid dot indicates the direction pointing out of the paper.
5.7 Simulation of Thermal Annealing of Thin Film Under Uni-axial Stresses

As the limitation of the annealing method (refer to Chapter 2.3), not all the nucleation mechanisms are obtained in this kind of simulations. Only the glissile type of dislocations can be observed under the same conditions under compression / tension. It is because the nucleation process of a sessile half-loop cannot proceed, as there is no further growth of the film. This is the limitation of the annealing method. In our study, we use the annealing method for the two cases under the same uni-axial stresses in case (1) and (2) to verify our results by deposition. They are described in the following sub-sections in detail.

Under uni-axial compression (compare with case (1)), only the first nucleation event (5.3.1) is observed. A dislocation is nucleated along the [1 1 1] step with three atomic distances on the (0 1 1) surface. It is consistent with the result we obtain in section 5.3.1, and is nucleated on the groove along the [1 1 1] direction. Figure 5-37 shows the (0 1 1) surface with a step. The relationship between the direction of the step and the propagation direction are given in a series of snapshots. We conclude that it starts to nucleate close to the [1 1 1] edge of the step (figure 5-37b). Then, it propagates along the step and reaches the end of the [1 1 1] edge (figure 5-37c). For further growth, it propagates without any guide of the step (figure 5-37d). Again, the later stage of the propagation is not investigated in detail, because the periodic boundary condition may have introduced artifacts when a long dislocation interacts with infinite number of its own image.
Figure 5-37 Effect of surface steps on the horizontal $(0\overline{1}1)$ surface for the nucleation and propagation direction of dislocation under uni-axial compression. The dark atoms indicate those atoms chosen by lattice disregistry for the dislocation under the $(0\overline{1}1)$ surface.
Under uni-axial tension (compare with case (2)), only a glissile dislocation half-loop mechanism on one of the \{112\} plane is observed. This time, a dislocation is nucleated and propagates on the \{121\} layer (the other symmetric plane as case (2)) with Burgers vector in [\overline{1}1\overline{1}] direction. The snapshots of figure 5-38 indicate the nucleation and propagation of the dislocation half-loop with the atomic structure with a step on the surface. A dislocation is nucleated near the step, and propagates into the film as a half-loop, on the two neighboring \{121\} planes. This nucleus of dislocation propagates along the [\overline{3}11] line, but it is not a close-packed atomic direction on the horizontal \{0\overline{1}1\} surface. This process generates a dislocation with a whole Burgers vector \(\frac{1}{2}[\overline{1}1\overline{1}]\). Afterwards, the atoms at the upper edge of the step relax to eliminate the sharp step, as shown in figure 5-39; the energy is likely minimized by the elimination of the step.
Figure 5-38  Effect of surface steps on the horizontal \((0 \overline{1} 1)\) surface for the nucleation and propagation direction of dislocation under uni-axial tension. The dark atoms indicate those atoms chose by lattice disregistry for the dislocation under the \((0 \overline{1} 1)\) surface. The annealing time is (a)1824ps, (b)1842ps, and (c)1865ps.
The elimination of the step on the top $\{0\overline{1}1\}$ surface. The dark atoms under the surface plane indicate the dislocation half-loop by lattice disregistry. After the propagation of the glissile half-loop dislocation, the whole step in (c) relaxes down to eliminate the sharp step. The annealing time is (a) 1842ps, (b) 1842ps, and (c) 1850ps.
5.8 Discussion of the Simulation Results

To compare the predicted critical thickness between our simulation results, two classical approaches, the energy minimum approach and the energy balance approach, are calculated in Appendix III. Results from the energy minimum approach (equation AIII-8) and energy balance approach (equation AIII-11) are shown in figure 5-40. The solid line shows the critical layer thickness for the nucleation of dislocation calculated by the Matthews energy minimum approach\textsuperscript{22,48,181-183}, while the dotted line shows the critical layer thickness for the dislocation using the People and Beam energy balance approach \textsuperscript{47,50}. The two circles and two triangles are our simulation results. The filled circle represents the simulation condition under uni-axial compression, while the open circle represents the simulation condition under uni-axial tension. Similarly, the filled triangle represents the simulation condition under bi-axial compression, while the open triangle represents the simulation condition under bi-axial tension.

![Graph showing critical layer thickness vs misfit](image)

Figure 5-40: The solid line shows the critical layer thickness for the nucleation of dislocation by Matthews energy minimum approach, while the dotted line shows the critical layer thickness for dislocation by People and Beam energy balance approach. The filled circle represents our simulation results under uni-axial compression, while the open circle represents our simulation results under uni-axial tension. Similarly, the filled triangle represents our simulation results under bi-axial compression, while the open triangle represents our simulation results under bi-axial tension.
In most of the MD simulations, the critical thickness is larger than the theoretical one. It is because to reach the critical thickness of a film is a necessary but not a sufficient condition for formation of a half-loop. Nucleation of half-loop will not occur unless the activation energy needed to form the loop is available. People and Bean have calculated the activation energy for Ge$_2$Si$_{1-x}$/Si. It is in the range from 50 to 88kT $^{[50]}$. Large critical thickness values are also obtained for the calculation of the specific role of surface steps $^{[122]}$. This may explain why unexpectedly large values for critical thickness are always obtained in experiments, such as Ge on GaAs $^{[32]}$, and various rare-earth garnets on garnet substrates $^{[44]}$.

In our simulation results, it is interesting that the critical thickness depends on the sign of the misfit. The critical thickness of compressively strained films is smaller than that of films with the same magnitude of misfit, but in tension. The same results are obtained by Ichimura’s calculation for a surface step $^{[122]}$, and Dong’s MD simulation for film growth $^{[113]}$. They associated this behavior with the stress dependence of the surface energy.

The mechanism of dislocation nucleation is different in tension and compression, and in all cases, is associated with the roughness of the film surface. Development of the rough surface due to surface instability can be due to either tensile or compressive stresses $^{[177-178]}$. The critical thickness depends intimately on the film morphology, which is determined as an integral part of the film growth process. Therefore, the non-flat nature of a grown film plays a significant role in determining the critical thickness. The nucleation of the dislocation increases the surface roughness. Some studies have shown that stresses may affect the surface instability and result in the increase of surface roughness $^{[177-178]}$. In our simulations, it is worth mentioning that an equivalent amount of surface diffusion, although not sufficient guarantee the equivalence of low and high temperature simulations, does minimize the risk of artificial roughness.

In our simulation results under both uni-axial and bi-axial tension, dislocation half-loops nucleate but are absorbed by the surface frequently. An energy barrier exists for the propagation of the dislocation half-loop from the surface to the interface. Again, Ichimura and Narayan $^{[122]}$ also observed an energetic barrier associated with the propagation of a dislocation loop from the surface towards the interface, which they associated with the activation barrier for misfit dislocation nucleation.
5.9 Conclusion

Using the three-dimensional molecular dynamics method, we have studied dislocation nucleation and propagation during deposition of tungsten thin films on an uni-axially and bi-axially stressed tungsten substrate. Our results show that a dislocation nucleates near a surface step/groove through the ejection/insertion of an atom from a surface layer. Following the ejection/insertion, atoms in the surface layer relax along one of the $\langle 111 \rangle$ directions to accommodate the extra space required. Depending on the space available for nucleation, the corresponding dislocation can either be glissile or sessile. Different types of nucleation mechanisms are possible, depending on the available space relation. Under the four types of applied stresses, the nucleation of the glissile and sessile dislocation can be summarized as follow.

When the relax space is small, glissile dislocations form. For the glissile dislocations, they are formed by gliding along one of the $\langle 111 \rangle$ directions and align on the plane with the largest Schmid factor. The obtained Burgers vectors are all aligned on the glide plane with the largest shear stress. Therefore, movement of atoms along the slip direction, which results in the nucleation of the dislocation half-loop, is due to the large resolved shear stress.

When the relax space is large, sessile dislocation half-loop form in a way similar to a Frank loop in the F.C.C. metal. In this case, the Burgers vectors align in one of the $\langle 111 \rangle$ directions with the largest applied strain direction on the surface (011) plane. By annihilating a vacancy or an interstitial, the applied strain can be reduced. However, the displacement of the involved atoms is along the direction with the largest applied strain, they are usually out of the dislocation plane. This results in the formation of a sessile dislocation half-loop, and it moves by climbing.

For some of the simulation setups, both glissile and sessile dislocation half-loops nucleate. This is because during the deposition process, the film surface is never perfectly flat. This rough surface will result in uneven distribution of the strain and formation of either type of loop in different regions.

It is worth mentioning that the long-range stress field of dislocations will also play an important role during propagation, as well as nucleation. The present study focuses on dislocation nucleation, although propagation behavior is also outlined; at the propagation stage when the long-range stress field dominates, the results of molecular dynamics simulations using periodic boundary conditions become
questionable. To reliably model the propagation and patterning of dislocations, kinetic Monte Carlo \(^{179}\) and dislocation dynamics methods \(^{180}\) would be more effective.
CHAPTER SIX - SUMMARY AND CONCLUSION

We study the nucleation of dislocations and their subsequent propagation, during thin-film deposition, using the three-dimensional molecular dynamics method.

Thin films are employed in a wide range of engineering applications, especially in a form with low defect concentration. It is well known that grain boundaries and dislocations are open paths of fast diffusion, which is responsible for the electromigration failure. Fast diffusion can be reduced or eliminated if the microstructure, in particular the texture and the dislocation density, can be well controlled. This necessitates the understanding of the evolution of grains and the dynamics of dislocations. However, the effects of dislocations, their nucleation in particular, in polycrystalline thin films have not been well understood.

The nucleation of dislocations at surfaces and their subsequent propagation in polycrystalline thin films bears some similarities to the case in epitaxial thin films. In the polycrystalline thin films, dislocations nucleate during film growth, as if the films are deposited on a stressed substrate made of the same material. During epitaxy, on the other hand, dislocations nucleate when films are deposited on a substrate of different materials; mismatch strain exists in hetero-epitaxy. In view of the common features between the dislocation dynamics in the two types of thin films, it is worthwhile reviewing the studies of epitaxial thin films.

Aiming to reveal the generic mechanisms, tungsten, an almost elastically isotropic metal, is considered. Four cases of tungsten on a stressed substrate of the same material are investigated. The main factors related to the microstructure development, which will determine the final properties of PVD thin films are: (1) the condensation and nucleation of the deposited adatoms on the surfaces, and (2) the growth of deposited film on a stressed substrate. Therefore, diffusion of atoms/clusters on a surface of the same material is studied before any investigation of thin film deposition. Different crystallographic structures will have different surface free energies, which will affect the surface diffusion of the adatom. Effects of crystallography for the condensation of atoms on the surface are studied by investigating diffusion in two structures: titanium (hexagonal close packed) atoms on its (0001) surface, and tungsten (body center cubic) atoms on its (011) surface.

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Our results show that Ti adatom diffuses very fast, with a diffusion coefficient $4.1 \times 10^{-4} e^{-0.06eV/kT} \text{cm}^2/\text{s}$, similar to that of an Al adatom on the aluminum (111) surface. The diffusion is forward correlated due to the high frequency of the jumps. We cannot conclude any forward correlation for Ti clusters. The lack of correlation is a result of frequent rotation for small clusters, and also may be a result of large inertia of the large clusters. However, W adatom diffuses much slower, with diffusion coefficient $1.3 \times 10^{-3} e^{-0.54eV/kT} \text{cm}^2/\text{s}$. We cannot conclude any forward correlation in this case.

All the Ti clusters investigated, as large as heptamer, are highly mobile. Even the heptamer is able to migrate a distance of 60 nm at room temperature during the time period of growing one monolayer under typical conditions. Therefore, Ti clusters as large as a heptamer are not effective nuclei in the three-dimensional growth of thin films. The mobility of W clusters, on the other hand, is not as high as Ti. The W dimmer and trimmer are probably the critical nucleus in three-dimensional growth. Although varied in details, diffusion of all the Ti clusters investigated start with the jump of one atom. Therefore, in the mobility of clusters, not all the atoms in a cluster diffuse simultaneously; this is true at least for the clusters investigated here.

Knowing the diffusion coefficient of adatom on the surface, the movement of adatoms at a finite temperature can be calculated. Therefore, we can estimate the simulation temperature and deposition rate for film growth to obtain results comparable to experimental processing. For example, in the simulation of deposition of W thin film in Chapter 5, the deposition rate is 1 meter per second, in contrast to the typical value of 1 micron per minute. This high deposition rate is a result of the limitation of molecular dynamics simulations. The most serious consequence of this high deposition rate is the lack of diffusion during film deposition. To compensate, the substrate is kept at a very high temperature, say 2500K. As a result, the amount of atomic diffusion during the simulations is equivalent to that during an experiment at 340K at a deposition rate of 1 micron per minute.

Using the information obtained above, we then simulate the nucleation and propagation of dislocation during deposition of tungsten thin films on an uni-axially and bi-axially stressed tungsten substrate. Our results show that a dislocation nucleates near a surface step/groove through the ejection/insertion of an atom from a
surface layer. Following the ejection/insertion, atoms in the surface layer relax along one of the \(<111>\) directions to take up/fill in the extra space of the resulting vacancies.

Under uni-axial compressive stress, two types of dislocation loops are observed. The first dislocation half loop nucleates and propagates on the \((10\bar{1})\) plane with Burgers vector \(\frac{1}{2}[\overline{1}1\bar{1}]\), or the symmetric plane. Referring to our calculation in appendix II table AII-3, the \((10\bar{1})\) plane with slip direction \([\overline{1}1\bar{1}]\) gives the largest Schmid factor in the \(\{110\}\) plane sets. Another sessile dislocation half-loops nucleate on the \((0\bar{1}\bar{1})\) plane with Burgers vector \(\frac{1}{2}[11\bar{1}]\), which is the applied strain direction. We call it glissile dislocation half loop as it moves down by climbing, and its propagation speed is too slow to be detected during our simulation.

Under uni-axial tensile stress, glissile dislocation half loops are observed to nucleate and propagate by gliding on the \((11\bar{2})\) plane with Burgers vector \(\frac{1}{2}[\bar{1}1\bar{1}]\), or the symmetric plane. Referring to our calculation in appendix II table AII-3 again, the \((11\bar{2})\) plane with slip direction \([\overline{1}1\bar{1}]\) give the largest Schmid factor in both of the \(\{110\}\) and \(\{11\bar{2}\}\) plane sets. Sessile dislocation half-loop nucleates on the \((1\bar{1}0)\) plane with Burgers vector \(\frac{1}{2}[1\bar{1}1]\). Again, it propagates by climbing with Burgers vector on the surface along the applied strain direction.

Under bi-axial compressive stress, only sessile dislocation with Burgers vector \(\frac{1}{2}[\overline{1}1\bar{1}]\) are observed. Again, the Burgers vector is along the applied strain direction. To analyze the geometry of this Burgers vector, we consider the surface \((0\bar{1}\bar{1})\) plane. The close alignment of atoms is along the \([\overline{1}1\bar{1}]\) and \([11\bar{1}]\) directions (refer to geometry of the surface in figure 4-6 in Chapter 4.2).

Under bi-axial tensile stress, a glissile dislocation half-loop nucleates and propagates on the \((2\bar{1}\bar{1})\) plane by gliding with Burgers vector \(\frac{1}{2}[\overline{1}1\bar{1}]\), or on the symmetric plane. As calculated in appendix II table AII-2, the \((2\bar{1}\bar{1})\) plane with slip direction \([\overline{1}1\bar{1}]\) gives the largest Schmid factor in both the \(\{110\}\) and \(\{11\bar{2}\}\) plane sets.
Sessile dislocation half-loop nucleates on the (121) plane with Burgers vector $\frac{1}{2}[\bar{1}11]$. Again, the Burgers vector aligns on the surface with one of the $<111>$ directions.

To conclude our simulation results, we find that the relaxation may lead to dislocations with Burgers vectors that are either in or out of the plane of the dislocation. Therefore, the corresponding dislocation can either be glissile or sessile. Also, all of them have the possibility for different types of nucleation mechanisms, especially when the relax space is small. Under the four types of applied stresses, the relationship for the nucleation of the glissile and sessile dislocation can be summarized as follows.

When the relax space is small, glissile dislocations form. For the glissile dislocations, they are formed by glide along one of the $<111>$ directions and align on the plane with the largest Schmid factor. The Burgers vectors of the loops formed are all aligned on the glide plane with the largest shear stress. Therefore, movement of atoms along the slip direction, which results in the nucleation dislocation half-loop, is due to the large resolved shear stress.

When the relax space is large, sessile dislocation half-loop form by climb. In this case, the Burgers vectors align in one of the $<111>$ directions on the surface (011) plane. This results in the formation of a sessile dislocation half-loop.

For some of the simulation setups, both the glissile and sessile dislocation half-loops nucleate. The observation results give evidence of the above nucleation mechanisms. This is because, during the deposition process, the film surface is never perfectly flat. This rough surface results in uneven distribution of the strain.

The critical thicknesses obtained are larger than the theoretical approaches (energy minimum approach and energy balance approach given in Appendix III). In most of the MD simulations, the critical thickness is larger than the theoretical one. It is because to reach the critical thickness of a film is a necessary but not a sufficient condition for formation of a half-loop. Nucleation of half-loop will not occur unless the activation energy needed to form the loop is available. People and Bean have calculated the activation energy for $\text{Ge}_x\text{Si}_{1-x}/\text{Si}$. It is in the range from 50 to 88kT $^{[50]}$. Large critical thickness values are also obtained for the calculation of the specific role of surface steps $^{[122]}$. This may explain why unexpectedly large values for critical
thickness are always obtained in experiments, such as Ge on GaAs $^{32}$, and various rare-earth garnets on garnet substrates $^{48}$.

In our simulation results, it is interesting that the critical thickness depends on the sign of the misfit. The critical thickness of compressively strained films is smaller than that of films with the same magnitude of misfit, but in tension. The same results are obtained by Ichimura's calculation for a surface step $^{122}$, and Dong's MD simulation for film growth $^{113}$. They associated this behavior with the stress dependence of the surface energy.

It is worth mentioning that the long-range stress field of dislocations will also play an important role during the propagation stage, as well as the nucleation stage. The present study focuses on dislocation nucleation, although propagation behavior is also outlined; at the propagation stage when the long-range stress field dominates, the results of molecular dynamics simulations using periodic boundary conditions become questionable. To reliably model the propagation and patterning of dislocations, kinetic Monte Carlo and dislocation dynamics methods would be more effective.

In this thesis, we first focus on the mechanisms of condensation and nucleation of the deposited adatoms on the surface formation, and migration energies of those adatom and clusters. They provide the input to both of the Monte Carlo simulations of thin film growth, and our MD simulation conditions for deposition of thin film. Then, we focus on the growth mechanisms of deposited film on a stressed substrate. The above mechanisms studied are the main factors related to the microstructure development, which will determine the final properties of PVD thin films. Knowing the above mechanisms, we can control the film properties in a more easy way.
APPENDIX

Appendix I  Lattice Disregistry for 3-dimensions

1. Calculations of Lattice Disregistry

Lattice disregistry method is limited to 2-dimensions; it is only possible to investigate a plane where a dislocation is located. But in our simulation, we want to verify the plane where the dislocation is located. Therefore, another program based on the same idea is developed. The new developed method can show those atoms around a dislocation core in 3-dimensions, but it cannot give the numerical magnitude of the vector. For a clear explanation, we simplify the 3-dimensional case into 2-dimensions in figure AI-1. The open circles indicate atoms in the lattice sites of a perfect crystal. The solid circles indicate atoms in the lattice sites with dislocation. Consider displacements of atoms with dislocation present (solid circles) and atoms without dislocation (open circles), we conclude that atoms ‘A’, ‘B’, ‘C’, ‘D’ and ‘E’ are the dislocation core in figure AI-1.

![Diagram of lattice disregistry](image)

Figure AI-1  Displacements of atoms with its perfect lattice sites. The open circles indicate atoms in the lattice sites of a prefect crystal. The solid circles indicate atoms in the lattice sites with dislocation.
The original method for lattice disregistry is considered the atoms above and below the slip plane. These displacements \( u \) will be different at the same distance \( x \) from the centerline of the dislocation. As an example in figure AI-1, the disregistry \( \Delta u \) is the difference between these displacements.

\[
\Delta u = u_a - u_s \quad \text{(AI-1)}
\]

Usually, width of the core is defined as the width of the region within which \( \Delta u \) is greater than half of its maximum value \((1/2 \ a)^{184}\).

However, the limitation is that we must choose the plane where dislocation located before the calculation of disregistry. It is not suitable in our case, as we want to check/verify/confirm which plane the dislocation is located. Therefore, another method based on this calculation is developed in our program and described in the following.

We should decide which structure (in our case, it is body center cubic lattice) we considered first. Then, we get the position of the first nearest neighbors and the second nearest neighbors for this structure. Now, consider all the atoms one by one and take the considered atoms as the center of the other neighbors. Then, the shift of the neighbors from their original perfect sites becomes \( \Delta u \). Similarly as before, we can set the acceptable range for \( \Delta u \). If one of the considered neighbors exceeds the acceptable range, then that center atom is considered as ‘disregistry’. On the other hands, if all the neighbors fulfill the requirements of the lattice neighbors, then that center atom is considered as ‘registry’. As an example, we consider only the first close neighbors for a 2-dimension dislocation in figure AI-1. Atoms are checked one by one and we get the result of table AI-1:
<table>
<thead>
<tr>
<th>Center atom</th>
<th>First close neighbors</th>
<th>Registry/Disregistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>I, J, K, E, C, B, D</td>
<td>Disregistry</td>
</tr>
<tr>
<td>B</td>
<td>F, D, A, Q, P, U, T</td>
<td>Disregistry</td>
</tr>
<tr>
<td>C</td>
<td>E, G, R, S, Q P</td>
<td>Disregistry</td>
</tr>
<tr>
<td>D</td>
<td>H, I, J, A, B, T, F</td>
<td>Disregistry</td>
</tr>
<tr>
<td>E</td>
<td>J, K, L, G, R, C, A</td>
<td>Disregistry</td>
</tr>
<tr>
<td>J</td>
<td>M, N, O, K, E, A, D, I</td>
<td>Registry</td>
</tr>
</tbody>
</table>

Table AI-1  Atoms that are disregistered from their sites.

Therefore, we conclude that only atoms ‘A’, ‘B’, ‘C’, ‘D’ and ‘E’ are ‘disregistry’ atoms. They form a dislocation core while all other atoms are ‘registry’.

By the calculation, we can identify the dislocation core for any dislocation loop in our simulation cell in 3-dimensions without the limitation of first choosing a dislocation plane.
2. Verify the 3-D Lattice Disregistry Program

To check our ‘lattice disregistry’ program for 3-D, two standard dislocations, a screw dislocation (figure AI-2) and an edge dislocation loop (figure AI-5) are created. Figure AI-2 is the set-up of a screw dislocation, with dislocation line along the [111] direction, and Burgers vector $\frac{1}{2}[111]$. To verify the screw dislocation, we select one of the planes, the (111) plane, and check its atomic positions along the [111] direction by original lattice disregistry $^{184}$; $\Delta u$ for B.C.C. tungsten. The changes of atomic positions along the $[\bar{2}11]$ direction are plotted in figure AI-3. With this figure, we have confirmation on the screw dislocation we created.

![Dislocation Diagram](image)

**Figure AI-2** Geometry of a screw dislocation created, with periodic boundary along [111] direction for a B.C.C. tungsten structure.
Figure AI-3    Atomic positions of disregistry $\Delta u$ of the created screw dislocation in [111] plane of figure AI-2.

Figure AI-4    Atoms selected by lattice disregistry for a screw dislocation mentioned above in figure AI-2. The lighter atoms represent the coordinates of our setup. The darker atoms indicate the dislocation core in the center of the model along the [111] direction.
To test our disregistry program, we applied it to the above screw dislocation we created. We observed the same dislocation line in the center along the [111] direction, indicated by those darker atoms in figure AI-4. It shows that our program is correct for detecting the pure screw dislocation core.

To create a dislocation loop (with both screw and edge dislocation), a circular interstitial (011) plane is inserted into the bulk with the set-up coordinate mentioned in figure AI-5. After relaxation, a dislocation loop in (011) plane with Burgers vector $\frac{1}{2}[111]$ is created. Again, to verify the dislocation loop created, we select one of the planes, the $\{211\}$ plane, and check its atomic positions by the original lattice disregistry $^{184}$, $\Delta u$ for B.C.C. tungsten. The changes of atomic positions along the [111] direction are plotted in figure AI-6. With this figure, we have evidence of the dislocation loop. The simulation method for creation of the dislocation loop can be refer other works done by our co-workers $^{185}$.

![Diagram of dislocation loop](image)

**Figure AI-5** Geometry of a dislocation loop formed by relaxation of an interstitial circular (011) plane in a B.C.C. tungsten structure.
Figure AI-6  Atomic positions of disregistry $\Delta \mu$ of the created dislocation loop in $(\overline{2}11)$ plane of figure AI-5.

Again, to test our disregistry program, we applied it to the above edge dislocation loop. Figure AI-7 shows those atoms selected with lattice disregistry (darker atoms), with top and bottom atoms indicating the direction of our coordinates. We observed a dislocation core in the shape of a ring located on the [011] plane, with the same location that the interstitial circular plane inserted. That is what exactly we created in our data.

As all dislocations are based on the above two types; screw and edge dislocations, we have evidenced that our lattice disregistry programs for 3-D are applicable for all dislocations.
Figure AI-7  Atoms selected by lattice disregistry for a dislocation loop mentioned above in figure AI-5. The lighter atoms represent the coordinates of our setup. The darker atoms indicate a circular dislocation core in the center of the (011) plane.
Appendix II  Strain Energy Analysis

The applied strains in our simulation set-up are not along the original coordinate; [100], [010] and [001] for the cubic crystal. In this section, we would like to do the transfer between the two coordinates and calculate the effective stresses on the crystal.

1. Direction Cosine for Transfer Between Two Coordinates for Strain Energy

Figure AII-1 The two coordinates of the simulated crystal.
Figure AII-1 shows the traditional coordinates and the new coordinates in our simulations. x, y and z are the three traditional coordinates inside a cubic crystal where,

x corresponds to the [100] lattice direction,
y corresponds to the [010] lattice direction,
z corresponds to the [001] lattice direction.

X', y' and z' are the new coordinates perpendicular to each other inside the same cubic crystal where

x' corresponds to the [111] lattice direction,
y' corresponds to the [211] lattice direction,
z' corresponds to the [011] lattice direction.

For general cases, let the direction cosine between the old coordinates and the new coordinates are as below:

<table>
<thead>
<tr>
<th></th>
<th>x</th>
<th>y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>x'</td>
<td>l₁</td>
<td>m₁</td>
<td>n₁</td>
</tr>
<tr>
<td>y'</td>
<td>l₂</td>
<td>m₂</td>
<td>n₂</td>
</tr>
<tr>
<td>z'</td>
<td>l₃</td>
<td>m₃</td>
<td>n₃</td>
</tr>
</tbody>
</table>

(AII-1)

And stress tensor changes between the old and the new coordinates are:

\[
\begin{bmatrix}
\sigma_{x'} & \tau_{x'y'} & \tau_{x'z'} \\
\tau_{y'x'} & \sigma_{y'} & \tau_{y'z'} \\
\tau_{z'x'} & \tau_{z'y'} & \sigma_{z'}
\end{bmatrix}
\begin{bmatrix}
l₁ & m₁ & n₁ \\
l₂ & m₂ & n₂ \\
l₃ & m₃ & n₃
\end{bmatrix}
= 
\begin{bmatrix}
\sigma_x & \tau_{xy} & \tau_{xz} \\
\tau_{yx} & \sigma_y & \tau_{yz} \\
\tau_{zx} & \tau_{zy} & \sigma_z
\end{bmatrix}
\begin{bmatrix}
l₁ & l₂ & l₃
\end{bmatrix}
\]

(AII-2)
For isotropic materials, we can rewrite the stress tensor in equation AII-2 in a vector form as:

\[
\begin{bmatrix}
\sigma_x \\
\sigma_y \\
\sigma_z \\
\tau_{yx} \\
\tau_{zx} \\
\tau_{xy}
\end{bmatrix} =
\begin{bmatrix}
l_1^2 & m_1^2 & n_1^2 & 2m_1n_1 & 2n_1l_1 & 2l_1m_1 \\
l_2^2 & m_2^2 & n_2^2 & 2m_2n_2 & 2n_2l_2 & 2l_2m_2 \\
l_3^2 & m_3^2 & n_3^2 & 2m_3n_3 & 2n_3l_3 & 2l_3m_3 \\
l_1l_3 & m_1m_3 & n_1n_3 & m_1n_3 + m_3n_1 & n_1l_3 + n_3l_1 & l_1m_3 + l_3m_1 \\
l_2l_3 & m_2m_3 & n_2n_3 & m_2n_3 + m_3n_2 & n_2l_3 + n_3l_2 & l_2m_3 + l_3m_2 \\
l_1l_2 & m_1m_2 & n_1n_2 & m_1n_2 + m_2n_1 & n_1l_2 + n_2l_1 & l_1m_2 + l_2m_1
\end{bmatrix} \begin{bmatrix}
\sigma_x \\
\sigma_y \\
\sigma_z \\
\tau_{yx} \\
\tau_{zx} \\
\tau_{xy}
\end{bmatrix}
\]  

(AII-3)

As matrix \( \sigma' = T\sigma \) where

\[
T =
\begin{bmatrix}
l_1^2 & m_1^2 & n_1^2 & 2m_1n_1 & 2n_1l_1 & 2l_1m_1 \\
l_2^2 & m_2^2 & n_2^2 & 2m_2n_2 & 2n_2l_2 & 2l_2m_2 \\
l_3^2 & m_3^2 & n_3^2 & 2m_3n_3 & 2n_3l_3 & 2l_3m_3 \\
l_1l_3 & m_1m_3 & n_1n_3 & m_1n_3 + m_3n_1 & n_1l_3 + n_3l_1 & l_1m_3 + l_3m_1 \\
l_2l_3 & m_2m_3 & n_2n_3 & m_2n_3 + m_3n_2 & n_2l_3 + n_3l_2 & l_2m_3 + l_3m_2 \\
l_1l_2 & m_1m_2 & n_1n_2 & m_1n_2 + m_2n_1 & n_1l_2 + n_2l_1 & l_1m_2 + l_2m_1
\end{bmatrix}
\]  

(AII-4)

Then transpose of matrix \( T \) becomes

\[
T' =
\begin{bmatrix}
l_1^2 & l_2^2 & l_3^2 & l_1l_3 & l_2l_3 & l_3l_1 \\
m_1^2 & m_2^2 & m_3^2 & m_1m_3 & m_3m_1 & m_1m_2 \\
n_1^2 & n_2^2 & n_3^2 & n_1n_3 & n_3n_1 & n_1n_2 \\
2m_1n_1 & 2m_2n_2 & 2m_3n_3 & m_1n_3 + m_3n_1 & m_2n_3 + m_3n_2 & m_1n_2 + m_2n_1 \\
2n_1l_1 & 2n_2l_2 & 2n_3l_3 & n_1l_3 + n_3l_1 & n_2l_3 + n_3l_2 & n_1l_2 + n_2l_1 \\
2l_1m_1 & 2l_2m_2 & 2l_3m_3 & l_1m_3 + l_3m_1 & l_2m_3 + l_3m_2 & l_1m_2 + l_2m_1
\end{bmatrix}
\]  

(AII-5)

For isotropic materials, the elastic constants matrix corresponds to the new coordinates are, \[ C' = TCT' \]

where

180
\[
C = \begin{bmatrix}
  C_{11} & C_{12} & C_{12} & 0 & 0 & 0 \\
  C_{12} & C_{11} & C_{12} & 0 & 0 & 0 \\
  C_{12} & C_{12} & C_{11} & 0 & 0 & 0 \\
  0 & 0 & 0 & C_{44} & 0 & 0 \\
  0 & 0 & 0 & 0 & C_{44} & 0 \\
  0 & 0 & 0 & 0 & 0 & C_{44}
\end{bmatrix}
\]

(All-6)

For the new coordinate \(x', y'\) and \(z'\) inside the same cubic crystal where \(x', y'\) and \(z'\) corresponds to the \([111]\), \([211]\) and \([0\bar{1}1]\) lattice direction. The direction cosine of equation All-1 becomes:

<table>
<thead>
<tr>
<th></th>
<th>(x)</th>
<th>(y)</th>
<th>(Z)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(x')</td>
<td>(\frac{1}{\sqrt{3}})</td>
<td>(\frac{1}{\sqrt{3}})</td>
<td>(\frac{1}{\sqrt{3}})</td>
</tr>
<tr>
<td>(y')</td>
<td>(-\frac{2}{\sqrt{6}})</td>
<td>(\frac{1}{\sqrt{6}})</td>
<td>(\frac{1}{\sqrt{6}})</td>
</tr>
<tr>
<td>(z')</td>
<td>(0)</td>
<td>(-\frac{1}{\sqrt{2}})</td>
<td>(\frac{1}{\sqrt{2}})</td>
</tr>
</tbody>
</table>

(All-7)

Calculated by equation All-4, All-5, All-6 and All-7, we get:
\[
C' = \begin{bmatrix}
\frac{1}{3}C_{11} + \frac{2}{3}C_{12} + \frac{4}{3}C_{44} & \frac{1}{3}C_{11} + \frac{2}{3}C_{12} - \frac{2}{3}C_{44} & \frac{1}{3}C_{11} + \frac{2}{3}C_{12} - \frac{2}{3}C_{44} \\
\frac{1}{3}C_{11} + \frac{2}{3}C_{12} - \frac{2}{3}C_{44} & \frac{1}{2}C_{11} + \frac{1}{2}C_{12} + C_{44} & \frac{1}{6}C_{11} + \frac{5}{6}C_{12} - \frac{1}{3}C_{44} \\
\frac{1}{3}C_{11} + \frac{2}{3}C_{12} - \frac{2}{3}C_{44} & \frac{1}{6}C_{11} + \frac{5}{6}C_{12} - \frac{1}{3}C_{44} & 0 \\
0 & \frac{1}{3\sqrt{2}}C_{11} + \frac{1}{3\sqrt{2}}C_{12} + \frac{2}{3\sqrt{2}}C_{44} & \frac{1}{3\sqrt{2}}C_{11} - \frac{1}{3\sqrt{2}}C_{12} - \frac{2}{3\sqrt{2}}C_{44} \\
0 & 0 & \frac{1}{3\sqrt{2}}C_{11} + \frac{1}{3\sqrt{2}}C_{12} + \frac{2}{3\sqrt{2}}C_{44} \\
0 & 0 & \frac{1}{3\sqrt{2}}C_{11} - \frac{1}{3\sqrt{2}}C_{12} - \frac{2}{3\sqrt{2}}C_{44} \\
\frac{1}{6}C_{11} - \frac{1}{6}C_{12} + \frac{2}{3}C_{44} & \frac{1}{3\sqrt{2}}C_{11} - \frac{1}{3\sqrt{2}}C_{12} - \frac{2}{3\sqrt{2}}C_{44} & 0 \\
\frac{1}{3\sqrt{2}}C_{11} - \frac{1}{3\sqrt{2}}C_{12} - \frac{2}{3\sqrt{2}}C_{44} & \frac{1}{3}\ C_{11} - \frac{1}{3}C_{12} + \frac{1}{3}C_{44} & 0 \\
0 & 0 & \frac{1}{3}\ C_{11} - \frac{1}{3}C_{12} + \frac{1}{3}C_{44}
\end{bmatrix}
\]

(All-8)

For Tungsten at high temperature \(^{186}\), the constants are:

\[C_{11} = 3.2000\]
\[C_{12} = 0.8500\]
\[C_{44} = 0.6470\]

By equation All-8, \(C'\) becomes:
\[
C' = \begin{bmatrix}
2.496 & 1.202 & 1.202 & 0 & 0 & 0 \\
1.202 & 2.672 & 1.026 & 0 & 0 & -0.249 \\
1.202 & 1.026 & 2.672 & 0 & 0 & 0.249 \\
0 & 0 & 0 & 0.823 & 0.249 & 0 \\
0 & 0 & 0 & 0.249 & 0.999 & 0 \\
0 & -0.249 & 0.249 & 0 & 0 & 0.999 \\
\end{bmatrix}
\]  
(AII-9)

We now rename the matrix \( C' \) as
\[
C' = \begin{bmatrix}
C_{11}' & C_{12}' & C_{13}' & 0 & 0 & 0 \\
C_{21}' & C_{22}' & C_{23}' & 0 & 0 & C_{26}' \\
C_{31}' & C_{32}' & C_{33}' & 0 & 0 & C_{36}' \\
0 & 0 & 0 & C_{44}' & C_{45}' & 0 \\
0 & 0 & 0 & C_{54}' & C_{55}' & 0 \\
0 & C_{62}' & C_{63}' & 0 & 0 & C_{66}' \\
\end{bmatrix}
\]  
(AII-10)

where \( C_{ij} \) corresponds to equation 6.9.

Relationship between strain \( \varepsilon_x', \varepsilon_y' \) and \( \varepsilon_z' \)
\[
\sigma' = C' \varepsilon'
\]  
(AII-11)

In our simulation under bi-axial stresses, \( \varepsilon_x' \) and \( \varepsilon_y' \) are set constant, and \( \varepsilon_z' \) are set zero (relax); i.e.
\[
\sigma' = \begin{bmatrix}
\sigma_{x}' \\
\sigma_{y}' \\
0 \\
\tau_{yz}' \\
\tau_{zx}' \\
\tau_{xy}' \\
\end{bmatrix}
\]

Then, equation AII-11 becomes

183
\[
\begin{bmatrix}
\sigma_x' \\
\sigma_y' \\
\tau_{xy}' \\
\tau_{x'y}'
\end{bmatrix}
= \begin{bmatrix}
C_{11}' & C_{12}' & C_{13}' & 0 & 0 & 0 \\
C_{21}' & C_{22}' & C_{23}' & 0 & 0 & C_{26}' \\
C_{31}' & C_{32}' & C_{33}' & 0 & 0 & C_{36}' \\
0 & 0 & 0 & C_{44}' & C_{45}' & 0 \\
0 & 0 & 0 & C_{54}' & C_{55}' & 0 \\
0 & C_{62}' & C_{63}' & 0 & 0 & C_{66}'
\end{bmatrix}
\begin{bmatrix}
\varepsilon_x' \\
\varepsilon_y' \\
\gamma_{xy}'
\end{bmatrix}
\]  
(AII-12)

By equation AII-12,

\[
\varepsilon_x' = \frac{-C_{31}' \varepsilon_x' \quad -C_{32}' \varepsilon_y'}{C_{33}'}
\]  
(AII-13)
2. *Condition Under Bi-axial Compressive Strain*

For the simulation case under bi-axial compressive strain of 0.02 along x' and y' direction, i.e.

\[ \varepsilon_{x'} = \varepsilon_{y'} = -0.02 \]

By equation All-13,

\[ \varepsilon_{z'} = 0.017 \]

Now, equation All-11 becomes

\[
\begin{bmatrix}
\sigma_{x'} \\ \sigma_{y'} \\ \sigma_{z'} \\ \tau_{y'z'} \\ \tau_{z'x'} \\ \tau_{x'y'}
\end{bmatrix} =
\begin{bmatrix}
2.496 & 1.202 & 1.202 & 0 & 0 & 0 \\ 1.202 & 2.672 & 1.026 & 0 & 0 & -0.249 \\ 1.202 & 1.026 & 2.672 & 0 & 0 & 0.249 \\ 0 & 0 & 0 & 0.823 & 0.249 & 0 \\ 0 & 0 & 0 & 0.249 & 0.999 & 0 \\ 0 & -0.249 & 0.249 & 0 & 0 & 0.999
\end{bmatrix}
\begin{bmatrix}
-0.02 \\ -0.249 \\ 0.249 \\ 0.249 \\ 0.999 \\ 0
\end{bmatrix}
\]  \( \text{(All-14)} \)

Finally,

\[
\begin{bmatrix}
\sigma_{x'} \\ \sigma_{y'} \\ \sigma_{z'} \\ \tau_{y'z'} \\ \tau_{z'x'} \\ \tau_{x'y'}
\end{bmatrix} =
\begin{bmatrix}
-0.094 \\ -0.060 \\ 0 \\ 0 \\ 0 \\ 0.009
\end{bmatrix}
\]

in the unit of Mbar.

In this case, a shear stress, \( \tau_{x'y'} \) is created. By coordinate rotation, using equation All-1 again (direction cosine), the shear stress on each of the following planes with one of a whole Burgers vector is shown in table All-1
<table>
<thead>
<tr>
<th>Plane</th>
<th>Slip Direction</th>
<th>New Coordinates</th>
<th>Direction Cosine</th>
<th>Shear Stress Along Slip Direction (Mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>[111]</td>
<td>x'=[110]</td>
<td>$l_1 = \frac{2}{\sqrt{6}}$; $m_1 = \frac{1}{\sqrt{12}}$; $n_1 = -\frac{1}{\sqrt{2}}$</td>
<td>-0.034</td>
</tr>
<tr>
<td></td>
<td></td>
<td>y'=[111]</td>
<td>$l_2 = \frac{1}{3}$; $m_2 = \frac{4}{\sqrt{18}}$; $n_2 = 0$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>z'=[112]</td>
<td>$l_3 = \frac{2}{\sqrt{18}}$; $m_3 = \frac{1}{6}$; $n_3 = \frac{3}{\sqrt{12}}$</td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td>[111]</td>
<td>x'=[110]</td>
<td>$l_1 = \frac{2}{\sqrt{6}}$; $m_1 = \frac{1}{\sqrt{12}}$; $n_1 = -\frac{1}{\sqrt{2}}$</td>
<td>-0.020</td>
</tr>
<tr>
<td></td>
<td></td>
<td>y'=[111]</td>
<td>$l_2 = \frac{1}{3}$; $m_2 = -\frac{2}{\sqrt{18}}$; $n_2 = \frac{2}{\sqrt{6}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>z'=[112]</td>
<td>$l_3 = \frac{2}{\sqrt{18}}$; $m_3 = \frac{5}{6}$; $n_3 = \frac{1}{\sqrt{12}}$</td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td>[111]</td>
<td>x'=[110]</td>
<td>$l_1 = 0$; $m_1 = -\frac{3}{\sqrt{12}}$; $n_1 = \frac{1}{2}$</td>
<td>-0.027</td>
</tr>
<tr>
<td></td>
<td></td>
<td>y'=[111]</td>
<td>$l_2 = \frac{1}{3}$; $m_2 = -\frac{2}{\sqrt{18}}$; $n_2 = -\frac{2}{\sqrt{6}}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>z'=[112]</td>
<td>$l_3 = \frac{4}{\sqrt{18}}$; $m_3 = \frac{1}{6}$; $n_3 = -\frac{1}{\sqrt{12}}$</td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td>[111]</td>
<td>x'=[110]</td>
<td>$l_1 = 0$; $m_1 = -\frac{3}{\sqrt{12}}$; $n_1 = \frac{1}{2}$</td>
<td>-0.008</td>
</tr>
<tr>
<td></td>
<td></td>
<td>y'=[111]</td>
<td>$l_2 = 1$; $m_2 = 0$; $n_2 = 0$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>z'=[112]</td>
<td>$l_3 = 0$; $m_3 = -\frac{1}{2}$; $n_3 = -\frac{3}{\sqrt{12}}$</td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td>[111]</td>
<td>x'=[110]</td>
<td>$l_1 = \frac{2}{\sqrt{6}}$; $m_1 = -\frac{1}{\sqrt{12}}$; $n_1 = \frac{1}{2}$</td>
<td>-0.003</td>
</tr>
<tr>
<td></td>
<td></td>
<td>y'=[111]</td>
<td>$l_2 = \frac{1}{3}$; $m_2 = -\frac{4}{\sqrt{18}}$; $n_2 = 0$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>z'=[121]</td>
<td>$l_3 = \frac{2}{\sqrt{18}}$; $m_3 = -\frac{1}{6}$; $n_3 = -\frac{3}{\sqrt{12}}$</td>
<td></td>
</tr>
<tr>
<td>(101)</td>
<td>[111]</td>
<td>(x''=[101])</td>
<td>(y''=[111])</td>
<td>(z''=[121])</td>
</tr>
<tr>
<td>(10̅1)</td>
<td>[111]</td>
<td>(x''=[10\overline{1}])</td>
<td>(y''=[1\overline{1}1])</td>
<td>(z''=[\overline{1}21])</td>
</tr>
<tr>
<td>(10ı)</td>
<td>[ı1ı]</td>
<td>(x''=[10ı])</td>
<td>(y''=[ı1ı])</td>
<td>(z''=[ı21])</td>
</tr>
<tr>
<td>(1ıı)</td>
<td>[ııı]</td>
<td>(x''=[1ıı])</td>
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<tr>
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<td>(z''=[ı0ı])</td>
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187
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<th>(z''=[011])</th>
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<th>(l_3=\frac{2}{\sqrt{6}}; m_3=-\frac{1}{\sqrt{12}}; n_3=\frac{1}{2})</th>
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<td>(l_3=0; m_3=0; n_3=1)</td>
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<tr>
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<td>(l_3=0; m_3=0; n_3=1)</td>
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</table>

Original Coordinate

0.009

188
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<th>$x''=[\bar{1}2]$</th>
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</tr>
<tr>
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<td></td>
<td>$z''=[110]$</td>
<td>$l_3=\frac{2}{\sqrt{6}}; m_3=\frac{2}{\sqrt{12}}; n_3=0$</td>
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<table>
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<tr>
<th>(2\bar{i})</th>
<th>[11]</th>
<th>$x''=[\bar{1}12]$</th>
<th>$l_1=\frac{2}{\sqrt{18}}; m_1=\frac{2}{3}; n_1=\frac{2}{\sqrt{12}}$</th>
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</tr>
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<td></td>
<td>$z''=[110]$</td>
<td>$l_3=\frac{2}{\sqrt{6}}; m_3=\frac{2}{\sqrt{12}}; n_3=0$</td>
<td></td>
</tr>
</tbody>
</table>

Table AII-1  Shear stress on each of the possible plane under bi-axial compressive strain.
3. **Condition Under Bi-axial Tensile Strain**

For the simulation case under bi-axial tensile strain of 0.04 along $x'$ and $y'$ direction, i.e.

\[ \varepsilon_{x'} = \varepsilon_{y'} = 0.04 \]

By equation AII-13,

\[ \varepsilon_{x'} = -0.033 \]

Now, equation AII-11 becomes:

\[
\begin{bmatrix}
\sigma_{x'} \\
\sigma_{y'} \\
\sigma_{x'} \\
\tau_{y'x'} \\
\tau_{x'y'}
\end{bmatrix} =
\begin{bmatrix}
2.496 & 1.202 & 1.202 & 0 & 0 & 0 & 0.04 \\
1.202 & 2.672 & 1.026 & 0 & 0 & -0.249 & 0.04 \\
1.202 & 1.026 & 2.672 & 0 & 0 & 0.249 & -0.033 \\
0 & 0 & 0 & 0.823 & 0.249 & 0 & 0 \\
0 & 0 & 0 & 0.249 & 0.999 & 0 & 0 \\
0 & -0.249 & 0.249 & 0 & 0 & 0.999 & 0
\end{bmatrix}
\] (AII-15)

Finally,

\[
\begin{bmatrix}
\sigma_{x'} \\
\sigma_{y'} \\
\sigma_{x'} \\
\tau_{y'x'} \\
\tau_{x'y'} \\
\tau_{x'y'}
\end{bmatrix} =
\begin{bmatrix}
0.101 \\
0.121 \\
0 \\
0 \\
0 \\
-0.018
\end{bmatrix}
\]

in the unit of Mbar.

In this case, a shear stress, $\tau_{x'y'}$ created. The shear stress on each of the following plane with a whole Burgers vector are shown in table AII-2.

In this case, a shear stress, $\tau_{x'y'}$ created. By coordinate rotation using equation AII-1 again (direction cosine), the shear stress on each of the following plane with one of a whole Burgers vector is shown in table AII-2.
<table>
<thead>
<tr>
<th>Plane</th>
<th>Slip Direction</th>
<th>New Coordinates</th>
<th>Direction Cosine</th>
<th>Shear Stress Along Slip Direction (Mbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>[111]</td>
<td>(x''=[110])</td>
<td>(l_1=\frac{2}{\sqrt{6}}); (m_1=\frac{1}{\sqrt{12}}); (n_1=-\frac{1}{\sqrt{2}})</td>
<td>0.045</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(y''=[\bar{1}11])</td>
<td>(l_2=\frac{1}{3}); (m_2=-\frac{4}{\sqrt{18}}); (n_2=0)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(z''=[\bar{1}12])</td>
<td>(l_3=\frac{2}{\sqrt{18}}); (m_3=-\frac{1}{6}); (n_3=\frac{3}{\sqrt{12}})</td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td>[\bar{1}11]</td>
<td>(x''=[110])</td>
<td>(l_1=\frac{2}{\sqrt{6}}); (m_1=\frac{1}{\sqrt{12}}); (n_1=-\frac{1}{\sqrt{2}})</td>
<td>0.016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(y''=[\bar{1}11])</td>
<td>(l_2=\frac{1}{3}); (m_2=-\frac{2}{\sqrt{18}}); (n_2=\frac{2}{\sqrt{6}})</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(z''=[\bar{1}12])</td>
<td>(l_3=\frac{2}{\sqrt{18}}); (m_3=\frac{5}{6}); (n_3=\frac{1}{\sqrt{12}})</td>
<td></td>
</tr>
<tr>
<td>(\bar{1}10)</td>
<td>[1\bar{1}1]</td>
<td>(x''=[\bar{1}10])</td>
<td>(l_1=0); (m_1=-\frac{3}{\sqrt{12}}); (n_1=\frac{1}{2})</td>
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<td></td>
<td>(y''=[1\bar{1}1])</td>
<td>(l_2=\frac{1}{3}); (m_2=-\frac{2}{\sqrt{18}}); (n_2=\frac{2}{\sqrt{6}})</td>
<td></td>
</tr>
<tr>
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<td></td>
<td>(z''=[112])</td>
<td>(l_3=\frac{4}{\sqrt{18}}); (m_3=\frac{1}{6}); (n_3=\frac{1}{\sqrt{12}})</td>
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<td>(\bar{1}10)</td>
<td>[111]</td>
<td>(x''=[\bar{1}10])</td>
<td>(l_1=0); (m_1=-\frac{3}{\sqrt{12}}); (n_1=\frac{1}{2})</td>
<td>0.016</td>
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<td>(z''=[112])</td>
<td>(l_3=0); (m_3=-\frac{1}{2}); (n_3=-\frac{3}{\sqrt{12}})</td>
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<td>[\bar{1}11]</td>
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<td>(l_3=\frac{2}{\sqrt{18}}); (m_3=-\frac{1}{6}); (n_3=-\frac{3}{\sqrt{12}})</td>
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<td>[101]</td>
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<p>|  ( {10\bar{1}} ) | ( {11\bar{1}} ) | ( l = 0 ); ( m_1 = -\frac{3}{\sqrt{12}} ); ( m_1 = -\frac{1}{2} ) | ( l_2 = 1 ); ( m_2 = 0 ); ( n_2 = 0 ) | ( l_3 = 0 ); ( m_3 = -\frac{1}{2} ); ( n_3 = -\frac{3}{\sqrt{12}} ) | 0.016 |
| ( {10\bar{1}} ) | ( {1\bar{1}} ) | ( l = 0 ); ( m_1 = -\frac{3}{\sqrt{12}} ); ( m_1 = -\frac{1}{2} ) | ( l_2 = \frac{1}{3} ); ( m_2 = -\frac{2}{\sqrt{18}} ); ( n_2 = \frac{2}{\sqrt{6}} ) | ( l_3 = \frac{4}{\sqrt{18}} ); ( m_3 = \frac{1}{6} ); ( n_3 = -\frac{1}{\sqrt{12}} ) | 0.055 |
| ( {12\bar{1}} ) | ( {\bar{1}1} ) | ( l = 0 ); ( m_1 = -\frac{3}{\sqrt{12}} ); ( m_1 = -\frac{1}{2} ) | ( l_2 = \frac{1}{3} ); ( m_2 = -\frac{2}{\sqrt{18}} ); ( n_2 = \frac{2}{\sqrt{6}} ) | ( l_3 = 0 ); ( m_3 = -\frac{3}{\sqrt{12}} ); ( n_3 = -\frac{1}{2} ) | 0.029 |
| ( {\bar{1}2} ) | ( {1\bar{1}} ) | ( l = \frac{2}{\sqrt{18}} ); ( m_1 = \frac{5}{6} ); ( n_1 = -\frac{1}{\sqrt{12}} ) | ( l_2 = 0 ); ( m_2 = -\frac{1}{2} ); ( n_2 = -\frac{3}{\sqrt{12}} ) | ( l_3 = \frac{2}{\sqrt{6}} ); ( m_3 = -\frac{1}{\sqrt{12}} ); ( n_3 = \frac{1}{2} ) | -0.032 |
| ( {1\bar{2}} ) | ( {1\bar{1}} ) | ( l = 0 ); ( m_1 = -\frac{3}{\sqrt{12}} ); ( m_1 = -\frac{1}{2} ) | ( l_2 = 1 ); ( m_2 = 0 ); ( n_2 = 0 ) | ( l_3 = 0 ); ( m_3 = \frac{3}{\sqrt{12}} ); ( n_3 = \frac{1}{2} ) | 0.009 |
| ( {\bar{1}2} ) | ( {\bar{1}\bar{1}} ) | ( l = 0 ); ( m_1 = -\frac{3}{\sqrt{12}} ); ( m_1 = -\frac{1}{2} ) | ( l_2 = \frac{1}{3} ); ( m_2 = \frac{4}{\sqrt{18}} ); ( n_2 = 0 ) | ( l_3 = 0 ); ( m_3 = \frac{3}{\sqrt{12}} ); ( n_3 = \frac{1}{2} ) | -0.010 |</p>
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<td></td>
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<td></td>
<td></td>
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<td>0.009</td>
</tr>
<tr>
<td>(211)</td>
<td>[\bar{1}11]</td>
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<td>( l_1 = \frac{4}{\sqrt{18}} ); ( m_1 = -\frac{1}{3} ); ( n_1 = 0 )</td>
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</tr>
<tr>
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<td></td>
<td>( z''=[1\bar{1}0] )</td>
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<td>Original Coordinate</td>
</tr>
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<td></td>
<td>( y''=[1\bar{1}1] )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( z''=[0\bar{1}1] )</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>-0.018</td>
</tr>
<tr>
<td>(2\bar{1}1)</td>
<td>[111]</td>
<td>( x''=[\bar{1}12] )</td>
<td>( l_1 = \frac{2}{\sqrt{18}} ); ( m_1 = -\frac{2}{3} ); ( n_1 = 0 )</td>
</tr>
</tbody>
</table>

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| \( (2\bar{1}1) \) | \( [\bar{1}11] \) | \( y''= [\bar{1}11] \) | \( z''= [110] \) | \( l_2 = \frac{1}{3} ; m_2 = -\frac{2}{\sqrt{18}} ; m_3 = \frac{2}{\sqrt{6}} \) |
| | | \( l_3 = \frac{2}{\sqrt{6}} ; m_3 = \frac{2}{\sqrt{12}} ; n_3 = 0 \) | \( 0.062 \) |
| \( (2\bar{1}1) \) | \( [1\bar{1}1] \) | \( x''= [\bar{1}12] \) | \( y''= [\bar{1}11] \) | \( z''= [110] \) | \( l_1 = \frac{2}{\sqrt{18}} ; m_1 = -\frac{2}{3} ; m_1 = \frac{2}{\sqrt{12}} \) |
| | | \( l_2 = \frac{1}{3} ; m_2 = -\frac{2}{\sqrt{18}} ; m_2 = -\frac{2}{\sqrt{6}} \) | \( l_3 = \frac{2}{\sqrt{6}} ; m_3 = -\frac{2}{\sqrt{12}} ; n_3 = 0 \) | \( 0.062 \) |

Table AII-2  Shear stress on each of the possible plane under bi-axial tensile strain.

Therefore, the two symmetric glide planes \( (2\bar{1}1) \) and \( (2\bar{1}1) \) with glide direction \( [\bar{1}11] \) and \( [1\bar{1}1] \), respectively, have the largest Schmid factor under the simulation conditions. These two planes are also the glide planes for the dislocation half-loop propagate in our simulation results (refer to Chapter 5).
4. *Condition Under Uni-axial Stress*

For the simulation case under uni-axial compression/tension $\sigma_z$ along [111] direction, a shear stress will create on glide planes. The shear stress on each of the following planes with a whole Burgers vector is shown in table AII-3.

<table>
<thead>
<tr>
<th>Glide Plane</th>
<th>Glide Direction</th>
<th>$\cos \phi$ where $\phi$ is the angle between applied stress and glide plane</th>
<th>$\cos \lambda$ where $\lambda$ is the angle between applied stress and glide direction</th>
<th>Schmid factor $(\cos \phi \cos \lambda)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(110)</td>
<td>[111]</td>
<td>$\frac{2}{\sqrt{6}}$</td>
<td>$\frac{1}{\sqrt{9}}$</td>
<td>0.27</td>
</tr>
<tr>
<td>(110)</td>
<td>[111]</td>
<td>$\frac{2}{\sqrt{6}}$</td>
<td>$\frac{1}{\sqrt{9}}$</td>
<td>0.27</td>
</tr>
<tr>
<td>(011)</td>
<td>[111]</td>
<td>$\frac{2}{\sqrt{6}}$</td>
<td>$\frac{1}{\sqrt{9}}$</td>
<td>0.27</td>
</tr>
<tr>
<td>(011)</td>
<td>[111]</td>
<td>$\frac{2}{\sqrt{6}}$</td>
<td>$\frac{1}{\sqrt{9}}$</td>
<td>0.27</td>
</tr>
<tr>
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<td>[111]</td>
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<td>$\frac{1}{\sqrt{9}}$</td>
<td>0</td>
</tr>
<tr>
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<tr>
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Table AII-3  Shear stress on each of the possible planes under uni-axial strain.

The set of \{112\} glide planes; \(12\), \(11\) and \(21\) planes with glide direction [i\̅11], [1i̅1], and [i\̅11] directions respectively, have the largest Schmid factor under the simulation conditions. Two of this planes are also the glide planes for the dislocation half-loop propagate in our simulation results (refer to Chapter 5).
Appendix III  Energy Calculations for Epitaxy Growth

Two approaches of calculations for the nucleation and formation of a dislocation for thin film is given in this section. One of them is by energy minimum/balance approach, and the other is by force equilibrium approach.

1. Energy Minimum/Balance Approach

There are two approaches for the nucleation of dislocation mechanisms in thin film; (1) nucleation of a half-loop on the film surface \(^{[48]}\), and (2) threading dislocation which nucleates on the interface.

Figure AIII-1 shows stages in the formation of a misfit dislocation by the nucleation and expansion of a half-loop. Curve (a) represents a sub-critical dislocation half-loop; (b) represents a half-loop which is stable under the influence of the misfit stress; and (c) depicts a loop which has grown to generate a length \(LL'\) of misfit dislocation line.

![Figure AIII-1 Nucleation and growth of a dislocation half-loop](image)

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Figure AIII-2 shows the mechanism for the formation of grown-in threading dislocation. Line (a) represents the initial stage when the interface is coherent. When the film growth to a thickness $h_b$, the interface is critical and the dislocation is represented by line (b). For the film thickness growth to $h_c$, the dislocation line (c) elongated in the interface plane, thereby producing a length $LL'$ of misfit dislocation line.

**Figure AIII-2 Elongation of a grown-in threading dislocation.**

Under energy minimum approach $[^{22,48,181-183}]$, we assume that (1) the misfit between the substrate and film are small so that all misfits will be accommodated by elastic strain, (2) film and substrate are cubic and elastically isotropic, (3) deviations from Hooke's law are neglected, (4) elastic constants of substrate and film are equal (same materials in my study), (5) misfit dislocations are in square network, in edge orientation, and (6) Burgers vectors are in the interface plane.

Symbols and abbreviations for the following calculations are as below:

- $G$ is shear modulus
- $\nu$ is Poisson's ratio
- $\varepsilon$ is elastic strain
$h$ is film thickness

$b$ is strength of dislocation (Burgers vector)

$\lambda$ is angle between slip direction and that direction in the interface which is perpendicular to the line of intersection of the slip plane and the interface.

$f$ is the misfit between the substrate and film

$a_s$ is the lattice constant of the substrate

$a_0$ is the lattice constant of the film

Under energy minimum approach, the calculations consider the formation of edge dislocation on the surface as following:

Energy of an edge dislocation is:

$$E_{edge} = \frac{Gb^2(1+\nu)}{4\pi(1-\nu)} \left( \ln \frac{h}{b} + 1 \right)$$  \hspace{1cm} (AIII-1)

Separation of adjacent misfit dislocation is:

$$dl = \frac{b}{f-\varepsilon}$$  \hspace{1cm} (AIII-2)

and we define

$$\delta = f - \varepsilon$$  \hspace{1cm} (AIII-3)

Energy of a square grid made up of two perpendicular and non-interacting arrays of edge dislocation

$$E_\delta = \frac{E_{edge}}{dl} = (f-\varepsilon) \frac{Gb}{2\pi(1-\nu)} \left( \ln \frac{h}{b} + 1 \right)$$  \hspace{1cm} (AIII-4)

The energy associated with the elastic strain in the film is

$$E_\varepsilon = \frac{2G(1+\nu)}{1-\nu} \varepsilon^2 h$$  \hspace{1cm} (AIII-5)

The value of strain $\varepsilon$ which minimizes $E_\delta + E_\varepsilon$:

$$\frac{\partial(E_\delta + E_\varepsilon)}{\partial \varepsilon} = 0$$

$$\varepsilon^* = \frac{b}{(1+\nu)8\pi h} \left( \ln \frac{h}{b} + 1 \right)$$  \hspace{1cm} (AIII-6)

where the largest value of $\varepsilon^*$ is when
\[ \varepsilon^* = f = \frac{a_s - a_b}{a_0} \]  \hspace{1cm} (AIII-7)

When \( \varepsilon^* \geq f \), the film will strain to match its substrate exactly and \( \varepsilon^* = f \).

When \( \varepsilon^* < f \), a portion of the misfit, \( \delta = f - \varepsilon^* \), will be accommodated by misfit dislocation.

When \( \varepsilon^* = f \), the first dislocation made and critical thickness of the film is

\[ h_{cr} = \frac{b}{8\pi f (1 + \nu)} (\ln \frac{h}{b} + 1) \]  \hspace{1cm} (AIII-8)

Equation AIII-8 agrees fairly well with Hirth’s energy calculations for the nucleation of a semicircular loop \(^{[40]}\).

Under energy balance approach \(^{[50]}\), the calculations are considering the formation of threading dislocation.

Force exerted on the dislocation line by misfit stress is \(^{[47]}\):

\[ F_H = G \frac{1 + \nu}{1 - \nu} bh \varepsilon \]  \hspace{1cm} (AIII-9)

Tension in the dislocation line is approximately \(^{[11]}\):

\[ F_D = \frac{Gb^2}{4\pi (1 - \nu)} (\ln \frac{h}{b} + 1) \]  \hspace{1cm} (AIII-10)

When \( F_H > F_D \), dislocations move and hence \( h_{cr} \) is obtained when we put \( F_H = F_D \) and \( h = h_{cr} \) and \( \varepsilon = f \):

\[ h_{cr} = \frac{b}{4\pi f (1 + \nu)} (\ln \frac{h}{b} + 1) \]  \hspace{1cm} (AIII-11)

Analysis of our results with equations AIII-8 and AIII-11 are given in the section 5.8 in Chapter 5.
2. *Matthews Force Equilibrium Calculation for Gliding Dislocation* \(^{[48]}\)

Another approach by force equilibrium is to consider more factors such as stacking force for formation of gliding dislocation with the assumptions (1)-(5) in Energy Minimum/Balance Approach in section 1 are given below.

Symbols and abbreviations for the following calculations are as below:

*G* is shear modulus

*v* is Poisson's ratio

*ε* is elastic strain

*h* is film thickness

*b* is strength of dislocation (Burgers vector)

*λ* is angle between slip direction and that direction in the interface which is perpendicular to the line of intersection of the slip plane and the interface.

*α* is angle between dislocation line and Burgers vector

*φ* is angle between the specimen surface and the normal to the slip plane

*σ* is surface tension of the film

*γ* is stacking fault energy

Force exerted by misfit strain

\[ F_\varepsilon = \frac{2G(1+\nu)}{1-\nu} h b \cos \lambda \]  
\[ (AII-12) \]

Line Tensile Force in the misfit dislocation

\[ F_i = \frac{Gb^2(1-\nu \cos^2 \alpha)}{4\pi(1-\nu)} (\ln \frac{h}{b} + 1) \]  
\[ (AII-13) \]

Tensile Force in the surface step created by the moving dislocation is

\[ F_s = \sigma b \sin \alpha \]  
\[ (AII-14) \]
Tensile Force in stacking fault

\[ F_r = \frac{\gamma h}{\cos \varphi} \]  
\hspace{1cm} (AIII-15)

We assume that interaction between moving dislocations will be neglected.

Peierls-Nabarro stress is neglected in our calculation as it is small in metals (but it is large in semi-conductors).

By force equilibrium,

\[ F_c = F_i + F_s + F_r \]  
\hspace{1cm} (AIII-16)

When \( h = h_{crit} \), \( \varepsilon = f \). We get the critical thickness of the film.

\[ h_{crit} = \frac{G b^2 (1 - \nu \cos^2 \alpha)}{4 \pi (1 - \nu)} \ln \left( \frac{h_{crit} + 1}{b} \right) + \sigma b \sin \alpha \]

\[ \frac{1}{2G(1 + \nu)} \frac{2b \cos \lambda}{1 - \nu} \frac{\gamma}{\cos \varphi} \]  
\hspace{1cm} (AIII-17)

where \( h > h_{crit} \), \( \varepsilon \) decrease to hold the equilibrium (by force equilibrium in equation AIII-16).
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