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STUDY OF HfO$_2$ BASED HIGH-$k$ GATE DIELECTRIC THIN FILMS GROWN BY PULSED LASER DEPOSITION

SUBMITTED BY
LEE PUI FAI

A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF PHILOSOPHY IN PHYSICS AT THE DEPARTMENT OF APPLIED PHYSICS

THE HONG KONG POLYTECHNIC UNIVERSITY

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Lee Pui Fai (Name of student)
Abstract

The current SiO₂ gate dielectric with a relatively low permittivity is reaching its limit of usefulness as the feature size of complementary metal oxide semiconductor (CMOS) devices shrinks to nanometer range. Alternative gate oxide with higher relative permittivity is necessary so that thicker films can be used in the future advanced CMOS technology. This can eliminate the problem associated with low-k SiO₂ such as high leakage current density due to direct tunneling. Among many alternative gate dielectrics, HfO₂ and its aluminates have received much attention and been considered as promising candidates.

Epitaxial yttrium stabilized HfO₂ thin films were deposited on p-type (100) Si substrates by pulsed laser deposition at a relatively low substrate temperature of 550°C. Transmission electron microscopy observation illustrated a fixed orientation relationship between the epitaxial film and Si, i.e. (100)Si//(100)HfO₂ and [001]Si//[001]HfO₂. The film/Si interface is not atomically flat and sharp, suggesting possible interfacial reaction and diffusion. The interfacial reaction and diffusion were further confirmed by X-ray photoelectron spectrum (XPS) analysis showing Hf silicate and Hf-Si bonds formation at the interface. The epitaxial growth of the yttrium stabilized HfO₂ thin film on bare Si is by a direct growth mechanism without involving the reaction between Hf atoms and SiO₂ layer. High frequency capacitance-voltage (C-V) measurement revealed that the relative permittivity of an as-grown 40 Å-thick yttrium stabilized HfO₂ is about 14 and the equivalent oxide thickness (EOT, here “oxide” refers to SiO₂) is 12 Å. The leakage current density is $7.0 \times 10^{-2} \, \text{A/cm}^2$ at 1 V gate bias voltage.

In order to obtain a stable amorphous structure under thermal annealing and
suppress the tunnelling leakage current, Al₂O₃ has been selected to alloy with HfO₂. Ultrathin amorphous Hf-aluminate (Hf-Al-O) films have been deposited on p-type (100) Si substrates by pulsed-laser deposition using a composite target containing HfO₂ and Al₂O₃ plates. Transmission electron microscopy observation of the Hf-Al-O films showed that the amorphous structure of Hf-Al-O films was stable under rapid thermal annealing at temperatures up to at least 1000°C. C-V measurement of a 38 Å Hf-Al-O film revealed that the relative permittivity of the film was about 16. The film showed very low leakage current density of 4.6 × 10⁻³ A/cm² at 1 V gate bias. The Hf-Al-O film under optimized condition did not show any significant interfacial layer at the interface and an equivalent oxide thickness of less than 10 Å has been achieved. The formation of Hf-O and Al-O bonds in the film was revealed by XPS.

However, for the films deposited in a high vacuum environment without introducing any gases, islands of Hf silicide formed from interfacial reaction have been observed on the surface of Si substrate. The formation of Hf silicide is attributed to the presence of Al oxide in the films that triggers the reaction between Hf atoms in the amorphous Hf-Al-O films and Si under an oxygen deficient condition. Impact of silicide formation on the electric properties has been studied by means of high-frequency C-V measurements at 1 MHz on the metal-oxide-semiconductor capacitors.

Based on our preliminary results on the growth and characterization of HfO₂-based thin films, we conclude that Hf-Al-O is very promising as high-κ gate dielectric to replace SiO₂.
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Chapter 1 Introduction

With the complementary-metal-oxide-semiconductor (CMOS) feature size shrinking from 0.25 to 0.13 and even to 0.1 μm, a revolution in microelectronic materials for the new generation ultra large scale integrated (ULSI) circuits is happening. Examples are the implementations of Cu metal line replacing Al, Co salicidation replacing Ti salicidation, and low relative permittivity (low-κ) materials for inter-metallic dielectrics (IMD). All of these new microelectronic materials developments have dramatically increased the density and working speed of the devices.

However, further shrinking of the feature size to sub 0.1 μm will depend on the successful development of high-κ gate dielectric materials in replacement of the currently used SiO₂ [1]. Based on a theoretical calculation, a minimum of 7 Å of SiO₂ is required to obtain bulk properties as gate oxide [2]. While in practice, 10-12 Å is reported to be the limit for reducing SiO₂ thickness for 0.1μm CMOS device [3]. This limitation severely restricts the further development of CMOS technology. However, if a single layer of high-κ dielectric oxide can be used, it can substantially reduce the equivalent oxide thickness (EOT) and leakage current [1].

Figure 1.1 illustrates the calculation of the equivalent thickness for a high-κ gate dielectric. Considering a parallel plate capacitor, the gate capacitance can be expressed as:

\[ C = \frac{k \varepsilon_0 A}{t} \]  

(1)

Here \( k \) is relative permittivity of the material, \( \varepsilon_0 \) is the permittivity of free space, \( A \) is the area of the capacitor, and \( t \) is the thickness of the dielectric.
Therefore, the relation of equivalent thickness referring to SiO₂, \( t_{eq} \), and a high-\( k \) gate dielectric with permittivity of \( k_{\text{high-}k} \) and thickness of \( t_{\text{high-}k} \) is:

\[
 t_{\text{high-}k} = t_{eq} \frac{k_{\text{high-}k}}{k_{ox}}. \tag{2}
\]

Here \( k_{ox} = 3.9 \) is the relative permittivity of SiO₂. For example, an equivalent of 10Å SiO₂ can be achieved with 40Å thick (physical thickness) of a material with a moderate permittivity of \( k = 16 \). In most of the literatures, the equivalent oxide thickness, here the “oxide” refers to SiO₂, was defined as EOT.

![A parallel plate capacitor.](image)

**FIG. 1.1** A parallel plate capacitor.

Many materials are currently under investigation as a potential replacement for SiO₂ as the gate dielectric material to meet the next generation CMOS technology requirement. Among the reported materials, Ta₂O₅, TiO₂, Al₂O₃, SrTiO₃, HfO₂, ZrO₂ and pseudobinary systems (Zr-Si-O and Hf-Si-O, Hf-Al-O) have been thought of being possible candidates [4-72]. However, before any candidates can be selected for use, a systematic study of the required properties of gate dielectrics is needed. Some key guidelines for selecting an
alternative gate dielectric are (a) permittivity, band gap, and band alignment to Si, (b) thermodynamic stability, (c) film morphology, (d) interface quality, (e) process compatibility, and (f) reliability [1].

The above-mentioned dielectrics appear favorable in some of these areas, but very few materials are promising with respect to all of these guidelines. For example, except Al₂O₃, all the other dielectric materials suffer from reaction with Si substrate to form SiO₂ and thus downgrade the high-k property and increase the tₑq. This is a severe limitation as a gate dielectric. For Al₂O₃, however, a layer of SiO₂ can still be formed during Al₂O₃ deposition by most of the techniques. In addition, due to the relatively lower relative permittivity (k=9) of Al₂O₃ and easy path for boron diffusion, when polysilicon is used as electrode, it is only possible for short-term solution [7]. Table 1 compares the relevant properties for some high-k candidates [1,73]:

Table 1 Comparison of relevant properties for some high-k candidates.

<table>
<thead>
<tr>
<th>Material</th>
<th>Relative Permittivity (k)</th>
<th>Barrier height ΔEC (eV) to Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>3.9</td>
<td>3.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9</td>
<td>2.8</td>
</tr>
<tr>
<td>Ta₂O₅</td>
<td>26</td>
<td>1.5</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>25</td>
<td>1.4</td>
</tr>
<tr>
<td>HfO₂</td>
<td>25</td>
<td>1.5</td>
</tr>
</tbody>
</table>
1.1 Material Properties Considerations

1.1.1 Permittivity and leakage current

Higher permittivity of ultra thin HfO\textsubscript{2} film is highly desirable for gate dielectric application. The relative permittivity for HfO\textsubscript{2} bulk materials is 25 [73]. However, effect of film thickness, method of film deposition, and local electronic structure within the dielectrics may cause discrepancy between the films and bulk [1]. More experimental data is needed for measurement of dielectric constant based on capacitance-voltage measurement on the established parallel plate capacitor. Capacitance-voltage measurements are also useful in determining many of the characteristics of a particular MOS device and modeling of the MOS structure for circuits.

Leakage current will also be measured before the film can be considered to be an alternative high-\(k\) gate dielectric to replace SiO\textsubscript{2}. Current-voltage measurement at the capacitor will be carried out for the current leakage measurement. The leakage current density for SiO\textsubscript{2} at 15Å thickness is 1-10 A/cm\textsuperscript{2} [1], and the leakage current of suitable high-\(k\) gate dielectric with the same equivalent oxide thickness should be of at least one order of magnitude lower.

1.1.2 Thermodynamic stability on Si

For all the thin gate dielectrics, the interface with Si plays a key role, and in most cases is the dominant factor in determining the overall electrical properties [1]. Therefore,
it is important to understand the thermodynamics in these systems, and thereby attempt to control the interface with Si. So far, most of the high-\(k\) metal oxide systems investigated have unstable interface with Si; that is, SiO\(_2\) interfacial layer will be formed under high temperature annealing. In this project, thermal stability of epitaxial HfO\(_2\) film on Si will be investigated by high-resolution transmission electron microscope (TEM).

1.1.3 Interface quality

It is crucial to understand the interfacial properties so that an optimized high-\(k\)/Si interface may be obtained. Different bonding structures of HfO\(_2\) with Si will result in different electrical properties. For example, it is desirable if the first atomic layer of HfO\(_2\) on Si is the oxygen forming Si-O bond, since SiO\(_2\) and Si interface is the most favorite interface. However, if the Hf-Si bonding is formed at the Si channel (not necessarily a full silicide phase), it will lead to poor leakage current and electron channel mobility [1]. In this project, the interfacial chemical state (atomic-bonding) will be studied by depth profile X-ray photoelectron spectroscopy (XPS). The formation of silicide will be studied.

1.1.4 Gate compatibility

The compatibility of high-\(k\) gate dielectric with standard CMOS process is a significant issue. So far, all the high-\(k\) gate dielectrics that have been studied are facing problems such as interfacial reaction with poly-Si gate materials or dopant diffusion for pMOS or nMOS poly-Si gate [1]. It is desirable to focus efforts on HfO\(_2\) gate dielectric on
the compatibility with potential metal gate materials, since for CMOS scaling in the longer term (beyond 0.07μm), poly-Si gate technology will be phased out as current roadmap predicted [74]. In addition, the use of metal gates require relatively lower thermal budget compared to poly-Si gate since there is no dopant activation annealing process for metal gate. However, gate electrode work function (Fermi level) is a big concern while selecting the materials. Chemical stability (interfacial reaction with gate dielectric) and process capability is another issue which needs to be addressed.

Conducting metal oxide is another choice as an alternative due to its process compatibility and achievable desired work function. For example, important properties of RuO₂ has been studied as gate material with both SiO₂ and Zr-Si-O dielectrics [75]. In this project, Pt is selected as the electrode for simplicity reason. However, for the case of HfO₂, more work need to be done for a better understanding of the alternative metal electrode and metallic oxide electrode, especially on the interfacial stability.
1.2 Yttrium Stabilized HfO₂ Epitaxial Film – Approach I

Most recently, researchers have successfully deposited crystalline yttrium-stabilized zirconia (YSZ) on a silicon wafer without any interfacial amorphous SiO₂ layer by Laser MBE [40]. The results demonstrated that ultrathin YSZ film might be a promising gate dielectric as an alternative to SiO₂ for reducing the feature size of devices. It has been reported that a 90 Å thick YSZ thin film with equivalent oxide thickness down to 17.7 Å, had a leakage current density of $1.5 \times 10^{-5}$ A/cm² at a bias voltage of 1 V. This is some five orders of magnitude lower than that for a SiO₂ film of the same equivalent oxide thickness to produce the same capacitance. However, due to the high density of interfacial dislocations and the lattice strain, the number of dangling bonds and state density are expected to be higher and this may cause reliability issues.

Among the candidates mentioned before, HfO₂ is one of the most attractive candidates due to its relatively higher stability on Si substrate and better reliability [1,76]. Compared to cubic ZrO₂ with a lattice constant of $a=5.07$ Å, HfO₂ has the same structure with larger lattice constant $a=5.12$Å and therefore will have lower lattice mismatch with Si ($a=5.43$ Å) [77]. Data in Table 1 also indicates that the barrier height of HfO₂ relative to Si (1.5eV) is higher than that of ZrO₂ which is 1.4 eV. That means the tunneling current injected from Si to gate through HfO₂ dielectric will be lower than that of ZrO₂ because the energy barrier to overcome is higher for HfO₂. In addition, amorphous HfO₂ shows encouraging result during mean time failure experiments [76]. Therefore, it is reasonable to expect that epitaxial HfO₂ on Si without SiO₂ interfacial layer may contain relatively lower density of interfacial dislocations and density of states and thus results in lower
leakage current and higher reliability. Reference [78] also reported $k=40$ for HfO$_2$, but this value has not been confirmed in more recent studies.

Even though the amorphous structure has been commonly accepted as the approach to select high-$k$ gate dielectric candidates, epitaxial single crystalline films are still of significant fundamental and technological interest. It is well known that epitaxial growth of metal oxide films on Si is a great technical challenge due to the easily formed amorphous silicon oxide layer on Si surface in an oxygen atmosphere preventing the intended oxide heteroepitaxy on Si substrate [79]. Nevertheless, epitaxial growth of yttrium stabilized ZrO$_2$ (YSZ) and SrTiO$_3$ high-$k$ gate dielectrics on bare Si has been successfully demonstrated [39-40, 80]. However, to the best of our knowledge, there is no report of epitaxial HfO$_2$ on bare Si.

Single-crystal oxides grown by molecular-beam epitaxy (MBE) methods can in principle be obtained, but the requirement of ultrahigh-vacuum limits its application due to low-wafer-throughput. In this project, we report the successful deposit of thin epitaxial yttrium stabilized HfO$_2$ film on bare Si at relatively lower substrate temperature by pulsed laser deposition (PLD). Electric properties of the epitaxial films, mechanism for the epitaxial growth and chemical reaction at the film/Si interface were also studied.
1.3 Hf-aluminate Amorphous Film – Approach II

One of the problems for HfO₂ as gate dielectric is that it crystallizes at temperatures higher than 500°C. Therefore, SiO₂ has been commonly used alloying with HfO₂ to form amorphous Hf silicate that is thermodynamically stable under high temperature annealing up to more than 1000°C. Compounds, such as (ZrO₂)ₓ(SiO₂)₁₋ₓ and (HfO₂)ₓ(SiO₂)₁₋ₓ, have been considered as encouraging systems due to their thermal stability on Si and lower leakage current [10,11]. However, the overall permittivity of the compound is inevitably lower (k=10-20) than that of the pure metal oxide (k=25 for ZrO₂ and HfO₂) [1].

Another problem for HfO₂ and ZrO₂ is that they are poor oxygen diffusion barriers. Therefore, during the deposition and the following annealing processes, excess oxygen can easily diffuse through the HfO₂ or ZrO₂ films into the interface area and oxidize the Si substrate. The formation of interfacial SiO₂ rich layer in contact with Si substrate or polysilicon gate material is still a problem affecting the application. Formation of silicide at the interface under condition lacking of oxygen is another serious problem. HfO₂ and ZrO₂ are expected to be thermodynamically stable with Si substrate based on Gibbs free energy analysis under equilibrium condition [81,82]. In practice, however, during the film deposition or the high temperature annealing process, interfacial reactions have been observed at the HfO₂/Si and ZrO₂/Si interfaces. Several authors have reported the formation of ZrSi₂ in the ZrO₂/Si interface under ultra high vacuum annealing due to the oxygen deficiency [83,84].

Similar to SiO₂ alloying with HfO₂ or ZrO₂, adding Al₂O₃ into HfO₂ or ZrO₂ films can also help to stabilize them in amorphous structure during high temperature annealing.
However, compared with SiO$_2$, Al$_2$O$_3$ possesses a larger relative permittivity and thus will reduce the overall relative permittivity less when alloyed with HfO$_2$ or ZrO$_2$. In addition, Al$_2$O$_3$ has its unique advantages such as large band gap (about 8.8eV) and large band offset with Si, and Al$_2$O$_3$ is also a good oxygen diffusion barrier to protect Si surface from oxidation [1,87]. In order to maximize the advantages offered by HfO$_2$ and Al$_2$O$_3$, it is desirable to make a Hf-Al-O film as high-$k$ gate dielectric. Recent reports on aluminates of Zr (Zr-Al-O) [85,86] and Hf (Hf-Al-O) [68,71,73,88-89] showed that such material systems exhibit encouraging gate dielectric properties. Cho and co-workers have reported thermal stability of Al$_2$O$_3$/HfO$_2$ nano laminates structure on Si [90]. Electrical properties such as electron trapping and band alignment in amorphous Hf-Al-O have also been reported [68,71]. However, the understanding of thermodynamic stability and interfacial structure of the Hf-Al-O thin film is still limited.

In this project, we also carried out another approach for the Hf based high-$k$ gate dielectric by depositing the Hf-aluminate thin films. The electric properties of the Hf-aluminate films in the MOS structure and the interfacial reaction, and its impact to the electric properties [72,75] were also studied.
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Chapter 2 Film Growth / MOS Physics / Characterization

In this research program, we attempted to carry out some in-depth investigations regarding to the epitaxial HfO$_2$ and amorphous Hf-aluminate thin films on bare Si as a high-k gate dielectric. In the following sections, the growth and characterization of dielectric films will be introduced. Some of the theories and terminologies in MOS physics that are related to the project will also be explained.

2.1 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a proven technique for depositing high quality thin oxide films on different substrates. The PLD system can be used to fabricate films by using a non-volatile target, a multi-component target and even a multi-target for multi-layer or alloy films. Films can be grown by PLD under conditions of ambient gas with a relatively low substrate temperature.

Figure 2.1 shows a schematic diagram of the PLD deposition system. During film deposition, a laser beam is focused on to the surface of a rotating target to ablate the target materials. By modifying different parameters, such as the substrate temperature, oxygen ambient, laser frequency and fluence, films with different structures may be deposited.
2.1.1 Laser ablation

Laser ablation is typically divided in two domains: thermal and non-thermal processes. The thermal process is mainly due to the irradiation of a laser with a photon energy smaller than the binding energy of the chemical bonds of the materials (i.e. $E_{hv} < E_b$). This process can be described by the thermal equilibrium, Maxwellian velocity distribution (half-Maxwellian distribution) and standard heat conduction model. Non-thermal processes includes the electronic process, bond breaking process and congruent evaporation and subsurface superboiling. In the electronic process, lattice localized relaxation occurs due to the formation of an electron-hole pair and/or an exciton after irradiation by the laser ($E_{hv} > E_{gap}$, $E_{hv} > E_{excit}$). This causes a transition to an anti-bonding potential energy on the target surface, thus, desorption of atoms from the surface will occur. Any desorption of surface atoms through bond breaking is categorized under the bond breaking process ($E_{hv} > E_b$). For some large molecules target materials, the bond breaking process changes the molecular structure resulting in a sudden change in
volume. As a consequence, the ejection of surface atoms, molecules, clusters and also particulates by microexplosions and blast waves occurs.

![Diagram](image)

**FIG 2.2** Schematic diagram of the basic thermal cycle induced by a laser pulser. (a) Laser pulse is absorbed, melting and vaporization begin (shaded area indicates melted material, arrows indicate motion of the solid-liquid interface). (b) Melt front propagates into the solid, accompanied by vaporization. (c) Melt front recedes (cross-hatched area indicates resolidified material). (d) Solidification complete, frozen capillary waves alter surface topography. The next laser pulse will interact with some or all of the resolidified material [1].

A thermal cycle induced by a pulsed laser is illustrated in Fig. 2.2. The thermal cycle depends on laser fluence and pulse length, the optical absorption coefficient, and the thermal properties of the solid such as heat capacity and conductivity. The following is a brief qualitative summary of points relevant to surface modification [1]:

1. The maximum temperature reached in the solid and the melt depth increase with laser fluence.
2. The thermal pulse penetrates deeper into solids with low absorption coefficients and high thermal conductivities.
3. Shorter pulse lengths produce higher melting and solidification velocities.
2.1.2 Film deposition

When the target material is irradiated by high fluence laser energy, a plume containing particles such as ions, atoms, molecules, clusters and even particulates will be formed. These particles, with a translational energy of about 10-100 eV, will finally arrive at the substrate surface and, consequently, a layer of film will be deposited.

Based on the microstructure of the film, the films deposited by PLD can be cataloged into three types: Epitaxial, polycrystalline and amorphous. Epitaxy refers to the phenomenon of film growth where a relation between the structure of the film and the substrate exists. In particular, it commonly denotes a single crystalline layer grown on a single crystal surface. If the single crystalline film and the single crystalline substrate are of the same material, we call the growth homoepitaxy. If the film and the substrate are of different materials, we call the growth heteroepitaxy. A film with randomly oriented grains is known as polycrystalline. In an amorphous film, the atoms only have a short-range order but no long-range order. Therefore, no crystal structure and grains can be identified. The processes of film growth are usually described by the following three different modes [2-4]:

1. Volmer-Weber, three-dimensional island growth. The deposited atoms are more strongly bonded to each other than they are to the substrate.

2. Frank-van der Merwe, two-dimensional full-monolayer growth. This is a layer-by-layer growth mode. The atoms of the deposited material are more strongly attracted to the substrate than they are to themselves.

3. Stranski-Krastinov, two-dimensional growth of full monolayers followed by the nucleation and growth of three-dimensional islands. This is also known as the
layer-plus-island growth mode.

Frank-van der Merwe  Volmer-Weber  Stranski-Krastinov

FIG. 2.3 Three modes of film growth [3,5-6]. Layer-by-layer (Frank-Van der Merwe) growth consists of deposition of one monolayer at a time and results in a very smooth epitaxial film. Island (Volmer-Weber) growth results in the formation and growth of isolated islands. Mixed (Stranski-Krastanov) growth consists of island growth after the first monolayer forms successfully.

2.1.3 Parameters that altering the film properties

When films are deposited in vacuum, the effect of the target-to-substrate distance is mainly reflected in the angular spread of the ejected flux. In general, the particulate trajectories are more divergent when a defocused laser beam is used, as opposed to emerging as a collimated jet for a tightly focused beam. However, when a PLD experiment is done in a poor vacuum, with an ambient gas, or at a substantially large target-to-substrate distance at which particulates can coalesce, the appearance of the particulates may be markedly different, depending on the position of the substrate [7].

The specific effects of target-to-substrate distance and ambient pressure are interrelated. Due to the increased numbers of collisions between the laser-produced plume and the background gas, the plume dimension decreases as the background gas pressure increases. Dyer et al. (1990) [8] have shown that $E/P_0$ is the scaling parameter for plume range, where $E$ is the laser-pulse energy, and $P_0$ is the background gas pressure.

The length of the plume is $L \propto \left( \frac{E}{P_0} \right)^{\frac{1}{2\gamma}}$, where $\gamma$ is the ratio of the specific heats of the
elements in the plume. For an ambient pressure of 35 mTorr and a laser fluence of 4J/cm², the plume range \( L \) corresponds to approximately 5.5 cm [9]. When the target-to-substrate distance is much smaller than \( L \), there is no marked difference in particulate size and density. As the target-to-substrate distance increases, the proportion of the smaller particulates decreases, and a few larger particulates appear [10], indicating merging during flight. Once the substrate is located far beyond \( \sim L \), the adhesion to the substrate of the ejected matter, including the particulates and atomic species, is poor.

The use of an ambient gas is mainly to compensate for some loss of a constituent element such as oxygen or nitrogen in ceramics. It mainly affects the oxygen content of the deposited thin film. For example, the deposited oxide tends to be deficient in oxygen when the ablation experiment is done in vacuum. When a laser ablation deposition experiment is done in vacuum, there are virtually no collisions between the ejected species before they reach the substrate. Thus, the establishment of the epitaxial thin film and the control of the crystal structure of the thin film can be done by varying the ambient gas with suitable values.

The surface mobility of the ablated species is greatly affected by substrate temperature. One of the possible effects is that metastable microstructures will be formed as insufficient thermal energy at very low temperature [11].

Investigation of the structural properties and the stoichiometry of the layers, deposited at different conditions (substrate temperature; substrate-target distance, \( l \); laser pulse energy, \( E \)) has shown that there is a critical substrate temperature, \( T_c \), below which the structure of the films is not completely monocristalline and the film composition deviates significantly from the stoichiometric one [12-13].
2.2 MOS Physics

2.2.1 MOS structure

The MOS capacitor is a simple two-terminal device composed of a thin SiO₂ layer sandwiched between a silicon substrate and a metallic field plate [14, 15]. A typical parallel plate MOS capacitor is illustrated in Figure 2.4. The visualized layer-by-layer structure as shown in the figure presents the three-layer structure of a typical MOS capacitor: metal, gate dielectric and semiconductor (usually Si).

![MOS capacitor diagram](image)

**FIG. 2.4** A parallel plate MOS capacitor.
Figure 2.5 is an energy band diagram of an ideal MOS capacitor when a bias voltage is added across it. As for metal, the minimum energy above the Fermi-level for the emission of an electron to the outside is defined as workfunction ($\phi_M$). For a semiconductor, the minimum energy above the conduction band edge for the emission is defined as electron affinity ($\chi_S$), while the energy above the Fermi-level is known as the workfunction of semiconductor($\phi_S$).

![Diagram of an ideal MOS structure](image)

**FIG. 2.5 The band diagram for an ideal MOS structure.**

An ideal MOS structure mainly has the following characteristics: (1) no work function difference between the gate metal and the semiconductor substrate ($\phi_M = \phi_S$); (2) no fixed charge locating at the oxide/semiconductor interface; (3) no mobile ions trapped in the oxide layer and (4) no interface states at the oxide/semiconductor interface. All of these imply that the electric field across the MOS capacitor equals zero; thus, no gate bias voltage is presented and the energy band is flat ($V_G = 0$ and $V_{FB} = 0$). However, no ideal MOS system exists in the normal systems that we normally come across. In the following sections, some important terminologies such as flat-band voltage, threshold voltage and their correlation to the MOS properties will be introduced.
2.2.2 Flat band voltage

As revealed in the previous section, for an ideal MOS capacitor, the electric field inside the system would be zero if the applied voltage $V_G$ across the metal and semiconductor is zero; i.e., $V_{FB}$ is zero. In practice, however, due to the work function difference between the metal electrode and semiconductor, and the charges in the oxide-semiconductor interface, a flat-band voltage $V_{FB}$ has to be applied at the metal to maintain a zero electric field in the semiconductor. Therefore, in a real MOS system, the band diagram of the substrate is usually not flat at equilibrium state and the $V_{FB}$ is expressed as:

$$V_{FB} = V_{ms} + V_{interface} + V_{mobile}, \quad (1)$$

where $V_{ms}$ is the workfunction difference between the metal and semiconductor; $V_{interface}$ is the flat band voltage associates with the interface charges in the oxide layer close to the oxide/semiconductor interface, and $V_{mobile}$ is the flat band voltage associates with the mobile ions in the oxide layer.

Assuming that the workfunction of the metal ($\phi_m$) is larger than the workfunction of the semiconductor ($\phi_s$), as illustrated in the band diagram 2.6(a), the band of the substrate curves upward towards the equilibrium state(Fig 2.6(b)). This indicates a positive flat band voltage; i.e. a negative voltage is needed to recover a flat band as shown in the band diagram (Fig. 2.6(c)).
Figure 2.7 shows the nature and location of charges in the non-flat band MOS structures. As illustrated in Fig. 2.7, the mobile ions are usually the ions of alkali elements trapped in the oxide layer. Those mobile ions can create electric field in the Si substrate region and thus affect the band structure in the substrate as the interface charges do. When the gate bias voltage is applied across the MOS capacitor, the mobile ions can move due to the electromotive force (emf). Therefore, their positions in the oxide layer are not fixed.

During the process of the gate-oxide fabrication in the MOS capacitor, there are always charges, called fixed charges, trapped near the oxide/semiconductor interface. Assume the trapped charge is positive with a real concentration, say, Q. The electric field lines generated by those fixed charges will enter the substrate and deplete part of the
semiconductor, causing a non-flat band at equilibrium. To eliminate the influence of these charges, an equal amount of charges $Q$ has to accumulate on the gate metal so that all of the electric field lines from the interfacial charges are attracted towards the metal side [14].

The interface traps, when occupied by electrons, will affect the substrate as the interface charges. For carefully treated SiO$_2$ interfaces, a typical charge density due to interface traps and interface fixed charges are about $10^{10}$ charges/cm$^2$ for Si with $\{100\}$ surfaces [14].

![Diagram of MOS structure with mobile ions, fixed charges, and interfacial traps](image)

FIG. 2.7 Nature and location of charge centres in MOS structures [16,17].
2.2.3 Accumulation, depletion and inversion

FIG. 2.8 Accumulation of majority charge carriers (holes) near the p-type substrate surface.

FIG. 2.9 Formation of depletion layer.

FIG. 2.10 Inversion state (high minority carriers – electrons concentration in p-type substrate).
For p-type Si, when there is a negative bias voltage ($V_G - V_{FB} < 0$), majority carrier holes will accumulate near the semiconductor surface. The energy band in the semiconductor thus curves upwards due to the accumulation of majority charge carriers (holes). When there is a positive gate bias voltage ($V_G - V_{FB} > 0$), holes will be expelled from the surface area and thus form a depletion layer, where "Θ" in the figure represents the ionized acceptor atoms, and "•" represents electrons accumulated at the interface. The depletion layer expands as the gate bias voltage $V_G$ increases. Finally electrons start to accumulate at the oxide/semiconductor interface. There is a tendency for the p-type Si to gradually changes to an n-type semiconductor near the surface area, thus building an inversion layer.
2.3 Measurement and Characterization

To evaluate the dielectric property, a parallel plate capacitor structure has to be built by growing a suitable electrode on top of the dielectric thin film. Since metal electrodes are thought to be a dominant technology for sub 0.1μm CMOS devices, sputter-coated Pt has been selected as the electrode material in this project.

The structural and bonding properties of the dielectric films were investigated using a transmission electron microscope (TEM) and an X-ray photoelectron spectroscopy (XPS). The MOS performance was characterized by the capacitance-voltage (C-V) and leakage current-voltage (I-V) measurements. The C-V and I-V measurements were performed using an impedances analyzer (HP 4194A) and an electrometer (Asvantest TR8652), respectively. The details of these characterizations are introduced as follows.
2.3.1 Transmission electron microscope (TEM)

Transmission electron microscope (TEM) is an important tool for studying the microstructure of materials. For thin gate dielectric films with thicknesses of usually less than 100Å, a cross-section high-resolution TEM (HRTEM) is the final judgment on the microstructure. HRTEM is also a very powerful tool for investigating the interfacial reaction that may happen at the dielectric/Si interface. The cross-section TEM samples were made by conventional methods, including mounting the sample with film side face-to-face, mechanical polishing and ion-milling.

2.3.2 X-ray photoelectron spectrometry (XPS)

X-ray photoelectron spectrometry (XPS) is based on a photoemission technique that is able to examine the composition and chemical state of species at a solid surface. The deposited thin film dielectric chemical state and interfacial reaction were characterized using a Physical Electronics Quantum 2000 X-ray photoelectron spectroscope with a monochromatic Al Kα (1486.7 eV) source.
2.3.3 $C-V$ characterization

The MOS capacitor is used to monitor the integrated circuit fabrication and to study the electrical properties of the MOS system. The MOS capacitor has the advantages of simplicity of fabrication and analysis.

During the $C-V$ measurement, some special points should be noted: a) the metal electrode should be made as small as possible to minimize leakage which may greatly affect the accuracy. The following figure is the kind of real case that we come across mostly during the fabrication of the MOS capacitor. A thin layer of SiO$_2$ present in between the gate dielectric and the Si substrate.

![Diagram of MOS capacitor with $C-V$ curves and a schematic of a MOS structure.]

FIG 2.11 High frequency $C-V$ curves.
For a pMOS, when a negative gate bias \( V_G < 0 \) is applied, holes will accumulate near the oxide/semiconductor interface. Therefore, the MOS capacitor behaves like a parallel plate capacitor in the case of accumulation; i.e.,

\[
C(V) = C_{ox} = \frac{\varepsilon_{ox} \varepsilon_0 A}{d_{ox}}.
\]

When there is a positive gate bias \( V_G - V_{TH} > 0 \), the width of the depletion layer increases with the gate bias voltage. The MOS capacitance in the depletion region is thus the resultant capacitance of \( C_{ox} \) in series with the depletion capacitance \( C_s \).

\[
C(V_G) = \frac{C_{ox} C_s}{C_{ox} + C_s}.
\]

When the positive gate bias \( V_G \geq V_{TH} \), where \( V_{TH} \) is the threshold voltage, so the depletion layer increases to a maximum thickness \( x_{dmax} \). Beyond this voltage, the variation in electron concentration may be at the oxide/semiconductor interface (low-frequency response) or at the outer boundary of the depletion layer (high-frequency response). The change in \( V_G \) is so rapid such that electrons do not have time to pass through the depletion layer. Electrons can only pass in and out of the outer boundary. The measured capacitance is therefore a minimum and is a constant.

\[
\frac{1}{C_{\min}} = \frac{1}{C_{ox}} + \frac{1}{C_{d_{max}}}.
\]

*C-V* characteristics describe the variation in the differential capacitance \( C = \frac{dQ}{dV} \) of
the MOS capacitor as a function of the gate bias voltage. In Fig. 2.11, the flat band capacitance $C_{FB}$ corresponds to the flat band gate voltage, $V_{FB}$. (In an ideal MOS system, $V_{FB}$ is zero), $C_{FB}$ is useful in determining the $V_{FB}$ in a real MOS system. The $C-V$ curve of a real MOS capacitor shifts in an amount of the "flat band voltage" with reference to an ideal $C-V$ curve. Once a $C-V$ curve is obtained from the measurement, $V_{FB}$ can be deduced from the measured $C_{FB}$. In Eq.(1) mentioned in the previous section, $V_{FB}$ equals a group of values that may be found experimentally. $V_{MS}$ can be found through the known data $\phi_m$ and $\chi_s$ from material handbooks, and $\phi_s$ can be calculated from the Si substrate doping concentration. $V_{mobile}$ may be obtained by conducting the bias-temperature test which measures the concentration of mobile ions trapped in the gate oxide.
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Chapter 3 Epitaxial HfO$_2$ Thin Films

Conditions for the epitaxial growth of HfO$_2$ films by PLD have been investigated by varying the growth conditions such as oxygen partial pressures, different targets (pure HfO$_2$ and yttrium stabilized HfO$_2$) and substrate temperatures. The thin yttrium stabilized HfO$_2$ (with 10% of yttrium) epitaxial films on p-type (100) Si substrates with resistivity of 5-25 ohm-cm were deposited at conditions described below. Si substrates were treated by a conventional HF-last process before film deposition leaving hydrogen terminal surface. The base vacuum of the PLD chamber is of $5 \times 10^{-5}$ Pa. After heating up the substrate to 550$^\circ$C, the vacuum decreased to $2 \times 10^{-4}$ Pa due to degassing. The wavelength of the Excimer laser is 248 nm and the energy density is 6 J/cm$^2$ with a repetition rate of 2 Hz. In order to prevent the formation of SiO$_2$ interfacial layer during deposition, the films were deposited at $2 \times 10^{-4}$ Pa without inducing any oxygen gas. The Pt dot electrode was formed on top of the films by subsequent deposition of Pt by PLD at 200$^\circ$C in the same chamber with a shadow mask of 0.25 mm$^2$ area. The so-formed MOS capacitors were evaluated by high frequency capacitance-voltage (C-$V$) and conductance-voltage (G-$V$) measurements using an HP 4194A impedance analyzer. The leakage current of the MOS capacitor was characterized by current-voltage ($I$-$V$) measurement performed with an Advantest TR8652 Digital Electrometer. The film microstructure and interfacial structure were studied by high-resolution transmission electron microscopy (TEM) with a JEOL 2010 microscope, and the film surface roughness was evaluated by an atomic force microscope. The depth profile photoelectron spectroscopy (XPS) of the film was characterized using a Physical Electronics Quantum 2000 XPS with a monochromatic Al K$_\alpha$ (1486.7 eV) source.
Figure 3.1 shows cross-sectional high-resolution TEM images of the as-grown 40Å yttrium stabilized HfO$_2$ film on Si substrate. As mentioned in previous section, alloying with yttrium can be stabilized HfO$_2$ in its cubic structure. Within all the TEM observation areas, there is no distinguishable grain boundary in the film and the film shows a fixed orientation relationship with the Si substrate. This characteristic suggests that the film is highly epitaxial. From the enlarged high-resolution TEM image as shown in Fig. 3.1(b), the orientation relationship between cubic HfO$_2$ and Si substrate can be determined as (100)HfO$_2$/|(100)Si, and [001]HfO$_2$/|[001]Si. One can also see that the interface is free from any SiO$_2$ amorphous layer. However, due to a large (5.7 %) lattice mismatch between HfO$_2$ and Si, the interface is actually not atomically flat and sharp. This interface characteristic suggests that lattice strain and interdiffusion at the interface may happen. In addition, interfacial dislocations at the interface can also be identified by careful examination of the lattice image.
FIG. 3.1. High-resolution TEM image of epitaxial yttrium stabilized HfO₂ film (expressed as YSH in the figure) on (001) Si observed along the [110] direction of Si. (a) is a lower magnification image, and (b) a higher magnification image.

Figure 3.2 shows $C-V$ and $G-V$ curves of the epitaxial yttrium stabilized HfO₂ films on the MOS capacitor measured at 1 MHz. Due to the presence of oxygen deficiencies in the film, the as-grown samples show large leakage current ($7.0 \times 10^{-2}$ A/cm² at gate voltage of 1 V) as shown in the inset in Fig. 3.2, and thus $C-V$ measurements at different frequencies exhibited large discrepancy (only the result measured at 1 MHz is shown).

The relative permittivity of the yttrium stabilized HfO₂ film from the series capacitance analysis as shown in Fig. 3.2 is about 14 and the equivalent oxide thickness (EOT) is 12 Å. However, a parallel capacitance analysis yields a relative permittivity smaller than 1. The large discrepancy between the series and parallel analysis revealed a large dissipation of
the capacitor (dissipation factor is calculated to be 5.1 at 1 MHz from the admittance).

Since the as-grown film/Si interface may contain Hf-Si bonds and interfacial dislocations, the interface trap density and flat-band voltage are expected to be much higher than acceptable values, as suggested by Fig. 3.2. However, for a very thin yttrium stabilized HfO₂ film, it is difficult to optimize the annealing condition in oxygen ambient, since the resistance to oxygen diffusion for HfO₂ film is very low. Therefore, a layer of SiO₂ will normally be formed at Si interface after thermal annealing in oxygen ambient. The effort to find an optimized annealing condition without forming SiO₂ interfacial layer was not successful and it deserves further studies.

![Graph](image)

**FIG. 3.2.** High frequency (1MHz) C-V and G-V curves of the parallel plate capacitor of the as-grown 40Å yttrium stabilized HfO₂ epitaxial film. The inset is a characteristic I-V curve of the epitaxial film.

In order to study the epitaxial growth mechanism, some comparison experiments were carried out. Pure HfO₂ ceramic target was used to grow HfO₂ films under the same condition for the epitaxial growth of yttrium stabilized HfO₂ films. TEM observations of the pure HfO₂ films revealed that the films are polycrystalline even though there is no
SiO\textsubscript{2} layer present at the interface. Figure 3.3 shows a TEM image of a few HfO\textsubscript{2} grains with different orientations in the film. Polycrystalline HfO\textsubscript{2} film on bare Si grown by PLD has been reported by Ikeda and co-workers [1]. However, due to the large stress at the interface and the possible phase transformation from cubic to tetragonal structures in the film, it is difficult to grow pure HfO\textsubscript{2} epitaxial films on Si. This is due to the well-known instability of HfO\textsubscript{2} cubic structure that undergoes Martensitic phase transformation to tetragonal and monoclinic structures under stress.

![Image of TEM image showing SiO\textsubscript{2} layer, HfO\textsubscript{2} film, and Si substrate with 2 nm scale]

FIG 3.3. High-resolution TEM image of a polycrystalline HfO\textsubscript{2} film on Si.

Substrate temperature was found to be a critical parameter for the epitaxial growth of yttrium stabilized HfO\textsubscript{2} films. TEM observations revealed that higher substrate temperature at 600°C caused SiO\textsubscript{2} formation on Si surface before film deposition and therefore prevented the epitaxial growth of the films (see Fig. 3.4 (a)). On the other hand, the films grown at lower substrate temperature of 450°C also resulted in polycrystalline structure even the interface is free from SiO\textsubscript{2} layer (Fig. 3.4 (b)). This can be understood by considering the different mobility of atoms arrive at the Si surface at different temperatures. Higher substrate temperature results in higher atom mobility and allows the
atoms move into low energy lattice sites thus leads to a layer-by-layer growth. Lower substrate temperature results in lower atom mobility and thus the atoms do not have sufficient kinetic energy to overcome the energy barrier to reach the epitaxial lattice sites and the film growth is basically by island growth mechanism forming columnar grains with different orientations. Again one can see that the film/Si interface is rough suggesting interfacial diffusion and reaction.

FIG. 3.4. High-resolution TEM image of polycrystalline yttrium stabilized HfO\textsubscript{2} film on Si. (a) grown at 600°C, and (b) grown at 450°C.
The process window for yttrium stabilized HfO$_2$ epitaxial growth on bare Si in our case is very narrow. We believe this is due to the relatively lower vacuum of the system compared to ultra-high vacuum (UHV) system. For a relatively lower vacuum, due to the residue oxygen gas in the chamber, there is a temperature limit above which SiO$_2$ will be formed on Si surface preventing the epitaxial growth of the intended oxide films. For UHV system in which SiO$_2$ and SiO can be vaporized at high temperature, the epitaxial growth can be realized within a large range of temperatures. This suggests that the quality of yttrium stabilized HfO$_2$ epitaxial films may be improved by growing the films in an UHV system at higher temperatures. The oxygen content in the yttrium stabilized HfO$_2$ films is another issue since it is very difficult to be optimized. However, well-controlled and optimized SiO$_2$ layer less than 10 Å can result in a compromised effect between a decreased gate stack capacitance and improved interfacial quality to Si, since no high-k system has yet shown an interfacial quality equal to that of SiO$_2$ [2].

The advantages of the yttrium stabilized HfO$_2$ epitaxial films over the HfO$_2$ polycrystalline films have been studied in terms of surface flatness.Atomic force microscope analysis revealed that the surface root-mean-square roughness for the yttrium stabilized HfO$_2$ epitaxial film is 2.5 Å, and 5.4 Å for pure HfO$_2$ film. Therefore, the surface flatness for epitaxial yttrium stabilized HfO$_2$ films is better than that of polycrystalline HfO$_2$ films.

XPS technique has been commonly used in the study of thin film chemical structure and interfacial reaction of HfO$_2$ and Hf silicate on Si [3-10]. In order to study the interfacial reaction and diffusion that may happen at the interface of the epitaxial yttrium stabilized HfO$_2$ film on Si, the as-grown film was subjected to XPS analysis. Figure 3.5 shows the depth profile XPS binding energy of Hf 4f and Si 2p peaks, while the film was
subsequently removed by Ar⁺ in-situ sputtering. One can see from Fig. 3.5 (a) that with increasing depth, the peak position of Hf 4f shifted from HfO₂ (17.6 eV) to elemental Hf (~ 14.6 eV). The presence of elemental Hf peak inside the film illustrates the existence of oxygen vacancies. The dominated elemental Hf peak at the interfacial area suggests more oxygen deficiencies during the earlier stage of film growth and also possible Hf silicide formation since Hf-Si binding energy is very close to the elemental Hf peak [3-5].

FIG. 3.5. XPS depth profile of epitaxial yttrium stabilized HfO₂ film on Si: (a) Hf 4f peak, (b) Si 2p peak.
The sequence of the spectra are as follow: (i) film surface, (ii) after a 150s sputtering, (iii) after a 270s sputtering, (iv) after a 750s sputtering, (v) after a 1110s sputtering, (vi) after a 1600s sputtering.

Since the film is only about 40Å, the XPS spectra from surface may also contain information from the interfacial area due to the penetration effect. The Si 2p peak at
~102.8 eV in spectrum (i) as shown in Fig. 3.5 (b) illustrates Hf-silicate formation close to the interfacial area [3]. The shifting to a higher binding energy of Hf 4f peak from spectrum (i) to (ii) as can be clearly seen in Fig. 3.5 (a) also evidences the presence of Hf-silicate at the interfacial area [3,5]. It can also be identified from Fig. 3.5 (b) that there is a shift of Si 2p peak from 99.3 eV to higher energy end in the first three spectra. This fact and the appearance of elemental Hf 4f peak when approaching the film/Si interface suggest that Hf silicide or Hf-Si bonds may be formed at the interfacial area, even though there is no evidence from TEM observation. The formation of Hf silicide or Hf-Si bonds can be understood by considering the fact of insufficient oxidation of Hf atoms at the beginning of film growth on bare Si surface leading to the reaction of Hf with Si. The Hf silicate formation is believed to be due to the further oxidation of Hf silicide that has been formed at the interface. Therefore, it is reasonable to expect that with sufficient oxygen during film growth, the Hf silicide formation can be suppressed at earlier stage of film growth or can be eliminated during subsequent film growth.

Wang and co-workers have reported the epitaxial growth of yttrium stabilized zirconia (YSZ) on Si [11,12]. A dynamic growth model during the first few atomic layers has been proposed in which the reaction of Zr with SiO₂ and the desorption of SiO were thought to be essential for the epitaxial growth. In the beginning, the in-coming Zr atoms react with the preformed SiO₂ and the product of SiO is desorbed leading to the epitaxial growth of ZrO₂ film. However, the yttrium stabilized HfO₂ epitaxy in our case is expected to follow a different mechanism, i.e. the film was epitaxially deposited on the crystalline Si surface directly without the reaction between Hf atoms and SiO₂. This assumption is based on two facts. First, the epitaxial growth was at substrate temperature of 550°C, which was much lower than the temperature of 730°C for the YSZ epitaxial growth.
[11,12]. At such a low temperature, the oxidation of hydrogen terminated Si surface at vacuum of $2 \times 10^{-4}$ Pa was difficult. The film growth condition of 550°C and $2 \times 10^{-4}$ Pa is actually close to the lower limit to form SiO$_2$ as reported by Seiple and co-workers [13]. Secondly, it is difficult to expect desorption of SiO at temperature of 550°C (if any). Therefore, we believe that the epitaxial deposition of yttrium stabilized HfO$_2$ on bare Si is by direct growth without formation of amorphous SiO$_2$ layer. In fact, the formation of Hf-Si bonds suggested by the XPS result also supports this direct growth mechanism.

In summary, epitaxial yttrium stabilized HfO$_2$ thin films have been deposited on p-type (100) Si substrates by pulsed laser deposition at low substrate temperature of 550°C. The orientation relationship between the epitaxial film and Si is (100)Si///(100)HfO$_2$ and [001]Si//[001]HfO$_2$. The relative permittivity of an as-grown 40Å yttrium stabilized HfO$_2$ epitaxial film was characterized to be about 14 and the equivalent oxide thickness (EOT) is 12 Å. The leakage current density is $7.0 \times 10^{-7}$ A/cm$^2$ at 1 V gate bias voltage. The mechanism of the epitaxial growth of the yttrium stabilized HfO$_2$ thin films on Si was discussed, and the interfacial diffusion and reaction have been illustrated by XPS analysis.
References


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Chapter 4 Hf-aluminate Thin Films

4.1 Hf-Al-O Thin Films

The Hf-Al-O ultrathin films on p-type (100) Si substrate were deposited by pulse-laser deposition (PLD) using a specially designed target containing HfO$_2$ and Al$_2$O$_3$ plates. As shown in Fig. 4.1, the laser frequency was set to 2 Hz and the target rotation was set to a speed in which the HfO$_2$ and Al$_2$O$_3$ targets were sequentially ablated only one pulse a time during ablation. Based on the experimental data, the HfO$_2$ and Al$_2$O$_3$ films' growth rate for each pulse is about 0.2 Å which is much smaller than one single atomic layer. Therefore, the composite films grown by this method can be considered as sublayer laminates of HfO$_2$-Al$_2$O$_3$, and we can expect that such films are comparable with the films made using target containing HfO$_2$ and Al$_2$O$_3$ particles. The base vacuum of the chamber is 5 ×10$^{-5}$ Pa, and in order to reduce the formation of interfacial SiO$_2$ layer, the films were deposited at a relatively lower substrate temperature of 550°C. Si substrates were treated by a conventional HF-last process before film deposition leaving hydrogen terminal surface. A KrF excimer laser (λ = 248nm) with laser fluence of 6 J/cm$^2$ is used for the film deposition. In order to study its structure stability under high temperature, the as-grown films were rapid thermal annealed (RTA) at 1000°C for 10s at a vacuum of 10$^{-3}$ Torr. RTA under reduced oxygen pressure (5 Pa) was also performed at 500°C for 1 min in order to compensate for the oxygen loss during film deposition. The structure of the films and the interface with Si substrates before and after annealing was characterized by means of high-resolution transmission electron microscopy (TEM) using a JEOL 2010 electron microscope equipped with energy dispersive X-ray (EDX) analysis. The
chemical structure of the film was characterized using Physical Electronics Quantum 2000 X-ray photoelectron spectrometer with a monochromatic Al Kα (1486.7 eV) source. The scans were done at pass energy of 23.5 eV and a take-off angle of 90°. All of the spectra are calibrated against C 1s peak (284.5 eV) of adventitious carbon and plotted with normalized intensities. Electrical properties of the MOS capacitors with Pt dot electrodes were studied by C-V measurements using a HP4194A impedance analyzer. Leakage current of the capacitors was characterized by means of an Advantest TR8652 Digital Electrometer. The electrode area was $2.5 \times 10^{-3}$ cm$^2$ for both C-V and I-V measurements.

FIG 4.1 The target rotation was set to a speed at which the HfO$_2$ and Al$_2$O$_3$ targets were sequentially ablated only one pulse a time during ablation. The composite films grown by this method can be considered as sublayer laminates of HfO$_2$-Al$_2$O$_3$. 
FIG. 4.2 Cross-sectional TEM images of thin Hf-Al-O films on p-type (100) Si substrates with different annealing conditions. (a) As-grown film, (b) annealed at 500°C for 1 min with oxygen partial pressure of 5 Pa, and (c) RTA at 1000°C for 10s.

EDX analysis of the as-grown Hf-Al-O films shows that the films generally have a composition of Hf$_{0.14}$Al$_{0.25}$O$_{0.61}$. TEM examinations of different temperature annealed Hf-Al-O films revealed that the amorphous structure of the films is stable under all the annealing temperatures up to at least 1000°C. Figure 4.2 shows TEM pictures of an ultrathin (about 38 Å) Hf-Al-O amorphous film grown on Si substrate before and after thermal annealing. In Fig. 4.2(a), the very thin white contrast interfacial layer in the as-grown sample indicating possible SiO$_2$ rich layer formed during film deposition. After annealing at 500°C for 1 min in oxygen ambient, there is no further oxidation of the Si
substrate as shown in Fig. 4.2(b). This indicates that the film has sufficient resistance to oxygen diffusion at this condition. It should be pointed out that the interface between Hf-Al-O film and epoxy is not sharp since both of them are amorphous structure. The Hf-Al-O film surface is very flat, in fact, as proved by atomic force microscope analysis that shows only 2Å of r.m.s. roughness.

No evidence of crystallization can be found within all the observed areas in the Hf-Al-O film after RTA performed at 1000°C for 10s. Figure 4.2 (c) is a representative high-resolution TEM picture showing amorphous structure of the Hf-Al-O film after 1000°C RTA. The interfacial layer formed as shown in Fig. 4.2 (c) is SiO₂ layer due to further oxidation of Si during RTA since the vacuum is not high enough for very high temperature annealing. The very recent report shows that the structural transition from amorphous to crystalline for the Al₂O₃-HfO₂ nanolaminates occurs at the temperature of 920°C and the laminate is drastically broken [1]. Therefore, the amorphous Hf-Al-O films under our deposition condition show much better thermodynamic stability compared to laminated structure. In fact, a comparison experiment has been carried out to illustrate the high resistance to oxygen diffusion of Hf-Al-O film using HfO₂ film as a control sample. The result revealed that the amorphous Hf-Al-O thin film has much better property to block the oxygen diffusion.
Figure 4.3 is a characteristic high frequency $C-V$ curve of the 38-Å Hf-Al-O film with bias voltage from -6V to 4V. The accumulation capacitance is 9 nF, and the peak near the transition on the accumulation side may be caused by too much series resistance [2,3]. The relative permittivity of the Hf-Al-O film is calculated to be about 16 and the equivalent oxide thickness (EOT) is 9.2 Å for the sample annealed at 500°C for 1 min in oxygen ambient. Inset in Fig. 4.3 is a typical current density-voltage curve of the MOS capacitor, and one can see that at 1 V gate bias voltage, the leakage current density is $4.6 \times 10^{-3}$ A/cm², which is 4 orders of magnitude higher than that of 15Å SiO₂ [4].

Formation of Hf-O and Al-O bonds is studied by XPS analysis as shown in Fig. 4.4. Figure 4.4 (a) shows the Al 2$p$ peak at 74.2 eV indicating Al₂O₃ formation in the film. The Hf 4$f$ peak is shown in Fig. 4.4 (b). It is worth noting that compared to the reported Hf 4$f$ peaks (16.8 and 18.5 eV) for HfO₂ [5], there is a 0.4 eV shift of Hf 4$f$ peaks toward higher binding energy for the Hf-Al-O film in our case. Yu et al stated that all the core level peak positions of Hf 4$f$, Al 2$p$, and O 1$s$, experience a shift to higher binding energy with the increase of Al₂O₃ concentration in Hf-Al-O system [6]. This shift may be attributed to the
fact that Hf is a more ionic cation than Al in Hf-Al-O system, and thus the charge transfer contribution changes with the increase of Al concentration [6-8].

![XPS spectra of annealed Hf-Al-O ultrathin film on Si substrate. (a) Al 2p spectra, and (b) Hf 4f spectra. The 4f (7/2) peak is 17.2 eV, separated by the 1.7 eV spin splitting from the Hf 4f (5/2) peak at 18.8 eV.](image)

**FIG. 4.4** XPS spectra of annealed Hf-Al-O ultrathin film on Si substrate. (a) Al 2p spectra, and (b) Hf 4f spectra. The 4f (7/2) peak is 17.2 eV, separated by the 1.7 eV spin splitting from the Hf 4f (5/2) peak at 18.8 eV.

In summary, ultrathin amorphous Hf-Al-O films have been deposited on p-type (100) Si substrates by PLD. TEM examinations of different temperature annealed Hf-Al-O films revealed that the amorphous structure of the film is stable up to at least 1000°C annealing. Relative permittivity of 16 and a EOT of 9.2 Å have been achieved by a 38-Å amorphous Hf-Al-O film and the film presents very a low leakage current density of $4.6 \times 10^{-3} \text{ A/cm}^2$. XPS analysis of the Hf-Al-O film shows the formation of Hf-aluminate in the film.
4.2 Silicide Formation

During the investigation of Hf-aluminate thin film properties as described in the former section, an interesting interfacial reaction phenomenon is presented in some of our films fabricated in a particular film growth condition. Such phenomenon was attributed to unstable Hf-Al-O/Si interface such that Hf-silicide is formed within the interfacial area.

![Image](image.png)

FIG 4.5. Cross-sectional TEM images of a thin Hf-Al-O film on a (100) Si substrate. (a) Low magnification and (b) high resolution. The circles indicate the interfacial reaction.

Figure 4.5 shows TEM pictures of a 60Å-thick Hf-Al-O thin film grown on Si substrate at 550°C. It can be seen that the Hf-Al-O film is of uniform amorphous structure possessing atomically flat surface and interface with Si. In fact, atomic force microscope analysis of the surface morphology revealed a r.m.s. roughness of only 2.5 Å. It can also be seen from the low magnification picture in Fig. 4.5 (a) that there are some island-shaped precipitates on the Si surface with darker contrast suggesting interfacial
reaction or diffusion at the interface. These interfacial reactions are generally observed in all the samples with different thicknesses deposited over a wide range of temperatures from 550°C to 700°C without introducing any oxygen gas, and it was found that the degree of reactions increases with growth temperature. The atomic ratio of Al/Hf in the films is about 1.4 as revealed by micro-beam EDX analysis. Nano-beam EDX analysis also proved that the island-shaped interfacial reaction productions are Hf silicide. This matches the fact that Al usually does not form silicide bond with Si.

![Image](image.png)

**FIG. 4.6** (a) Low magnification cross-sectional TEM image of a thin Hf-Al-O film on a Si substrate. (b) Cross-sectional TEM image of the same Hf-Al-O film on Si showing interfacial reaction at the interface. (c) Corresponding selected area electron diffraction pattern from the plan-view sample.

Figure 4.6 (a) is a plan-view TEM picture of another Hf-Al-O film grown at 700°C. Since plan-view TEM observation of amorphous film on Si should show uniform contrast, the grain-like features as appeared in Fig. 4.6 (a) indicate a very serious interfacial
reaction. It can also be seen that some Hf silicide islands are faceted into hexagons. The Moiré fringes that can be identified from the plan-view TEM picture are due to the overlapping of the silicide islands with Si substrate that was not milled off by ion beam. Figure 4.6 (b) is a cross-sectional TEM image of the same film on Si showing the interfacial reaction. The corresponding selected area electron diffraction pattern from the plan-view sample is shown in Fig. 4.6 (c), where the strong diffraction points is from Si [100] zone axis and the rings and weak points are from Hf silicide. Since the diffraction from Hf silicide contains rings and isolated dots, the silicide formed may contain more than one phase. The phase identification of Hf silicide formed at the interface will be further studied.

![TEM images](image)

**FIG. 4.7** High-resolution TEM images of thin films on Si. (a) pure Al₂O₃, and (b) pure HfO₂.

It is well known that the interfaces of HfO₂/Si and Al₂O₃/Si are thermodynamically stable. However, the formation of Hf silicide at the interface suggests that the interface of Hf-Al-O/Si is not stable. In fact, we have carried out a comparison experiment by depositing Al₂O₃ and HfO₂ films at the same condition as growing the Hf-Al-O films. The results showed that the interfaces of Al₂O₃/Si and HfO₂/Si were free from significant
silicidation reaction (see Fig. 4.7). An interesting question arises from this fact is that why HfO$_2$/Si and Al$_2$O$_3$/Si interfaces are stable (free from silicidation) but Hf-Al-O/Si interface is not. There are two approaches leading to the answer of the question. First, we believe that there is a competition between Hf and Al atoms in bonding with limited oxygen atoms when they arrive on the Si surface. Since Al has very strong affinity to oxygen atoms, some of the Hf atoms at the Si surface will be difficult to form oxide bond. The lack of oxygen for Hf atoms at the interface area is believed to be the reason of the Hf silicide formation. It has been reported earlier that oxygen-deficient Zr can react with SiO gas phase to form ZrSi$_2$ under high temperature annealing in ultra-high vacuum condition [9,10]. Similar mechanism may also be applicable to describe the Hf-Al-O/Si system.

The other approach is related to another question. It is well known that both amorphous and crystalline HfO$_2$ are thermodynamically stable in contact with Si. The question is that whether the interface is still stable or not if HfO$_2$ is in amorphous structure at temperatures much higher than its transition temperature from amorphous phase to crystalline phase. The answer is uncertain since the Gibbs free energies for HfO$_2$ in amorphous and crystalline phases at the same temperature are different, and thus the tendency of chemical reaction based on the Gibbs energy analysis may be changed. Our experimental result suggested that if HfO$_2$ is not in crystalline structure at high temperatures due to alloying with Al$_2$O$_3$, the HfO$_2$/Si interface may not be thermodynamically stable, especially at oxygen deficient conditions. Detailed thermodynamic analysis in this Hf-Al-O/Si system is not possible at present due to the lack of enough thermodynamic information.
This Hf silicide reaction is not usually seen in other deposition techniques such as jet-vapor-deposition [11], atomic layer deposition [6,12-13] and chemical vapor deposition [14], where oxygen source (or water vapor) and high temperature are involved during the deposition. Sufficient oxygen source and high temperature result in significant SiO₂ interfacial layer formation and thus the silicidation is suppressed. However, Hf aluminate can be grown by PLD without introducing oxygen gas during disposition and oxygen vacancies in the films can be filled by subsequent annealing in oxygen ambient. Therefore, the condition of lack of oxygen in PLD process may result in silicidation. In fact, when oxygen gas was introduced during the PLD process in our experiment, silicidation-free interface was obtained. By optimizing the oxygen pressure (≈10⁻⁴ Pa), SiO₂ interfacial layer can be controlled within 10Å, and silicidation was inhibited.

![Graph](image)

**FIG 4.8.** High frequency (1 MHz) C-V curve of a thin Hf-Al-O film with silicide reaction at the interface. The inset shows a well-behaved C-V curve of a sample without interfacial reaction.

Figure 4.8 is a high frequency C-V measurement of a thin Hf-Al-O film (60Å) parallel plate capacitor-containing silicide at the interface. Compared to the well-behaved
C-V curve from the sample without silicidation at the interface grown at an optimised oxygen partial pressure (inset in Fig.4.8), there is no saturation in accumulation region and a small hump near \( V_{\text{bias}} = -1.0 \text{V} \) is presented. Theses features suggest the presence of large amount of interface traps in the Si band gap [15]. Since the very thin Hf-Al-O film resulted in large leakage current, the C-V measurement at different frequencies showed large discrepancy. Therefore, only 1MHz results are shown in Fig. 4.8.

![Diagram](image)

**FIG 4.9.** Characteristic C-V curve of a thicker Hf-Al-O film with interface silicidation. The frequencies are (a) 100 kHz, (b) 200 kHz, (c) 300 kHz, (d) 500 kHz, (e) 1 MHz, (f) 2 MHz.

Figure 4.9 is a characteristic C-V curve of a thicker (30Å) Hf-Al-O film grown at 700°C containing silicide islands at the interface. The driving frequencies are from 100kHz to 2MHz. Besides the feature of non-saturating of accumulation capacitance similar to those of thinner film sample, there is another significant feature that need to be noted in this abnormal C-V curve. A step near the boundary of depletion and weak
inversion can be seen as indicated by the arrow, and from that point the capacitance shows continuous decrease against the gate bias voltage. This feature may due to the screening effect to the electric field by the Hf silicide islands.

The chemical structures of both the Hf-Al-O thin films with and without annealing were subjected to investigation by using XPS. XPS spectra for Hf 4f, Al 2p are shown in Fig. 4.10. One can see that silicidation occurs in the as-grown sample evidenced by presence of a peak at the lower binding energy end. The Hf 4f (7/2) peak is 17.1 eV, and the Hf 4f (5/2) peak is 18.9 eV with a electron spin separation of 1.8 eV. The peak appeared at 13.7 eV in the spectrum is due to the presence of Hf-Si bond [16-17]. The interfacial silicidation may be due to the oxygen deficient condition during thin film deposition. It is well known that the interfaces of HfO2/Si and Al2O3/Si are thermodynamically stable. Some more evidence can be found in the XPS analysis to support the two proposed explanations mentioned in the recent publication [18]. One of the explanations is the competition between Hf and Al atoms in bonding with limited oxygen atoms when they arrive on the Si surface. In Fig. 4.10, the inset is the spectra of Al 2p peak for various depth within the same sample. It indicated that the Al2O3 is mainly formed on the surface region of the Hf-Al-O film. This suggested that Al atoms have stronger affinity with oxygen to form Al2O3 and migrate outward to combine with the incoming excessive oxygen during annealing.
FIG 4.10. XPS spectra of as-grown and thermal annealed Hf-Al-O films on p-type (100) Si. The Hf 4f(7/2) peak is 17.1 eV for the thermal annealed sample. The inset is the XPS spectra of the Al 2p peak position taken for various depths within the same sample.

A similar condition of film fabrication was also carried out to deposit the film in a higher oxygen gas pressure ($\times 10^{-3}$ Pa) which is believed to be able to prevent the silicidation. Figure 4.11 shows high-resolution TEM images of an ultrathin (about 38 Å) Hf-Al-O amorphous film grown on Si substrate before and after thermal annealing. The thin white contrast layer in Fig. 4.11 is suggested to be a SiO$_2$ rich layer formed in the interfacial area. After the rapid thermal annealing at 1000°C for 10s in oxygen ambient, there is no further crystallization of the Hf-Al-O thin film as shown in Fig. 4.11(b). This indicates that the amorphous structure of the thin film can sustain a very high annealing temperature.
In summary, amorphous thin films of Hf-Al-O have been deposited on p-type (100) Si substrates by pulsed-laser deposition. TEM analysis revealed the Hf silicidation reaction at the Hf-Al-O/Si interface. Al oxide presented in the films retards the formation of crystalline HfO₂, and thus triggers the reaction between the Hf atoms in the amorphous Hf-Al-O film and Si at the oxygen deficient condition. Al atoms have a tendency to move outward to bond with oxygen to form Al₂O₃ in the surface of the Hf-Al-O film. High-frequency C-V measurements revealed the impact of silicide formation at the interface on electric properties, and this impact seems to be both frequency and dielectric thickness dependent.
References


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Chapter 5 Conclusion and Future Work

In conclusion, HfO$_2$ based high relative permittivity gate dielectrics have been studied in this project. The films are deposited on p-type (100) Si substrate by PLD system and the performance of different high-k gate dielectrics has been characterized. With a laser fluence of about 6 J/cm$^2$ and a relatively low substrate temperature (~550°C) in high vacuum condition, epitaxial yttrium stabilized HfO$_2$ thin films on bare Si have been grown. The orientation relationship between the epitaxial film and Si is (100)Si//(100)HfO$_2$ and [001]Si//[001]HfO$_2$. The relative permittivity of an as-grown 40 Å-thick yttrium stabilized yttrium stabilized HfO$_2$ epitaxial film was characterized to be about 14 and the equivalent oxide thickness (EOT) is 12 Å. The leakage current density is $7.0 \times 10^{-2}$ A/cm$^2$ at 1 V gate bias voltage.

Much better structural and electrical properties have been achieved in alloys of Al with HfO$_2$. TEM examinations of Hf-Al-O films annealed at different temperatures have revealed that the amorphous structure of the film is stable up to at least 1000°C annealing. Relative permittivity of 16 and an EOT of 9.2 Å have been achieved in a 38 Å amorphous Hf-Al-O film. The film shows a very low leakage current of $4.6 \times 10^{-3}$ A/cm$^2$. We believe that Hf-aluminate is very promising as an alternative gate dielectric due to its stabilized amorphous structure and low leakage current.

However, it must be pointed out that an oxygen deficient condition in high vacuum deposition process may result in a serious interfacial silicidation problem; i.e. Hf-silicide island formation on Si surface. This problem can be eliminated by introducing a proper amount of oxygen during the film growth.

Relationship between annealing temperatures and thin film properties has been
examined in several series of experiments. Although a final conclusion has not been reached, an optimized annealing condition has been identified as evidenced by reduced leakage current density after annealing. It is also worthy to notice that the size of the "silicide island" formed in the interfacial layer is related to the substrate temperatures during deposition and post annealing. Nevertheless, a detail understanding of the above phenomena needs further study.

Investigation of the electrical properties of HfO₂ and Hf-Al-O films in the present work is limited due to the lack of determinable information, even though we have put much effort on the electrical measurement of $C-V$ and $I-V$ characteristics. Instead we have emphasized on the study of the mechanism of thin film growth and physical characterizations, by TEM and XPS. More quantitative characterization such as flat band voltage ($V_{FB}$), interface density of state ($D_{in}$), time-dependent $I-V$ characteristics and reliability are highly desirable for further studies.
List of Publications


