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## The Hong Kong Polytechnic University

### The Department of Applied Physics

Development of novel low-temperature selective hydrogen

gas sensors made of palladium/oxide or nitride

capped Mg-transition metal hydride films

Tang Yu Ming

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

Feb 2011



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Tang, Yu Ming

### Abstract

Palladium capped Mg-based transition metal alloy film (Pd/Mg-TM) is a potentially useful hydrogen gas (H<sub>2</sub>) sensing material, which can operate at low temperature for detection of H<sub>2</sub> leakage in an environment to ensure safe use and storage of the gas. The Pd layer catalytically dissociates hydrogen molecules, and the hydrogen atoms produced can enter (hydridation) or be detached (dehydridation) from the alloy layer. These processes are reversible, such that the film is switchable between a metal state and a hydride state, giving rise to substantial changes in its optical transmittance/reflectance and electrical resistivity. Unlike a conventional metal-oxide (MO<sub>x</sub>) H<sub>2</sub> sensor, hydridation of an Mg-TM film is associated with relatively low enthalpy, and hence can perform at temperature much lower than the operation temperature of an MO<sub>x</sub> sensor (typically around 500°C or above). As such, an Mg-TM based sensor does not experience undesired annealing effect during operation, and hence is much more stable and durable. Furthermore, the detection selectivity of a Pd/Mg-TM film versus other reducing gases is superior to most conventional MO<sub>x</sub>-type hydrogen sensors. In this project, we systematically investigated the H<sub>2</sub> sensing properties of Pd/Mg-TM films. The emphases of our work and the major results obtained are briefly delineated in the following.

- The dependences of H<sub>2</sub> sensing properties of Pd/Mg-nickel (Ni) films on hydrogen partial pressure (P<sub>H2</sub>) and temperature were investigated with a specifically designed measurement system.
  - At 60°C, the changes of the resistance (R) and optical transmittance (T) with He-Ne laser as incident light of a Pd/Mg-Ni film were observed with  $P_{H_2}$

increased with a very slow rate (quasi-static mode). During measurements, the film in the measurement chamber was made to get contact and react with a H<sub>2</sub>-argon (Ar) mixture, where the gas was admitted into the chamber very slowly. The relationship obtained is referred to as the resistance-pressure isotherm (RPI) and optical transmittance-pressure isotherm (TPI) respectively. Each plot shows three different stages. In Region I of low  $P_{H_2}$ , both R and T increase linearly with increasing  $P_{H_2}$ , with relatively fast response and recovery times. In Region II of moderate  $P_{H_2}$ , both R and T increase more rapidly and non-linearly with  $P_{H_2}$ . In Region III of even higher  $P_{H_2}$ , the increasing rates of the responses with increasing  $P_{H_2}$  become slower.

The durability of the gas sensing response were investigated by exposing the film to air and H<sub>2</sub>-Ar (or H<sub>2</sub>-air) mixture with a fixed H<sub>2</sub> content alternatively. This testing method is referred to as the cyclic mode of measurement. Results show that the H<sub>2</sub> sensing response is most stable in Region I, because the hydrogen content in the film varies in a low range such that hydrogen atoms are only incorporated interstitially without affecting the network. As such, only a solution of hydrogen is formed, which is denoted as the α-phase of Mg-Ni alloy. In Region II, more hydrogen atoms are incorporated into the film, such that transitions between the α-phase and β-phase occur. The gas sensing responses are stronger, but H-induced volume expansion and contraction of the film material occur, which initiate cracking of the film surface and subsequent invasion of oxygen from the surrounding. The oxygen atoms tend to react with Mg

atoms and a surface oxide layer is formed to degrade the reproducibility of the gas sensing response of the film. In Region III, the film is mainly in the  $\beta$ -phase. The difference between the specific volumes of the alloy phase and  $\beta$ -phase are great (over 30%), such that cracking of the Pd cover layer and the alloy layer is more severely, and the gas sensing properties deteriorate very fast with increasing number of switching cycles.

- Data obtained at various measurement temperatures reflect that degradation of the gas sensing response of a Pd/Mg-Ni film is associated with a decrease in the enthalpy and entropy, and an increase in the activation energy of the hydridation processes. Combining with compositional and structural data, one expects to gain insights on the mechanisms governing the stability of switching responses of R and T.
- 2. Referring to the results on the gas sensing responses detected, we recognized that the durability of the gas sensing responses of Pd/Mg-Ni films was still a problem requiring further improvement. Three remedial schemes were implemented and the results are briefly described in the following.
  - Increase the thickness of the Pd cover layer ( $t_{Pd}$ ). In particular, the H<sub>2</sub> gas responses of two Pd/Mg-Ni (35 nm) films with 5 and 10 nm Pd cover layers respectively obtained in cyclic tests were compared. The test was performed by exposing a film to a 4% H<sub>2</sub>-argon (or 4% H<sub>2</sub>-air) mixture. The gas responses the one with a smaller  $t_{Pd}$  started to degrade substantially after around 400 cycles, but that of the one with a larger  $t_{Pd}$  can last to over 2000 cycles without significant deterioration. This suggests that a thicker Pd cover

layer can obstruct the invasion of oxygen into the alloy layer more effectively, and thus decelerates the formation of surface oxide. It also shortened the response time substantially, but the drawback was to cause a reduction in gas detection sensitivity.

- The next one was to increase the Ni content near the film surface before the addition of the Pd cover layer. This approach is based on the intention of obstructing the diffusion of the Pd atoms in the cover layer into the Mg-Ni layer and to alloy with Mg atoms. Results show that both the sensitivity and stability are prominently improved. The drift in enthalpy and entropy associated with the hydridation process are greatly suppressed. In addition, data of X-ray photoelectron spectroscopy (XPS) analyses showed that diffusion of Pd into the Mg-Ni layer was substantially reduced, explaining the observed improvement of the stability of the gas responses of the film.
- The third approach was to dope iron (Fe) into the Mg-Ni layer by means of co-sputtering when depositing the alloy film. Results show that stability of the gas sensing responses of the Fe-doped Pd/Mg-Ni films was also improved. The reason leading to the improvement was found to be similar to that of the surface Ni-enriched Mg-Ni film, namely by suppression of alloying between Pd and Mg atoms, but the switching rate of a Fe-doped one was found to even faster.
- 3. To further examine the possible mechanisms responsible for the hydridation of a Pd/Mg-Ni film, we tried to construct a simple four-step kinetic model consisting of physisorption, chemisorptions, surface penetration and hydride formation to

describe the process. A set of differential equations was established, which was expected to embrace the mechanisms controlling the temperature and  $P_{H_2}$  dependences of the absorption and desorption kinetics. The model was justified to be effective in describing the hydridation of a Pd/Mg-Ni film by reproducing the trends of the temperature and  $P_{H_2}$  dependence of the gas sensing responses observed experimentally. The model is not only useful in helping one to gain physical insight of the switching process of an Mg-Ni film, but may be also valuable in giving guidelines for optimizing the operation condition of the film for H<sub>2</sub> detection.

4. The response of the film to the variation in the relative humidity in the detected environment was observed. The presence of moisture was found to be influential to the degradation of the gas sensing properties of an Mg-Ni film, because water molecules can react with Mg atoms to form certain compounds, which eventually weaken the H-induced switching properties of the substance. This assertion is proposed according to the results of atomic force microscopy (AFM) analyses, which indicated that the surface morphology of the film sample after experiencing a certain number of switching cycles in a humid environment became very rough. We further found that the influence of moisture can be alleviated to a certain extent by adding a SiO<sub>2</sub> or SiN<sub>x</sub> layer on a Pd/Mg-Ni film. The durability of a film with such a water-resistant layer was found to be prominently improved.

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### Chapter 1

### Introduction

#### 1.1 Background

In today's industrialized society, hydrogen (H<sub>2</sub>) has been recognized to be one of the most useful gases. In many industries involving chemical and food production, semiconductor processing and transportation etc., H<sub>2</sub> plays important role as a raw material or fuel. In particular, recent development in the fuel cell industry further extends the consumption of H<sub>2</sub> in the both short- and long-term future.

However, problems are created from the increasing use of  $H_2$ .  $H_2$  is not easily stored due to its low mass and high diffusivity. Its molecule is so small, such that it has a higher risk of leakage. Being a colorless, odorless and tasteless gas,  $H_2$ detection devices are needed in workplaces far before its concentration is accumulated to reach the flammability limit (LFL) in air. The LFL for  $H_2$ , defined as the minimum concentration of  $H_2$  in air below which flame propagation does not occur, is 4 vol %.

At present, there are many types of commercial  $H_2$  gas sensors, for example, metal oxide type or hot-wire type, where the resistance of the sensor materials is changed when the sensor is exposed to  $H_2$ . There are thin film sensors like field effect transistors (FETs) with Pd catalyst or chemoresistive Pd alloy resistor, where  $H_2$  present at the Pd-gate interface results in a change of the current in the conduction channel and hence the resistivity of the device. There are other  $H_2$  sensor types based on different operating principles or different materials.

Many parameters are referred to for specifying the performance of  $H_2$  gas sensors, among which sensitivity is of primary concern, while recently more attentions are paid on lowering the operation temperature and improving the stability of  $H_2$  sensing properties.

Consider detection sensitivity first. The detection limits of most existing H<sub>2</sub> sensor products are in the range of 50 - 100 ppm. They include: (i) electrochemical (EC) type sensors, which give current signal through dissociation of  $H_2$  [Boon-Brett L 2010, Boon-Brett L 2009, Boon-Brett L 2008, Korotcenkov G 2009]; (ii) semiconducting metal-oxide  $(MO_x)$  type sensors, which give resistive response determined by equilibrium concentrations of surface sorbed oxygen (O) ions and conduction electrons in the oxide [Boon-Brett L 2010, Boon-Brett L 2009, Boon-Brett L 2008, Aroutiounian VM 2005, Korotcenkov G 2009, Shimizu Y 1998]; and (iii) catalytic combustion (CC) type sensors, which give resistive change of a platinum resistor component affected by catalytic oxidation of H<sub>2</sub> on its surface [Boon-Brett L 2010, Boon-Brett L 2009, Boon-Brett L 2008, Aroutiounian VM 2005, Korotcenkov G 2009, Han CH 2007]. Recently, great efforts have been made to apply nano materials to fabricate new H<sub>2</sub> sensors, based on the consideration that a nano material has a large effective area to give a high efficiency of gas detection. For example, a sensor made of palladium (Pd) decorated carbon nanotubes is found to be responsive to 30 ppm of H<sub>2</sub> [Sun Y 2007].

Consider the operation temperature of  $H_2$  sensors.  $MO_x$  and CC-type  $H_2$  sensors are widely used. However, they need to be operated at elevated operation temperatures in the range of  $300 - 500^{\circ}$ C, which lead to many disadvantages. First, each of them is equipped with a heater and controlling circuit, which complicate the

design and add to the production cost. The properties of the sensing element may be altered due to annealing effect, which causes the output to drift with time. The sensor is not convenient to be powered with a battery and is unlikely to be incorporated into a portable system. These drawbacks motivate the efforts to search for new H<sub>2</sub> sensing materials workable at ambient temperature [Yoshimura K 2004, Yoshimura K 2006, Yoshimura K 2009, Yoshimura K 2007b].

The performance of a  $H_2$  sensor is required to be as stable as possible. The baseline of the output of the sensor in a  $H_2$ -free environment, or the output corresponding to a steady  $H_2$  concentration should be stable enough. Moreover, a  $H_2$  sensor may be required to be exposed to  $H_2$  over and again, or the  $H_2$  concentration in the detected area may vary with time. In such a mode of use, the sensor needs to have satisfactory dynamic stability, which should be characterized specifically. To date, studies on dynamic stability of  $H_2$  sensors are quite premature. In most papers involving this topic, only data of a limited number of switching cycles are presented. They are not enough to be used for assessing the dynamic behavior of the samples [Yoshimura K 2007c].

#### 1.2 Pd capped Mg-based alloy - potential candidate of a good H<sub>2</sub> sensor material

More recently, palladium capped magnesium-nickel (Pd/Mg-Ni) film has emerged as a representative of the family of Pd/Mg-based film materials, which indicates excellent hydrogen detection capability [van Mechelen JLM 2004; Lohstroh W 2004; Hirata T 1981].

Hydrogen molecules are dissociated into hydrogen atoms (H) by Pd catalytically [Huot 2003]. The hydrogen atoms diffuse into the Mg-Ni layer and



locate interstitially to form a solid solution Mg<sub>2</sub>NiH<sub>x</sub>. At low hydrogen content, the lattice structure is not changed, and is named as the  $\alpha$ -phase, until the hydrogen content reaches the solubility of the solid at x = 0.3. When more hydrogen is added for x to exceed 0.3, the host metal lattice continues to expand [Schlapbach 1994]. Eventually, nucleation of a Mg<sub>2</sub>NiH<sub>4</sub> phase with a higher hydrogen concentration occurs, which is named as the  $\beta$ -phase. The  $\alpha$ -phase (Mg<sub>2</sub>NiH<sub>0.3</sub>) is supposed to be in a metallic state, hence exhibiting a high reflectance of 60-70 % in the wavelength range of 300-2500 nm [Richardson 2001; Yoshimura 2002; Lohstroh 2004]. On the other hand, the  $\beta$ -phase (Mg<sub>2</sub>NiH<sub>4</sub>) is known to be a semiconductor, and is found to have an optical band gap  $E_g$  as large as 2.0 eV, which is accompanied by low reflectance < 20% and large transmittance in the range of 40-60 % [Yoshimura Transitions between the metallic  $\alpha$ -phase and the semiconducting  $\beta$ -phase 20021. are reversible through hydridation and dehydridation respectively, hence exhibiting remarkable electrical and optical responses [van Mechelen JLM 2004, Lohstroh W 2004, Richardson TJ 2001, Hirata T 1981, Schefer J 1980, Reilly JJ 1968, Johansson E 2004, Yoshimura K 2002, Yoshimura K 2007a, Gremaud R 2009].

The above processes and changes in the material properties are found to be sensitive to present of H<sub>2</sub> at room temperature. The performance could be even better at a slightly heated environment. Compared with many existing semiconductor based H<sub>2</sub> sensors, elevated temperature normally above 300°C [Schefer J 1980; Reilly JJ 1968; Johansson E 2004; Yoshimura K 2002] are needed, which tends to cause many drawbacks including annealing effect and subsequent drift of the output.



To investigate the performance of a H<sub>2</sub> sensor, several performance indexes such as sensitivity (*S*), response time ( $t_{90}$ ), recovery time ( $t_{10}$ ), etc should be extracted and the evolution of these data under different operating conditions should be discussed. According to the data reported in literature, quantitative studies on H<sub>2</sub> sensing properties of an Mg-Ni film are not fully reported. Firstly, dynamic stability of an Mg-based alloy film H<sub>2</sub> sensor is affected by volume expansion induced irreversible structural changes [Bao S 2008a, Bao S 2008b]. However, these structural changes and quantitative H<sub>2</sub> sensing data (*S*,  $t_{90}$  and  $t_{10}$ ) are not well correlated. Secondly, it is found that the dynamic stability of a Mg-Ni film H<sub>2</sub> sensor can be improved by adding a thin metal buffered layer (e.g. titanium, aluminum) [Bao S 2008, Bao S 2006, Tajima K 2007] between the Pd and Mg-Ni layers or a polymer buffered layer on the top of Pd overcoat [Bao S 2007]. Nonetheless, an evolution on *S*,  $t_{90}$  and  $t_{10}$  under hydrogenation and dehydrogenation cycles are not discussed. Moreover, an influence of moisture on H<sub>2</sub> sensing properties of a Pd/Mg-Ni film has not reported so far.

#### **1.3** Scope of this study

On this background, this study was carried out and focused on the following issues.

The first was to investigate the general resistive and optical changes of a Pd/Mg-Ni film in  $H_2$  environment and its dynamic stability. We expect to identify the phases involved and the structural changes of the material under the influence of  $H_2$  (Chapter 3). The next purpose was to develop a model to describe the kinetics associated with the  $H_2$ -induced responses of a Pd/Mg-Ni film at different  $H_2$ 



pressures and temperatures (Chapter 4). The third purpose was to propose and test some methods aiming at improving the dynamic stability of a Pd/Mg-Ni film (Chapter 5, 6 and 7). Finally, the influence of moisture on the H<sub>2</sub>-sening properties of a Pd/Mg-Ni film was investigated. By adding a dielectric layer, the improvement in the dynamic stability of a Pd/Mg-Ni film operates in a humid environment was also investigated and discussed.

### **Chapter 2**

### **Sample Fabrication and Characterization**

#### 2.1 Sample Fabrication

A stainless steel chamber equipped with a diffusion pump and three magnetron sputtering guns as shown in Fig. 2.1 was used to prepare Pd coated magnesium-nickel (Mg-Ni) alloy bilayered films for this study. One of the sputtering guns has a design for the use of sputtering ferromagnetic material. The magnetic material to be sputtered in this study is Ni. Other two sputtering guns were used to sputter Mg and Pd, respectively. The targets were two 2-inch discs with purities of 99.9 and 99.95 % respectively. The chamber was first pumped down to a base pressure of 10<sup>-6</sup> Torr. Argon (Ar, 99.995 %) was then admitted into the chamber with a flow rate of 20 sccm by using a mass flow controller (MKS model: 1179A). Before starting a sputtering process, the pumping speed was reduced by adjusting the conductance of the high vacuum valve, until the Ar pressure was stabilized at 700 mTorr. Each sputter gun was then powered at 100 W for 5 min to pre-clean the surface of the target. The Ar pressure in the chamber was then further reduced to a lower pressure between 2 and 10 mTorr by readjusting the conductance of the high vacuum valve. This pressure level is referred to as the sputtering pressure  $(\phi)$ afterwards. The shutters in front of the Mg and Ni targets were then opened to start depositing an Mg-Ni alloy layer until the expected film thickness is reached. The

shutter in front of the Pd target was then opened to add a thin Pd cover layer. The substrate holder was rotated with a motor throughout the deposition process to ensure that the film thickness is uniform. The substrate temperature can be adjusted by means of a resistive heater regulated with a proportional-integration-differentiation (PID) temperature controller.

Table 2.1 lists the preparation conditions of the Pd/Mg-Ni film samples used for basic characterization. The sputtering pressure ( $\phi$ ) and ratio of the sputtering power of Mg to that of Ni denoted as  $P_{Mg}$ :  $P_{Ni}$  were fixed at 10 mTorr and 2.13, respectively. The thickness of an alloy layer is denoted as  $t_{Mg-Ni}$ . The thickness of the Pd layer is 5 nm. The first sample in the list, Sample Pd(5)/MN(30)\_RT, was used in most of the time for investigating the hydrogen sensing performance, the thermodynamic mechanisms of the switching processes, and sensitivity deterioration of the film material. Detailed discussions are presented in Chapter 3 and 4 respectively.

Four different fabrication approaches were implemented to improve the durability of H<sub>2</sub> sensing properties of Pd/Mg-Ni films. The first approach is to adjust the thickness of the Pd cover layer to reach the best compromise between H<sub>2</sub> detection sensitivity and protection of the alloy layer from oxidation. In this approach, the H<sub>2</sub> sensing properties of Sample Pd(5)/MN(30)\_RT with a 5-nm Pd cover layer were compared with those of Sample Pd(10)/MN(30) with a 10-nm Pd cover layer. Their preparation conditions are listed in Tables 2.1 and 2.2 respectively. The second approach is to dope Pd atoms into a Mg-Ni layer. The idea is to "pre-age" the alloy layer as if the degradation of H<sub>2</sub> sensing properties induced by interdiffusion of Pd and Mg in the Pd/Mg-Ni bilayer film. The preparation condition of samples,



Pd(5)/MN:Pd(30), used for this part of test is shown in Table 2.2. The third approach is to enrich the Ni content at the top surface of the Mg-Ni alloy layer by adding a thin Pd layer at the interface between the Pd and Mg-Ni alloy layer. The intention is to suppress inter-diffusion of Pd and Mg atoms. Three samples were prepared for this study, namely Sample Pd(5)/Ni(3)/MN(30) and Pd(5)/Ni(6)/MN(30) of 3-nm and a 6-nm thick interfacial Ni layers respectively, which preparation conditions are listed in Table 2.2. The fourth approach is to introduce iron (Fe) doping into the Mg-Ni layer, which is found (accidentally) to be able to suppress degradation of the H<sub>2</sub> sensing properties of the films. Two samples, namely Samples Pd(5)/MFN(30) and Pd(10)/MFN(30), were prepared to investigate this idea, which fabrication conditions are listed in Table 2.2. The sputtering pressure ( $\phi$ ) and the sputtering power ratio P<sub>Mg</sub>:P<sub>Ni</sub> were set at 10 mTorr and 2.13, respectively. All the samples used in this part of study are fabricated at room temperature.

Influence of moisture on the H<sub>2</sub> sensing properties of a Pd/Mg-Ni film sample was also investigated. Two samples with а layered structure of Pd/dielectric/Pd/Mg-Ni were fabricated. The dielectric layer was made of silicon dioxide  $(SiO_2)$  or silicon nitride  $(SiN_x)$ . Experiments were performed to investigate how the presence of a dielectric layer can protect the alloy layer from the influence of the moisture. The samples are named as  $Pd(5)/SiO_2(3)/Pd(5)/MN(30)$  and Pd(5)/SiN(3)/Pd(5)/MN(30). Their fabrication conditions are listed in Table 2.3. They were deposited at room temperature. The sputtering pressure  $\phi$  and power ratio  $P_{Mg}$ :  $P_{Ni}$  were set at 10 mTorr and 2.13, respectively.



Fig. 2.1 Schematic diagram of the magnetron sputtering system used for thin film deposition.

Table 2.1 Preparation conditions of Pd/Mg-Ni films. The Mg-Ni layers were made to have different thicknesses  $(t_{Mg-Ni})$  and at different substrate temperatures  $(T_s)$ . The ratio of sputtering power  $P_{Mg}$ :  $P_{Ni}$  was set at 2.3. The sputtering pressure  $\phi$  was set at 10 mTorr. The thickness of the Pd layer is 5 nm.

Sample code	P <sub>Mg</sub> :P <sub>Ni</sub>	$t_{Mg-Ni}(nm)$	$T_s(^{\circ}C)$
Pd(5)/MN(30)_RT	1.41	30	40
Pd(5)/MN(133)_RT	2.30	133	44
Pd(5)/MN(115)_150C	0.72	115	150
Pd(5)/MN(150)_350C	0.66	150	350

Table 2.2 Preparation conditions of two groups of film samples. One sample is doped with Pd. Two samples have Ni interfacial layers, with thickness  $t_{Ni}$  equal to 5 or 10 nm, respectively. Two samples were doped with Fe. The sputtering pressure  $\phi$  and power ratio  $P_{Mg}$ :  $P_{Ni}$  for the preparation the Mg-Ni layers were set 10 mTorr and 2.13.

Sample code	$t_{Pd}(\mathbf{nm})$	t <sub>Ni</sub> ( <b>nm</b> )	Dopant
Pd(10)/MN(30)	10	0	
Pd(5)/MN:Pd(30)	5	0	Pd
Pd(5)/Ni(3)/MN(30)	5	3	
Pd(5)/Ni(6)/MN(30)	5	6	
Pd(5)/MN(30):Fe	5	0	Fe
Pd(10)/MN(30):Fe	10	0	Fe



Table 2.3 Preparation conditions of film samples having a layered structure of Pd/dielectric/Pd/Mg-Ni. The dielectric material is either  $SiO_2$  or  $SiN_x$  which is prepared by using reactive sputtering with the presence of  $O_2$  or  $N_2$ . The sputtering pressure  $\phi$  and sputtering power ratio  $P_{Mg}$ : $P_{Ni}$  were set at 10 mTorr and 2.13. The sputtering power was set at 30 W. The numbers inside the brackets are the thicknesses (in nm) of the corresponding layers.

Samula aada	Duffer commons d	Thickness of the
Sample code	Buller compound	dielectric layer (nm)
Pd(5)/SiO <sub>2</sub> (3)/Pd(5)/MN(30)	SiO <sub>2</sub>	3
$Pd(5)/SiN_x(3)/Pd(5)/MN(30)$	SiN <sub>x</sub>	3

#### 2.2 Sample Characterization

#### 2.2.1 Thickness measurements

The thicknesses of the Mg-Ni layers ( $t_{Mg-Ni}$ ), Pd layers ( $t_{Pd}$ ) and dielectric layers were measured by using a surface profiler (KLA Tensor P-10) with a depth resolution of 0.1 nm. The surface profiler has a diamond stylus. To perform a measurement, the stylus is driven to scan across the edge of the film, where it experiences a vertical displacement (Fig. 2.2) to generate an electrical signal through a permanent magnet-coil coupling assembly. The signal can be converted into a reading of the step height (film thickness) based on the result of a calibration process.

#### 2.2.2 X-ray diffraction

X-ray diffraction was performed to investigate the film structure by using a Philips X'Pert system with a Cu K $\alpha$  radiation source (wavelength  $\lambda = 0.154$  nm). In order to enhance the signal of diffraction, we employed glancing-angle configuration, or 20-scan method. The incident beam was directed to strike on the film surface with a glancing angle of 3°. A diffraction peak would be detected if the Bragg condition

$$2 d \sin\theta = \lambda \tag{2.1}$$

is satisfied, where *d* is the lattice spacing and  $\theta$  the diffraction angle as shown in Fig. 2.3. If the full width at half maximum (FWHM) is small enough, the average grain size (*t*) can be estimated by applying the Scherrer equation:

$$t = \frac{\lambda}{FWHM\cos\theta}$$
(2.2)



Fig. 2.2 Schematic diagram of film thickness measurement by using a surface profiler.



Fig. 2.3 Schematic diagram showing the principle of X-ray diffraction.



#### 2.2.3 Compositional analyses by X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS, Phi 5600) was used to analyze the depth profiles of the relative contents of oxygen (O), Pd, Mg and Ni in the films. The system is equipped with an aluminium (Al)  $K_{\alpha}$  radiation with a characteristic energy of hv = 1486.6 eV. When an Al  $K_{\alpha}$  photon from the radiation source knocks out a core electron, the kinetic energy of the photoelectron ( $U_k$ ) is determined by an electron energy analyzer. The binding energy of the electron ( $U_B$ ) is:

$$U_{\rm B} = h\upsilon - U_{\rm k} \tag{2.3}$$

The relative content of a particular kind of atoms, specified by the index "i", is estimated by the expression:

$$C_{i} = \frac{A_{i}/S_{i}}{\sum_{j} A_{j}/S_{j}}$$
(2.4)

where  $A_i$  is the area of the XPS spectrum of that kind of atoms obtained after the removal of the Shirley background. The "*j*" is the index going through all kinds of atoms in the film. S<sub>j</sub> represents the sensitivity factor of the corresponding kind of atoms. The values of the sensitivity factors of the four kinds of atoms are provided by the manufacturer of the XPS system.

The depth profiles of XPS spectra were recorded. An ion gun installed in the measurement chamber of the system was used to generate an 2-keV Ar ion beam to etch the sample. The etching rate of film material (Pd and Mg-Ni alloy) is calibrated by referring to the thickness of a Pd/Mg-Ni film measured by using a surface profiler. In addition, a charge neutralizer is turned on to generate "soft" electrons for preventing surface charge up. Photoelectron spectra of Mg1s, Mg2p, Ni2p, Pd3d<sub>5/2</sub>

and O1s states are recorded. Meanwhile, the O1s and Pd  $3p_{3/2}$  spectra are detected, which are found to have some overlapping. Mg $2p_{1/2}$  and Pd $4p_{3/2}$  spectra also show some degree of overlapping.

The XPS spectra are deconvoluted by using a software (XPSpeak 4.1) developed by the Chemistry Department of The Chinese University of Hong Kong some years ago. The energy corresponding to the maximum intensities of a component is recorded and used to identify the chemical states of that group of atoms in the solid.

#### 2.2.4 Atomic force microscopy (AFM)

The surface morphology of the film samples was investigated with an atomic force microscopy (AFM) operating in tapping mode. AFM is a non-destructive technique useable for imaging the surface morphology of a specimen. From the surface profile, one can estimate the roughness of the film surface.

To generate an AFM image, a vibrating cantilever with a  $Si_3N_4$  tip in the system is driven to scan across the surface of a specimen. The undulation of the sample surface modulates the amplitude of the vibration of the cantilever. A laser beam is focused on a mirror mounted on the back side of the cantilever. The light is reflected and strikes on a position sensor. The sensor monitors the shift of the laser spot, which carries the information on the change of the vibration amplitude of the cantilever and hence the morphology of sample surface. This technique has very high depth and lateral resolutions, namely in the order of 0.1 nm and a few nanometers respectively.

Root mean square roughness ( $z_{RMS}$ ) is used to represent the roughness of a surface. The profile of a flat reference surface is recorded to reflect the tilting of the sample stage. The surface profile of the film surface is then collected and modified with the reference background. The value of  $z_{RMS}$  is defined by equation (2.4), where  $z_i$  is the deviation of a data from the mean vertical position, and *n* the number of the data points.

$$z_{\rm RMS} = \sqrt{\sum_{i} \frac{z_i^2}{n}}$$
(2.4)

The typical dimension of the area investigated in one signal test is  $1.5 \times 1.5 \ \mu m^2$ . In the tapping mode, the tip is driven to vibrate at a frequency of 0.825 Hz. The travelling speed of the tip on the sample surface is set to be 2.47  $\mu m s^{-1}$ .

#### 2.3 In-situ optical and electrical H<sub>2</sub> sensing property measurements

Fig. 2.4 shows the schematic diagram of the system used to investigate both the optical and electrical H<sub>2</sub> sensing response of the film samples. With this system, a sample can be exposed to a H<sub>2</sub>-containing gas and synthetic air alternatively. In the diagram,  $V_1$ ,  $V_2$  and  $V_3$  represent three pneumatic valves, and GV an electromagnetic gate valve. To generate a gas of a particular H<sub>2</sub> content, a 4%H<sub>2</sub>-96%Ar admixture and synthetic air with a certain ratio of respective molar numbers are emitted into a pre-loading chamber by means of two mass flow controllers. It is then admitted into the measurement chamber (a stainless steel six-way cross) to initiate hydrogenation of the film sample. On the other hand, synthetic air can be admitted into the measurement chamber via  $V_3$  to perform dehydrogenation of the film sample. The


information on the molar numbers of the gaseous components is attained from the readings of the pressure sensors attached to pre-loading chamber. Another pressure sensor is used to monitor the pressure in the measurement chamber for cross checking. A film sample was mounted in a six-way cross (measuring chamber) as shown in Fig. 2.4. It can be heated up by means of a resistive heater regulated by a PID temperature controller. For investigating the optical H<sub>2</sub> sensing response, a helium-neon laser (He-Ne) with a wavelength of 632.8 nm is generated and directed to shine on the film. The intensities of both the reflected and transmitted light beams are detected with two photodiodes to derive the changes of optical transmission ( $\Pi$ ) and reflection (R) of the film sample. The outputs from the photodiodes are collected with two lock-in amplifiers in order to diminish the influence of random noise.

The electrical H<sub>2</sub> sensing response of the film sample is monitored by measuring the change of the resistance of the film. The resistance of the film material between two parallel silver-paint electrodes separated by a distance of 5 mm was detected by using an electrometer. It is in fact an effective resistance of a co-planar structure. We used it to derive the effective resistivity,  $\langle \rho \rangle$ , of the bi-layered film. The movements of the valves and data acquisition are automatic with by using a LABVIEW program.

Two modes of measurements were employed. The first one is referred to as the quasi-static mode. For a test in this mode, the measurement chamber was first pumped down to rough vacuum (by opening the gate valve GV; closing valves  $V_1, V_2$  and  $V_3$ ). An admixture with a specific H<sub>2</sub> concentration formed in the pre-loading chamber. It is then released to the measurement chamber by closing GV,  $V_1$  and  $V_3$  and opening  $V_2$ . The film was then hydrogenated to a certain extent depending on the



 $H_2$  content in the gas. The changes the values of  $\langle \rho \rangle$ , T and R of the film sample were derived. The procedure was repeated, while the partial pressure of  $H_2$  ( $P_{H_2}$ ) was increased successively in a step-wise pattern with a very low increasing rate (20 minutes per step). Such a process is regarded to be quasi-static. The data of  $\langle \rho \rangle$  obtained from the test can be plotted as a function of  $P_{H_2}$ , which is named as the resistivity-pressure isotherm (RPI). Similarly, the plot of transmittance (T) of the film against  $P_{H_2}$  is named as the transmittance-pressure isotherm (TPI).

The second approach is referred to as the cyclic mode of measurement. To perform a cyclic test, the film sample was exposed alternatively to a H<sub>2</sub>-containing gas (for hydrogenation) and dry air (for dehydrogenation) for many cycles. The H<sub>2</sub>-containing gas is generated by mixing a 4% H<sub>2</sub>-96% Ar gas and synthetic air in a specific molar ratio, such that the H<sub>2</sub> partial pressure in the mixture is equal to the targeted value. A complete cycle includes a hydrogen charging process; evacuation of the preloading chamber and measurement chamber with a vacuum pump (by closing  $V_{1,3}$ ; opening  $V_2$  and GV), and filling up the measurement chamber with dry air to 1 atmosphere for dehydrogenation (by closing  $V_{1,2}$  and GV; opening  $V_3$ ).

In addition, the temperature of the film sample can be set with a resistive heater. The information obtained from the tests is very useful for analyzing the kinetics of the H<sub>2</sub>-induced transition processes of the film materials.



Fig. 2.4 Schematic diagram of the system used for observing the optical and electrical  $H_2$  sensing responses of film samples.



#### Chapter 3

# Basic analysis of the structure and H<sub>2</sub> sensing properties of palladium capped magnesium-nickel alloy films

In this chapter, we present the results of basic  $H_2$  sensing properties of Pd/Mg-Ni films. Studies cover (i) structure of the films, (ii)  $H_2$ -induced electrical and optical responses of Pd/Mg-Ni films detected in both the quasi-static mode and cyclic modes, which carry the information on detection sensitivity, response time and stability, and (iii) degradation mechanisms of  $H_2$  sensing responses. The knowledge gained in this part of study is used to analyze hydrogenation-dehydrogenation processes from thermodynamic point of view (Chapter 4); and helps to generate guidelines for improving the  $H_2$  properties of Pd/Mg-Ni films (Chapter 5 – 8).

#### 3.1 Film structure

Fig. 3.1 shows the XRD spectra of the Pd/Mg-Ni film samples with the alloy layers deposited at different substrate temperatures. All the films show a weak and broad halo with the maximum intensity roughly located at  $2\theta \approx 39.3^{\circ}$ . This broad halo is attributed to the (111) planes of the Pd cover layer [Yoshimura K 2007a]. In addition, Sample Pd(5)MN(30)\_RT deposited at room temperature is identified to be X-ray amorphous. Sample Pd(5)MN(115)\_150C with the Mg-Ni layer deposited at 150°C does not show any strong diffraction peak, but it should contain some crystallites because it has a low  $\langle \rho \rangle$  (see below). Sample Pd(5)MN(150)\_350C with the Mg-Ni layer deposited at 350°C shows two strong diffraction peaks, whose positions match with the positions of the (003) and (006) peaks of Mg\_Ni crystal

[Fardindoost S 2010]. This result shows that the film deposited at 350°C is crystallized.



Fig. 3.1 XRD spectra of Pd/Mg-Ni film samples prepared at various substrate temperatures.

## 3.2 Results of quasi-static tests: resistivity-pressure isotherm and optical transmittance-pressure isotherm

The solid curves shown in Fig. 3.2 (a) and (b) are the results of quasi-static measurements, presented in the form of resistivity-pressure isotherm (RPI) and optical transmittance-pressure isotherm (TPI) of Sample Pd(5)MN(30)\_RT measured at 60°C. During measurement, the hydrogen partial pressure,  $P_{H_2}$ , was controlled to vary very slowly from 17 to 3000 Pa (Section 2.3), and hence the process is considered to be quasi-static.  $P_{H_2}$  can also be expressed in another form, namely nominal hydrogen concentration,  $C_{H_2}$ , defined as the H<sub>2</sub> partial pressure normalized with respect to one atmospheric pressure.  $C_{H_2}$  is more intuitive when used in discussion. The range of  $C_{H_2}$  corresponding to that of  $P_{H_2}$  is easily calculated to be 170 - 30000 ppm.

Fig. 3.2 (a) shows the RPI curve, which behaves differently in three regions. Their boundaries are at  $C_{H_2}$  roughly equal to 1.1% and 2.2%, respectively. The effective electrical resistivity  $\langle \rho \rangle$  increases monotonically with increasing  $C_{H_2}$ . In particular, in Region I and III,  $\langle \rho \rangle$  depends approximately linearly on  $C_{H_2}$ , and the increasing rate of  $\langle \rho \rangle$  is relatively mild. However, the curve in Region II is much steeper. Fig. 3.2 (b) shows the TPI curve, which illustrates similar features as those of the RPI curve, indicating that both the H<sub>2</sub>-induced electrical and optical responses are based on the same physical origin.

It should be noted that a similar step-wise feature is also seen in a typical plot of the pressure-composition isotherm (PCI) of an Mg<sub>2</sub>Ni crystal during hydrogenation [Sun Y 2007]. An Mg<sub>2</sub>Ni crystal has a hexagonal structure with lattice constants *a* 



and *c* equal to 0.516 and 1.320 nm. When hydrogen atoms are first incorporated into the lattice, they are located interstitially to form a solid solution of hydrogen, denoted as  $\alpha$ -Mg<sub>2</sub>NiH<sub>x</sub> ( $x \le 0.3$ ). They become scattering centers of charge carries to result in a rise of electrical resistivity of the solid. At x = 0.3, *a* and *c* expand to 0.523 and 1.343 nm, corresponding to a 4.52% increase in volume [Han CH 2007]. For higher H<sub>2</sub> concentration in the surrounding, more H atoms are incorporate into the solid and initiate a transition from the  $\alpha$ -phase to a  $\beta$ -phase, denoted as Mg<sub>2</sub>NiH<sub>4</sub>. The  $\beta$ -phase has a tetragonal structure with lattice constants *a* and *c* equal to 0.6464 and 0.7033 nm. From the densities (3.44 and 2.57 g cm<sup>-3</sup>) and numbers of molecules per unit cell (6 and 4) of the two phases, one estimates that the specific volume of the solid is increased by 41.8%. More H atoms may still be added to the lattice without further phase change, but the volume and electrical resistivity may still be further increased mildly.

Our film samples are not crystalline, but the appearance of the step-wise feature in their RPI and TPI plots indicates that their atomic networks also experience similar structural transitions as in the case of a crystal, except that the processes now conduct among amorphous phases. In particular, major volume expansion of the Mg-Ni layer should occur in Region II of the RPI and TPI plot [Lohstroh W 2004]. It induces substantial irreversible deformation of the bi-layered film structure. Because the film-to-substrate adhesion constrains in-plane deformation, out-of-plane expansion along the normal direction of the substrate dominates the change of the volume of the film during the transitions.



Fig. 3.2 Plots of (a) RPI and (b) TPI of Sample Pd(5)MN(30)\_RT measured at 60°C immediately after deposition and after 40 switching cycles with  $C_{\rm H_2}$  = 40000 ppm; and cyclic response of measured at 60°C across Region I and II.

#### 3.3 Durability at different pressure

Results of three cyclic tests performed at  $60^{\circ}$ C on three specimens of Sample Pd5/MN30\_RT are presented in this section. The tests were conducted by using three different  $C_{\text{H}_2}$  values in respective hydrogenation processes. In each test, both the electrical and optical responses of the samples were recorded and analyzed.

In the first cyclic test, a  $C_{H_2}$  value of 6400 ppm lying in Region I of the RPI plot was used in the hydrogenation processes. The following features were observed. Fig. 3.3 (a) shows that over 40 cycles, the baseline of  $\langle \rho \rangle$  (dehydrogenated state 0% H<sub>2</sub>) remains stable and close to the as-deposited value of 0.38  $\mu\Omega$  m; but the saturation value (hydrogenated state 4% H<sub>2</sub>) drops mildly. The overall result is to cause the sensitivity S to drop slightly from 48 to 39% as shown in Fig. 3.3 (d), where S = $\Delta < \rho > / < \rho >_o \times 100\%$  with  $\Delta < \rho >$  being the rise of  $< \rho >$  in a hydrogenation process and  $\langle \rho \rangle_{o}$  is the as-deposited  $\langle \rho \rangle$ . Furthermore, the response and recovery rates of the cycles are fast, as reflected by short response time  $t_{90} \approx 15$  s required for  $<\rho>$  to increase by  $0.9 \times \Delta < \rho >$  in a hydrogenation process; and short recovery time  $t_{10} \approx 31$  s required for  $<\rho>$  to reduce by 90% of the total drop in a dehydrogenation process. Based on these findings, we have the following suggestions. (i)  $\Delta < \rho >$  and S varied so mildly, such that the film should remain in the amorphous  $\alpha$ -phase throughout the test. (ii) The volume of the film fluctuated with a small amplitude, such that irreversible deformation evolved gradually to result in the observed instability of  $\Delta < \rho >$  and S. (iii) H atoms only interact "interstitially" with the atomic network without forming strong chemical bonds with the metal atoms, so that they are relatively mobile in the film to give the observed fast response rate.



In the second cyclic test, a larger  $C_{H_2}$  of 12800 ppm lying in Region II of the RPI plot was used in hydrogenation processes. Fig. 3.3 (b) shows that  $\Delta < \rho >$  rises initially from a very small value to the maximum after a few cycles, and dropped continuously afterwards. Fig. 3.3 (d) shows that S has the same trend. Note that the shrinkage of  $\Delta < \rho >$  is due to the drift of both the baseline and saturation value of  $< \rho >$ . To explain these results, we point out that the  $C_{H_2}$  value used in this test is high enough for part of the amorphous  $\alpha$ -phase to be transformed to the amorphous  $\beta$ -phase. Since the transition is accompanied by a huge volume change, the transition cannot be completed in the first cycle. Instead, it needs a few cycles to fully evolve. After reaching a maximum response, volume breathing continues to extend deformation. Eventually, the alloy layer surface is less protected by the Pd cover layer and is more readily to be oxidized. The mobility of H atoms in the oxide is known to be low, such that H uptake and detachment are obstructed, giving rise to the drops in  $\Delta < \rho >$  and *S* as observed.

In the third cyclic test, a  $C_{H_2}$  of 40000 ppm lying in Region III was used in hydrogenation processes. Figs. 3.3 (c) and (d) show that  $\Delta < \rho >$  and S are the maximum in the first cycle, and then drop continuously in the following runs. One directly suggests that the  $\alpha$ -to- $\beta$  transition has been accomplished in the first cycle, and the ensuing drops of  $\Delta < \rho >$  and S are attributed to volume breathing effect and subsequent surface oxidation of the alloy layer. This viewpoint is strongly substantiated by the following facts and the results of XPS analyses (see next section). (i) The quasi-static RPI of the film recorded after 40 switching cycles shown in Fig. 3.2 (a) is found to deviate significantly from that of the one without



experiencing switching, indicating that irreversible structural changes are induced in a cyclic test. (ii) The thickness of the film is found to increase from the as-deposited value of 30 nm to 46 nm recorded after the dehydrogenation process of the last cycle. The thickening of the film represents a nearly unidirectional volume expansion above 50% along the normal direction of the substrate surface, assuming that the substrate restricts in-plane expansion of the film. Such a huge expansion has greatly exceeded the expected one associated with a typical  $\alpha$ -to- $\beta$  transition. Hollowing of the film structure in our case is thus expected. (iii) AFM images show that the film surface is roughened markedly after 40 switching cycles (Fig. 3.4 (a) and (b)), and the root mean square roughness is increased from 7.44 to 30.7 nm. This observation is consistent with the above argument.

We further note that the switching properties of the optical transmittance of the film are very similar to that of  $\langle \rho \rangle$ , as shown in Fig. 3.3 (e) – (h), and hence should be interpreted with the same arguments.



Fig. 3.3 (a) – (d) H-sensing response of  $\langle \rho \rangle$  of Sample Pd(5)MN(30)\_RT in three cyclic tests performed at 60°C, with  $C_{\rm H_2}$  = 6400, 12800 and 40000 ppm respectively; and (d) sensitivity  $S = \Delta \langle \rho \rangle / \langle \rho \rangle \times 100\%$ . (e) – (h) H-sensing response of  $\Pi$  of Sample Pd(5)MN(30)\_RT in three cyclic tests performed at 60°C, with  $C_{\rm H_2}$  = 6400, 12800 and 40000 ppm respectively; and (d) sensitivity  $S = \Delta \Pi / \Pi \times 100\%$ 



Fig. 3.4 AFM images and surface profiles of Sample Pd(5)MN(30)\_RT captioned (a) at as-deposited stage and (b) after 40 switching cycles with  $C_{\rm H_2}$  = 40000 ppm.

#### 3.4 Stability analysis based on XPS

Fig. 3.5 (a) and (b) show the binding energy spectra of the  $Pd3d_{3/2}$ ,  $Pd3d_{5/2}$ , Mg1s and O1s photoelectrons of Sample Pd(5)MN(30) RT from different depths collected at the as-deposited stage and after 40 switching cycles. The Pd3d<sub>3/2</sub> and Pd3d<sub>5/2</sub> spectra show peak energies at 341.0 and 335.7 eV respectively [Tang YM 2009]. An Mg1s spectrum is fitted to a three-component models, with the peak energies located at around 1303.1, 1304.8 and 1302.0 eV corresponding to the chemical states of the Mg atoms in the Mg-Ni alloy phase, Mg-O phase and Mg-OH phase respectively [Yoshimura K 2007b; Bao S 2008]. An O1s spectrum may contain two components corresponding to the oxygen atoms in the Mg-O and Mg-OH phases, but they are too close to be resolved [Bao S 2007]. The major features of the Ni2p photoelectron binding energy spectra do not change, indicating that they remain at the same chemical state throughout the test. The elemental compositions in different phases are thus deduced by dividing the areas of the components with respective sensitivity factors. Fig. 3.6 (a) and (b) show the depth profiles of the elemental contents in the metallic phases (including Pd and Mg-Ni) and non-metallic phases (including Mg-O and Mg-OH) at the as-deposited stage and after 40 switching cycles performed at  $C_{\rm H_2}$  = 40000 ppm and 60°C.

Referring to Fig. 3.6 (a), at the as-deposited stage, Pd atoms are mainly located in a depth of 5 nm below the film surface, consistent with that predicted value estimated from the coating rate of Pd. The film surface is Mg-rich, but the Mg-to-Ni ratio drops with depth and is stabilized at around 1.7. This reflected that Mg atoms tend to migrate towards the film surface. No oxide phase on the film surface is found, showing that the Pd layer provides excellent resistance against oxidation of the alloy

layer. An Mg-O phase is detected over a range of depth from 20 to 37 nm, and an Mg-OH phase is detected near the film-substrate interface. To interpret the origins of these two non-metallic phases, we consider that the formation energy of  $Mg(OH)_2$  (-211.00 kcal/mol) is more negative than that of MgO (-143.84 kcal/mol). At the start of the deposition process, the landing Mg atoms first react with the water molecules in the sputtering chamber to form the Mg-OH phase, and then react with the surface sorbed or background oxygen molecules to form the Mg-O phase.

Fig. 3.6 (a) and (b) show the depth profile of the elemental composition of a sample at the as-deposited stage and after 40 switching cycles. The structure is assumed to contain two phases, namely a metallic phase and an oxide phase. The summation of all elemental compositions in all the phases is normalized to 100%. After performing 40 switching cycles, Pd atoms penetrate much deeper into the film, because the film surface has become so rough that the Pd layer is fragmented and does not locate on a flat level. The alloy layer is less isolated from the environment, such that the Mg atoms near the film surface are oxidized more readily to form an Mg-O phase. Its presence does not favor the migration of hydrogen, such that the H-detection sensitivity is suppressed. The depletion of the Mg atoms in the alloy phase also ruins the switching ability of the film.





Fig. 3.5 Binding energies of Pd3d3/2, Pd3d5/2, Mg1s and O1s photoelectrons of Sample Pd(5)MN(30)\_RT from different depths below the film surface, which were collected (a) at as-deposited stage and (b) after 40 switching cycles.



Fig. 3.6 Depth profiles of elemental contents and chemical states of Sample Pd(5)MN(30)\_RT(a) at as-deposited state and (b) after 40 switching cycles.



# 3.5 Degradation of H<sub>2</sub> sensing properties of Pd/Mg-Ni films due to surface oxidation

To further illustrate the influence of surface oxidation on the switching properties of an Mg-Ni film, the cyclic response of  $\langle \rho \rangle$  of Sample Pd(5)/MN(115)\_150C and Sample Pd(5)/MN(150)\_350C working at  $C_{H_2} = 40000$  ppm and 60°C were measured and plotted in Fig. 8. Results shows that  $\langle \rho \rangle$  of both samples is insensitive to H<sub>2</sub>. When preparing these samples, the Mg-Ni layers were deposited at 150 and 350°C respectively, and then the substrate heater was turned off to allow the substrates to cool to room temperature in high vacuum. This took times of  $t_{delay} = 60$ and 120 min in the two cases, before the Pd cover layers were added. Meanwhile, residual oxygen in the chamber reacted with Mg atoms to form a surface Mg-O layer, which can greatly diminish the H-sensing response of the films. The presence of an Mg-O phase near the film surface is further confirmed by the results of XPS analysis performed on Sample Pd(5)MN(145)\_350C (Fig. 3.7). The Mg-O layer is located between the Pd and Mg-Ni layers, consistent very well with the time sequence used to prepare the layers.



Fig. 3.7 Cyclic resistive response of Sample Pd5MN110\_150C\_60 and Sample Pd5MN150\_350C\_120 measured at 60°C using  $C_{\rm H_2}$  = 40000 ppm in hydrogenation processes. Depth profiles of elemental composition and phases of as-deposited Sample Pd5MN150\_350C\_120.



At last, we estimate the H<sub>2</sub> detection limit based on a Wheatstone bridge using a Pd/Mg-Ni film as one of its resistive components. The output voltage of the circuit is expressed as  $\Delta V = S \times E \times C_{H_2}$ , where *E* is the input voltage. If the lowest detectable signal with an electrometer is 0.1 mV; *E* is set to be 0.5 V; and the lowest *S* value determined in this study is used, the lowest detectable value of  $C_{H_2}$  calculated from the formula is found to be 3 ppm. This detection limit is already lower than that of a typical MO<sub>x</sub>-type H<sub>2</sub> sensors. One more advantage of a Pd/Mg-Ni is that it is workable at ambient temperate with little problems associated with the need of an elevated operation temperature [Song SK 1998; Suehle JS 1993].

#### 3.6 Summary

We have the following findings from this part of study.

- All the film samples are amorphous, but all of them still exhibit outstanding H<sub>2</sub>-induced electrical and optical responses.
- When the ambient H<sub>2</sub> pressure increases quasi-statically, a Pd/Mg-Ni film goes through an amorphous α-phase which contains interstitial hydrogen atoms, and then experiences a transition from the amorphous α-phase to the amorphous β-phase accompanied with drastic volume changes in direction along the film thickness. In the latter process, the rise in is most substantial.
- When a Pd/Mg-Ni film works in the cyclic mode, both the electrical and optical responses degrade with increasing number of switching cycles. This is due to the substantial volumetric breathing effect, which causes successive cracking of the Pd cover layer to weaken protection of the alloy layer, and direct hollowing of the alloy layer during the switching process. At the same time, Mg atoms tend to migrate towards the film surface and be oxidized to form an Mg-O layer, which slows down the migration of H atoms to reduce the strength of the response to H<sub>2</sub>.

#### **Chapter 4**

#### Modelling of hydridation of Mg-Ni

The fundamental features of the hydrogen sensing properties of Pd/Mg-Ni films are described in the previous chapter. They seem to carry information on the mechanisms as well as the degradation of the H<sub>2</sub>-induced changes of electrical and optical properties of the films. In this chapter, we want to propose a model, based on thermodynamics and kinetics theories, to produce some trends matching with the results of observations. The model is made to include the contributions from (i) physisorption of hydrogen molecules, (ii) chemisorption of hydrogen atoms; (iii) penetration of the species into the alloy layer, and (iv) hydridation of the alloy layer. From the discussion, some quantities associated with hydridation of the film material, e.g. enthalpy, entropy and activation energy of hydridation, are derived.

#### 4.1 Model describing hydridation of a Pd/Mg-Ni film

#### 4.1.1 Four processes involved in constructing the model

The overall hydridation process is presented by a chemical formula:

$$H_{2(gas)} + Mg_2Ni_{(metal)} \Leftrightarrow Mg_2NiH_4$$

which is believed to contain at least four consecutive processes, i.e. physisorption of hydrogen molecules, chemisorptions of hydrogen atoms, penetration of hydrogen atoms into the Mg-Ni alloy layer, and hydridation of the Mg-Ni alloy layer [Fromm E 1998, Y. Fukai 2005.]. The last one is referred to an  $\alpha$ -to- $\beta$  transition occurring at

a high enough hydrogen concentration environment. They are described in the following.

(i) Physisorption of hydrogen molecules is presented by a chemical formula:

$$H_{2(gas)} \Leftrightarrow H_{2(physisorbed)}$$

It means that hydrogen molecules are physisorbed on the surface of a Pd cover layer [Fig. 4.1 (a)]. Meanwhile, no chemical bond is formed, but the adhesion of the molecules to the surface is based on van der Waals forces. The enthalpy is denoted as  $\Delta H_p$  (subscript "p" stands for "physisorption") usually in the order of 0.5–5 kJ mol<sup>-1</sup> [Borgschulte A 2008]. Physisorption is a reversible process strongly dependent on both ambient gaseous pressure (*P*) and temperature (*T*). For monolayer adsorption, the Langmuir isotherm describes the coverage ratio  $\theta_p$ , defined as fractional occupancy of the adsorption sites, as a function of *P*, *T*, and rate constants of forward and reverse reactions ( $k_{pa}$  and  $k_{pb}$ ) [Boris S 2005]:

$$\frac{d\theta_p}{dt} = k_{pa} \left(\frac{p}{\sqrt{T}}\right) (1 - \theta_p) - k_{pb} \theta_p \tag{4.1}$$

Two terms are included in the equation. The first one is associated with surface adsorption (forward reaction), and is proportional to the flux of  $H_2$  molecules bombarding on the absorbing surface (Pd layer surface). The second term is associated with detection of physisorpted hydrogen molecules (reverse reaction), and is proportional to the number of occupied sites.

(ii) Dissociation of H<sub>2</sub> and chemisorption of atomic H atoms at film surface:

$$H_{2(physisorbed)} \Leftrightarrow H_{(chemisorbed)}$$

At high *P* and *T*, the physisorpted hydrogen molecules could be dissociated and are chemisorbed [Fig. 4.1 (b)]. Chemisorption involves the formation of chemical bonds between hydrogen atoms and the Mg-Ni layer. The process is specified with an activation energy  $E_{ca} = 0$  to 23 kJ mol<sup>-1</sup> and enthalpy  $\Delta H_c = -1.1$  to -23 kJ mol<sup>-1</sup> [Borgschulte A 2008]. Assuming that the coverage of hydrogen atoms for chemisorption process is  $\theta_c$ , the rate of the change of the chemisorbed species is:

$$\frac{d\theta_c}{dt} = k_{ca} (1 - \theta_c)^2 \theta_p - k_{cb} (1 - \theta_p) \theta_c^2$$
(4.2)

where  $k_{ca}$  is a rate constant for chemisorptions and  $k_{cb}$  that of recombination process.

(iii) Surface penetration of reactant species into the alloy layer:

$$H_{(chemisorbed)} + Mg_2Ni_{(metal)} \Leftrightarrow Mg_2Ni - H_{(\alpha)}$$

Hydrogen atoms generated from this process could diffuse rapidly into the interior of the film material [Fig. 4.1 (c)]. The activation energy  $E_{\alpha}$  is 11.1 eV, and enthalpy  $\Delta H_{\alpha}$  is better to be described with a range of -2.9 to 14.5 kJ mol<sup>-1</sup> [Borgschulte A 2008]. The alloy layer is still assumed to be in the  $\alpha$ -phase at this moment. This

reaction is described by the following equation:

$$\frac{d[M]_{\alpha}}{dt} = k_{\alpha a} \theta_c[M] - k_{\alpha b} (1 - \theta_c)[M]_{\alpha}$$
(4.3)

where [M] and  $[M]_{\alpha}$  are the molar concentrations of the  $\alpha$ -Mg<sub>2</sub>Ni phase and  $\alpha$ -Mg<sub>2</sub>Ni-H phase which is referred to a solid solution of hydrogen.  $k_{\alpha a}$  and  $k_{\alpha b}$  are the rate constants of the forward and reverse reactions, respectively.

(iv) Hydridation in  $\alpha$ -to- $\beta$  transition :

$$4H_{(chemisorbal)} + Mg_2Ni - H_{(\alpha)} \Leftrightarrow Mg_2NiH_{4(\beta)}$$

When hydrogen content in the  $\alpha$ -phase increases, interactions between H atoms is more significant, such that an  $\beta$ -phase starts to nucleate [Fig. 4.1 (d)]. The rate equation can be expressed as:

$$\frac{d[M]_{\beta}}{dt} = k_{\beta a} \theta_c^4 [M]_{\alpha} - k_{\beta b} [M]_{\beta}$$
(4.4)

where  $[M]_{\beta}$  is the molar concentration of  $\beta$ -Mg<sub>2</sub>NiH<sub>4</sub>.  $k_{\beta a}$  and  $k_{\beta b}$  are the rate constant for the forward and reverse reactions of the  $\alpha$ -to- $\beta$  transition. The activation energy and heat of formation,  $E_{\beta a}$  and  $\Delta H_{\beta}$ , are around 23 and -24 kJ mol<sup>-1</sup>.

We summarize and renumber Eqs. (4.1) to (4.4) as follows:

$$\frac{d\theta_p}{dt} = k_{pa} \left(\frac{p}{\sqrt{T}}\right) (1 - \theta_p) - k_{pb} \theta_p \tag{4.5}$$

$$\frac{d\theta_c}{dt} = k_{ca} (1 - \theta_c)^2 \theta_p - k_{cb} (1 - \theta_p) \theta_c^2$$
(4.6)

$$\frac{d[M]_{\alpha}}{dt} = k_{\alpha a} \theta_c [M] - k_{\alpha b} (1 - \theta_c) [M]_{\alpha}$$
(4.7)

$$\frac{d[M]_{\beta}}{dt} = k_{\beta a} \theta_c^4 [M]_{\alpha} - k_{\beta b} [M]_{\beta}$$
(4.8)

They are referred to as the master equations when building up a model for describing the  $\alpha$ -to- $\beta$  hydridation of the Mg-Ni layer. Two key points should be highlighted first:

- Arrhenius' law is valid for all this equations, which means that the reaction rate constant  $k_i$  can be expressed as  $k_i = k_{io} \exp(-E_i / RT)$ , where  $k_{io}$  is the frequency factor and  $E_i$  the activation energy.
- A Mg-Ni film sample is as thick as < 40 nm. Referring to the typical value of diffusivity *D* of some atoms in Pd/Mg-Ni films, e.g.  $10^{-10}$  m<sup>2</sup>s<sup>-1</sup> for Pd atoms and  $4.0 \times 10^{-13}$  m<sup>2</sup>s<sup>-1</sup> for Mg atoms determined at 300 K [Fisher D.J. 1999], one estimates that the time required for the reactant species to diffuse through the film thickness is just about milliseconds, which is greatly shorter than the observed response time of magnitudes around 10 second. Therefore, diffusion process should not be the controlling mechanism to determine the rate of the  $\alpha$ -to- $\beta$  transition process.

In the following, we further modify Eqs. (4.5) to (4.8). According to the conservation of total mass, the sum of the molar concentrations of the metal phase Mg-Ni denoted as [M]; plus that in the  $\alpha$ -Mg-Ni:H phase denoted as  $[M]_{\alpha}$ ; and plus that in the  $\beta$ -Mg-Ni:H<sub>x</sub> phase noted as  $[M]_{\beta}$ , should be equal to the as-deposited total concentration of Mg-Ni denoted as  $[M]_{\circ}$ :

$$[M]_{o} = [M] + [M]_{\alpha} + [M]_{\beta}$$
(4.9)

From equation (4.9), the differential equation (4.7) becomes:

$$\frac{d[M]_{\alpha}}{dt} = k_{\alpha a} \theta_c \left( [M]_o - [M]_{\alpha} - [M]_{\beta} \right) - k_{\alpha b} (1 - \theta_c) [M]_{\alpha}$$
(4.10)

The next is to express the rate constants in Arrhenius' rate functions, such that Eq. (4.5) - (4.8) become:

$$\frac{d\theta_p}{dt} = k_{pa}^o e^{-E_{pa}/RT} \left(\frac{p}{\sqrt{T}}\right) (1 - \theta_p) - k_{pb}^o e^{-E_{pb}/RT} \theta_p \tag{4.11}$$

$$\frac{d\theta_{c}}{dt} = k_{ca}^{o} e^{-E_{ca}/RT} (1 - \theta_{c})^{2} \theta_{p} - k_{cb}^{o} e^{-E_{cb}/RT} (1 - \theta_{p}) \theta_{c}^{2}$$
(4.12)

$$\frac{d[M]_{\alpha}}{dt} = k_{\alpha a}^{o} e^{-E_{\alpha a}/RT} \theta_{c} \left( [M]_{o} - [M]_{\alpha} - [M]_{\beta} \right) - k_{\alpha b}^{o} e^{-E_{\alpha b}/RT} \left( 1 - \theta_{c} \right) [M]_{\alpha}$$
(4.13)

$$\frac{d[M]_{\beta}}{dt} = k_{\beta a}^{o} e^{-E_{\beta a}/RT} \theta_{c}^{4} [M]_{\alpha} - k_{\beta b}^{o} e^{-E_{\beta b}/RT} [M]_{\beta}$$
(4.14)

The enthalpy of hydridation associated with the  $\alpha$ -to- $\beta$  transition,  $\Delta H_{\beta}$ , can be expressed as the difference between activation energy of the forward  $E_{\beta a}$  reaction and that of the reverse reaction  $E_{\beta b}$ :

$$\Delta H_{\beta} = E_{\beta b} - E_{\beta a} \tag{4.15}$$

Also, from the definition of enthalpy,  $\Delta H_{\beta}$  can be expressed as:

$$dH_{\beta} = TdS + VdP + \sum_{i}^{k} \mu_{i} dn_{i}$$
  

$$\Delta H_{\beta} = T\Delta S + RT \ln(P/P_{o}) + \sum_{i}^{k} \mu_{i} \Delta n_{i}$$

$$E_{\beta b} = E_{\beta a} + T\Delta S + RT \ln(P/P_{o}) + \mu_{\beta} [M]_{\beta} - \mu_{\alpha} [M]_{\alpha} - \mu_{\theta_{c}} \theta_{c} \qquad (4.17)$$

Equation (4.14) can be rewritten as:

$$\frac{d[M]_{\beta}}{dt} = k_{\beta a}^{o} e^{-E_{\beta a}/RT} \theta_{c}^{4}[M]_{\alpha} - k_{\beta b}^{o} (\frac{P_{eq}}{P_{e}})^{RT} e^{-[E_{\beta a}+T\Delta S + (\mu_{\beta}[M]_{\beta} - \mu_{\alpha}[M]_{\alpha} - \mu_{\theta_{c}}\theta_{c})]/RT} [M]_{\beta}$$
$$= k_{\beta a}^{o} e^{-E_{\beta a}/RT} \theta_{c}^{4}[M]_{\alpha} - k_{\beta b}^{o} (\frac{P_{eq}}{P_{e}})^{RT} e^{-[E_{\beta a}+T\Delta S + \Delta G]/RT} [M]_{\beta}$$
(4.18)

The final form of the kinetic equation set can be expressed as the following:

$$\frac{d\theta_p}{dt} = k_{pa}^o e^{-E_{pa}/RT} \left(\frac{p}{\sqrt{T}}\right) (1-\theta_p) - k_{pb}^o e^{-E_{pb}/RT} \theta_p \tag{4.11}$$

$$\frac{d\theta_c}{dt} = k_{ca}^o e^{-E_{ca}/RT} (1 - \theta_c)^2 \theta_p - k_{cb}^o e^{-E_{cb}/RT} (1 - \theta_p) \theta_c^2$$
(4.12)

$$\frac{d[M]_{\alpha}}{dt} = k_{\alpha a}^{o} e^{-E_{\alpha a}/RT} \theta_{c} ([M]_{o} - [M]_{\alpha} - [M]_{\beta}) - k_{\alpha b}^{o} e^{-E_{\alpha b}/RT} (1 - \theta_{c})[M]_{\alpha}$$
(4.13)

$$\frac{d[M]_{\beta}}{dt} = k_{\beta a}^{o} e^{-E_{\beta a}/RT} \theta_{c}^{4} [M]_{\alpha} - k_{\beta b}^{o} (\frac{P_{eq}}{P_{o}})^{RT} e^{-[E_{\beta a}+T\Delta S+\Delta G]/RT} [M]_{\beta}$$
(4.18)



Fig. 4.1 Schematic diagrams showing the four basic processes involved in hydridation process associated with the  $\alpha$ -to- $\beta$  transition. They are (a) physisorption of H<sub>2</sub> molecules, (b) chemisorption of H atoms, (c) surface penetration of H atoms and (d) hydridation from  $\alpha$ -to- $\beta$ -phase.

#### 4.1.2 Quasi-static, Quasi-static isothermal and Dynamic processes

#### Quasi-static model

The quasi-static condition is used to analyze the experiment with the ambient hydrogen pressure, as well as other parameters, varies with a very low rate. This condition is suitable for analyzing the case where the hydrogen partial pressure ( $P_{H_2}$  from 17 to 3000 Pa) or nominal hydrogen concentration ( $C_{H_2}$ ) varies very slowly in the quasi static measurements of resistivity  $\langle \rho \rangle$ , or optical transmission or reflectance, from which the resistivity-pressure-isotherm (RPI) and optical transmittance-pressure-isotherm (TPI) are derived. Under this condition, concentrations of the constituents involved in all the reaction are fixed, or the changing rates, i.e. the left hand sides of Eqs. (4.11-13) and (4.18) are equal to zero:

$$\frac{d\theta_p^e}{dt} = \frac{d\theta_c^e}{dt} = \frac{d[M]_{\alpha}^e}{dt} = \frac{d[M]_{\beta}^e}{dt} = 0$$
(4.19)

The equation set is rewritten as:

$$0 = k_{pa}^{o} e^{-E_{pa}/RT} (\frac{p}{\sqrt{T}}) (1 - \theta_{p}^{e}) - k_{pb}^{o} e^{-E_{pb}/RT} \theta_{p}^{e}$$
(4.20)

$$0 = k_{ca}^{o} e^{-E_{ca}/RT} (1 - \theta_{c}^{e})^{2} \theta_{p}^{e} - k_{cb}^{o} e^{-E_{cb}/RT} (1 - \theta_{p}^{e}) \theta_{c}^{e^{2}}$$
(4.21)

$$0 = k_{\alpha\alpha}^{o} e^{-E_{\alpha\alpha}/RT} \theta_{c}^{e} ([M]_{o} - [M]_{\alpha}^{e} - [M]_{\beta}^{e}) - k_{\alphab}^{o} e^{-E_{\alphab}/RT} (1 - \theta_{c}^{e}) [M]_{\alpha}^{e}$$
(4.22)

$$0 = k_{\beta a}^{o} e^{-E_{\beta a}/RT} \theta_{p}^{e^{4}} [M]_{\alpha}^{e} - k_{\beta b}^{o} (\frac{P_{eq}}{P_{o}})^{RT} e^{-[E_{\beta a}+T\Delta S + (\mu_{\beta}[M]_{\beta} - \mu_{\alpha}[M]_{\alpha} - \mu_{\theta_{c}}\theta_{c})]/RT} [M]_{\beta}^{e}$$
(4.23)

Under this condition, the solutions of  $\theta_{c}^{e}$ ,  $[M]_{\alpha}^{e}$  and  $[M]_{\beta}^{e}$  are:

$$\theta_p^e = \frac{1}{1 + \frac{1}{K_p}} \tag{4.24}$$

$$\theta_{c}^{e} = \frac{1}{1 + \frac{1}{\sqrt{K_{c}K_{p}}}}$$
(4.25)

$$[M]_{\alpha}^{e} = \frac{[M]_{o}}{1 + K_{\beta} \theta_{c}^{e^{4}} + \frac{1}{K_{\alpha} \sqrt{K_{c} K_{p}}}}$$
(4.26)

$$[M]_{\beta}^{e} = \frac{[M]_{o} K_{\beta} \theta_{c}^{e^{4}}}{1 + K_{\beta} \theta_{c}^{e^{4}} + \frac{1}{K_{\alpha} \sqrt{K_{c} K_{p}}}}$$
(4.27)

where  $K_{\rm p}$ ,  $K_{\rm c}$ ,  $K_{\alpha}$  and  $K_{\beta}$  are the ratios of rate constants of the forward and reverse reactions. They are also referred to as the equilibrium constants.

$$K_{p} = \frac{k_{pa}^{o}}{k_{pb}^{o}} \left(\frac{p}{\sqrt{T}}\right) e^{\frac{E_{pb} - E_{pa}}{RT}},$$

$$K_{c} = \frac{k_{ca}^{o}}{k_{cb}^{o}} e^{\frac{E_{cb} - E_{ca}}{RT}},$$

$$K_{\alpha} = \frac{k_{aa}^{o}}{k_{ab}^{o}} e^{\frac{E_{ab} - E_{aa}}{RT}},$$
and
$$K_{\beta} = \frac{k_{\beta a}^{o}}{k_{\beta b}^{o}} e^{\frac{E_{\beta b} - E_{\beta a}}{RT}}$$

In these equations, a quantity with a superscript "e" means that it is evaluated at a quasi-equilibrium condition.

#### Quasi-static isothermal process:

The model is used for interpreting the results obtained in a resistive-pressure isotherm or optical transmittance-pressure isotherm, where the temperature is fixed and the ambient pressure is varied extremely slowly. More considerations are introduced. First, the difference in activation energy between forward and backward reaction can be represented as enthalpy  $\Delta H_i$ . Based on this relation,  $K_p$ ,  $K_e$ ,  $K_a$  and  $K_p$ 



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can be derived as:

$$K_{p} = K_{p}^{o} \left(\frac{p}{\sqrt{T}}\right) e^{\frac{\Delta H_{p}}{RT}},$$

$$K_{c} = K_{c}^{o} e^{\frac{\Delta H_{c}}{RT}},$$

$$K_{\alpha} = K_{\alpha}^{o} e^{\frac{\Delta H_{\beta}}{RT}}, \text{and}$$

$$K_{\beta} = K_{\beta}^{o} e^{\frac{\Delta H_{\beta}}{RT}} = K_{\beta}^{o} e^{\frac{T\Delta S + RT \ln \frac{P}{P_{o}} + (\mu_{\beta}[M]_{\beta}^{e} - \mu_{\alpha}[M]_{\alpha}^{e} - \mu_{\theta_{c}}\theta_{c}^{e})}}_{RT} = K_{\beta}^{o} \left(\frac{P}{P_{o}}\right) e^{\frac{T\Delta S + \Delta G}{RT}}$$

where

$$K_{p}^{o} = \frac{k_{pa}^{o}}{k_{pb}^{o}}$$
$$K_{c}^{o} = \frac{k_{ca}^{o}}{k_{cb}^{o}},$$
$$K_{\alpha}^{o} = \frac{k_{\alpha a}^{o}}{k_{\alpha b}^{o}}, \text{and}$$
$$K_{\beta}^{o} = \frac{k_{\beta a}^{o}}{k_{\beta b}^{o}}$$

It is noted that there are four groups of parameters appearing in equations 4.24 to 4.27 and they are summarized in the Table 4.1. The first group includes physical constants of chemical reactions, i.e. activation energies and enthalpies of formation, which can be directly found in literatures. The second group of parameters contains physical quantities which are determinable from experimental data as mentioned in the next section. The third group contains the parameters which values are assigned to give some plots with trends matching with the observed experimental result. They include the rate constants and temperature dependence of the Gibbs function. The last group contains unknowns to be solved by using Eqs. (4.24) to (4.27). They are  $\theta_{p}^{e}$ ,  $\theta_{c}^{e}$ ,  $[M]_{\alpha}^{e}$  and  $[M]_{\beta}^{e}$ . They are expected to produce some features correlated closely with the major trends of PCI, RPI or TPI.

Table 4.1 Four groups of parameters used in the model described by Eqs. (4.24) to (4.27). Note that "p" stands for physisorption"; and "c" for chemisorption".

	Parameters		Values	Ref.
Data from	Activation energy of "p" process	Ep	580 J mol <sup>-1</sup>	Borgschulte A
literatures	Activation energy of " <i>c</i> " process	E <sub>c</sub>	23000 J mol <sup>-1</sup>	2008
	Enthalpy of "p" process	$\Delta H_{\rm p}$	$-580 \text{ Jmol}^{-1}$	
	Enthalpy of " <i>c</i> " process	$\Delta H_{\rm c}$	-23000 Jmol <sup>-1</sup>	
	Enthalpy of $\alpha$ -formation	$\Delta H_{\alpha}$	-14500 Jmol <sup>-1</sup>	
Data from	Activation energy of $\alpha$ -formation	$E_{\alpha}$	$11100 \text{ J mol}^{-1}$	
derived	Activation energy of $\beta$ -formation	$E_{\beta}$	23700 J mol <sup>-1</sup>	
experimental	Enthalpy of $\alpha$ -to- $\beta$ transition	$\Delta H_{\beta}$	$-24500 \text{ Jmol}^{-1}$	
data	Entropy of $\alpha$ -to- $\beta$ transition	$\Delta S$	$40 \text{ JK}^{-1} \text{mol}^{-1}$	
Assigned	Frequency factor of reverse "p" process	$k^{\rm o}{}_{\rm pb}$	55.6 s <sup>-1</sup>	
parameters	Frequency factor of reverse " <i>c</i> " process	$k^{o}_{cb}$	$5 \times 10^5  \text{s}^{-1}$	
	Frequency factor of reverse $\alpha$ -formation	$k^{o}_{\alpha b}$	$20 \times 10^3  \mathrm{s}^{-1}$	
	Frequency factor of reverse $\alpha$ -to- $\beta$ transition	$k^{\rm o}{}_{\beta \rm b}$	$5 \times 10^9  \text{s}^{-1}$	
	Frequency factor of forward "p" process	$k^{\rm o}{}_{\rm pa}$	$5  \mathrm{s}^{-1}$	
	Frequency factor of forward "c" process	$k^{\rm o}{}_{\rm ca}$	$500 \text{ s}^{-1}$	
	Frequency factor of forward $\alpha$ -formation	$k^{0}_{\alpha a}$	$1000 \mathrm{s}^{-1}$	
	Frequency factor of forward $\alpha$ -to- $\beta$ transition	$k^{\rm o}{}_{\beta a}$	$5 \times 10^{5} \text{ s}^{-1}$	
	Chemical potential of $\alpha$ -phase	$\mu_{\alpha}$	$15 \text{ kJ mol}^{-1}$	
	Chemical potential of $\beta$ -phase	$\mu_{\beta}$	$-17 \text{ kJ mol}^{-1}$	
	Chemical potential of "c" phase	$\mu_{\theta}$	$10 \text{ kJ mol}^{-1}$	
Unknowns	Gibbs free energy of $\alpha$ -to- $\beta$ transition	$\Delta G$		
to be	Molar concentration of "p" phase	$\theta^{e}_{p}$		
determined	Molar concentration of " <i>c</i> " phase	$\theta^{\rm e}{}_{\rm c}$		
	Molar concentration of $\alpha$ -phase	$[M]^{e}_{\alpha}$		
	Molar concentration of $\beta$ -phase	$[M]^{e}_{\beta}$		

#### 4.1.3 Derivation of enthalpy $\Delta H_{\beta}$ and entropy $\Delta S$ from isotherms

A plot of pressure-composition isotherm (PCI) of an Mg-Ni material is commonly used to derive some important parameters associated with the  $\alpha$ -to- $\beta$ transition of the material [Orimo S, 2001, Verbetsky V.N, 1998, Vincent B, 2007]. The pressure  $P_{eq}$  at which hydridation occurs can be derived. On one hand,  $P_{eq}$  is the pressure (equivalent, hydrogen concentrations) at which the changes of hydrogen-induced electrical and/or optical responses at a fixed temperature are the maximum. On the other hand, thermodynamic quantities such as enthalpies and entropies of hydride formation reaction can also be derived from the temperature *T* dependence of  $P_{eq}$  according to the Van 't Hoff relation [Gremaud R 2007]:

$$\ln(P_{eq} / P_o) = \frac{\Delta H_{\beta}}{RT} - \frac{\Delta S}{R}$$
(4.33)

where  $\Delta H_{\beta}$  and  $\Delta S$  are the enthalpy of formation of  $\beta$ -phase and entropy associated with the  $\alpha$ -to- $\beta$  transition at standard pressure; *R* is the gas constant; *T* the absolute temperature;  $P_{o} = 1.013 \times 10^{5}$  Pa the standard atmospheric pressure, and  $P_{eq}$  the H<sub>2</sub> equilibrium plateau pressure of the PCI.

Since absorption of hydrogen by a Mg-Ni material is also accompanied by substantial changes in electrical and optical properties, the plot of electrical resistivity against hydrogen pressure (referred to as the resistivity-pressure isotherm, RPI), and the plot of optical transmittance versus hydrogen pressure (referred to as the optical transmittance-pressure isotherm, TPI) could also be used to derive the same set of parameters.

Fig. 4.2 (a) and (b) show the RPI and TPI of the sample Pd(5)/MN\_RT measured at different temperatures.  $\langle \rho \rangle$  and optical transmittance (II) increase slightly with  $P_{\rm H_2}$  when  $P_{\rm H_2} \langle P_{\rm eq}$  for the curves of all temperature where  $P_{\rm eq}$  is the mean value of *P* in the plateau. When  $P_{\rm H_2} = P_{\rm eq}$ ,  $\langle \rho \rangle$  and II increase sharply and are then saturated for further increase in  $P_{\rm H_2}$ .

The saturated value of  $\Pi$  decreases with increasing temperature. As a consequence, the electrical and optical H<sub>2</sub> detection sensitivity drop when temperature increases. Furthermore,  $P_{eq}$  increase with temperature for both ICP and TCP plots. It implies that if we increase the temperature of detection, Pd/Mg-Ni films become less sensitive to hydrogen pressure. For instance, considering an increase of hydrogen pressure from 0 to 5500 ppm, at a lower temperature of 30°C, the electrical and optical properties show substantial changes over 7 times (Fig. 4.2), but at a higher temperature of 60°C, the same increase in hydrogen pressure only causes a few percents of fractional changes of the properties.

Fig. 4.3 (a) and (b) show the Van 't Hoff plots obtained from RPI and TPI. The enthalpies obtained by means of Equation 4.1 are shown in Fig. 4.3 (a) and (b).  $\Delta H_{\beta}$ and  $\Delta S$  obtained from Fig. 4.3 (a) and (b) are -24.5 kJ mol<sup>-1</sup> and 40 JK<sup>-1</sup> mol<sup>-1</sup> respectively. The remarkable linearity of the plots shown in Fig. 4.3 (a) and (b), and the similarity of the values of  $\Delta H_{\beta}$  and  $\Delta S$  obtained from RPI and TPI respectively indicate that analyses based on  $\langle \rho \rangle$  and  $\Pi$  are thermodynamically equivalent.




Fig. 4.2 (a) RPI and (b) TPI of Pd(5)/Mg-Ni\_RT measured at 30 to 80°C.



Fig. 4.3 Van 't Hoff plots obtained from (a) RPI and (b) TPI plots.

#### 4.1.4 Derivation of $E_{\beta}$ from the data of reaction rates

In this section, we describe how to derive  $E_{\beta}$  from experimental data.

Fig. 4.4 (a) and (b) show the changes of  $\langle \rho \rangle$  and  $\Pi$  with time in the hydridation processes conducted at different temperatures. Both quantities increase with time in the process and finally approach to respective steady-state values. This trend is attributed to an  $\alpha$ -to- $\beta$  transition. The rises of both quantities are not sharp, suggesting that a Pd/Mg-Ni film needs some time to crystallize the  $\beta$ -phase during hydrogenation [Hydrogen in intermetallic compounds II]. The curves are further differentiated with respective to time to obtain the rate of changes of the constituents involved in reaction. Figs. 4.5 (a) and (b) show the rates of changes of  $<\rho>$  and  $\Pi$ against the time of reaction observed at different temperatures ranging from 30 to 80°C. Mostly, a curve shows two peaks, corresponding to the maximum reaction rates of two reactions. The amplitude and position of the first peak do not have prominent change. It is associated with a nucleation process which is insensitive to temperature from 30 to 90°C. The amplitude of the second peak decreases from 354.5  $\mu\Omega$  m<sup>-1</sup>s<sup>-1</sup> to a very low value with increasing temperature. Its position reaches a minimum when temperature increases to 65°C, and then increases again for higher temperature. The opposite trends may be due to the competition between the forward and reverse reactions of nucleation of the  $\beta$ -phase. At low temperature, the rate constant for the reverse reaction is negligibly small so that a large amount of the  $\beta$ -phase can be formed. At higher temperature, the rate constants for both forward and reserve reactions are increased, such that both the reaction rates of both

backward and reserve reactions are increased and comparable to each other. As a consequence, the formation range of the second  $\beta$ -phase is reduced.

Fig. 4.5 (b) show that each OPT plot only contains one peak at measurement temperature in the range of 30 to 90°C. The values of its amplitudes and positions are similar to the second peak of the RPI plots as shown in Fig. 4.5 (a). Therefore, the peak in an OPT is believed to have the same physical origin of the second peak shown in Fig. 4.5 (b).

Consider equation 4.8 which is used for describing a kinetic of hydridation:

$$\frac{d[M]_{\beta}}{dt} = k_{\beta a} \theta_c^4 [M]_{\alpha} - k_{\beta b} [M]_{\beta}$$
(4.8)

We assume that the rate constants  $k_{\beta a}$  and  $k_{\beta b}$  obey Arrhenius' rate equation, such that Eq.(4.8) can be written as:

$$\frac{d[M]_{\beta}}{dt} = k_{\beta a}^{o} \theta_{c}^{4} [M]_{\alpha} e^{-\frac{E_{\beta a}}{RT}} - k_{\beta b}^{o} [M]_{\beta} e^{-\frac{E_{\beta b}}{RT}}$$
(4.34)

In principle, this equation can be divided into two parts:  $k_{\beta a}^o \theta_c^4 [M]_{\alpha} e^{-\frac{E_{\beta a}}{RT}}$ 

(forward reaction: hydridation) and  $-k_{\beta b}^{o}[M]_{\beta}e^{\frac{E_{\beta b}}{RT}}$  (reverse reaction: dehydridation). Figs. 4.4 (c) and (d) indicate that if the operating temperature is smaller than 65°C, maximum  $\langle \rho \rangle$  and  $\Pi$  can be kept as a similar value, indicating that those processes are mainly governed by forward hydridation and hence the reverse dehydridation effect can be neglected in this temperature range. Therefore, equation 4.34 can be rewritten as:

$$\frac{d[M]_{\beta}}{dt} = k_{\beta a}^{o} \theta_{c}^{4}[M]_{\alpha} e^{-\frac{E_{\beta a}}{RT}}$$

By taking natural logarithm, it can further be rewritten as:

$$\ln(\frac{d[M]_{\beta}}{dt}) = \ln(k_{\beta a}^{o}\theta_{c}^{4}[M]_{\alpha}) - \frac{E_{\beta a}}{RT}$$
(4.35)

We further assume that the rate of change of  $[M]_{\beta}$  is equal to those of  $\langle \rho \rangle$  and  $\Pi$ .

By plotting  $\ln(\frac{d[M]_{\beta}}{dt})$  against 1/T,  $E_{\beta a}$  can be found. Fig. 4.6 (a) and (b) are the

plots of  $\ln(\frac{d < \rho >}{dt})$  and  $\ln(\frac{d\Pi}{dt}) \sim 1/T$  obtained from the data shown in Fig. 4.5 (a)

and (b). The activation energies of the formation of the  $\alpha$ -to- $\beta$  transition,  $E_{\beta a}$ , is obtained from Fig. 4.6 (a) and (b) are 22.9 and 23.7 kJ mol<sup>-1</sup> respectively.

Fig. 4.7 gives a plot showing a proposed energy diagram of different stages in a hydridation process of a Pd/Mg-Ni film. From thermodynamic theory, enthalpy of  $\beta$ -phase formation  $\Delta H_{\beta}$  is illustrated. From kinetics study, the values of activation energies for the formation of the  $\beta$ -phase ( $E_{\beta a}$ ) can be obtained.

It is noticed that the estimate standard error of  $E_{\beta a}$  obtained in Fig. 4.6 is 1.2 kJ mol<sup>-1</sup> which is 4.8% of the original value of  $E_{\beta a}$  (24.5 kJ mol<sup>-1</sup>), implying that the scattering of our data is not serious. If all data in Fig. 4.6 deviates 10%, the result of  $E_{\beta a}$  varies less than 15%. The increase of 5% out of 10% is acceptable in this case. Furthermore, according to literatures, temperature range from 25 to 65°C [Qua J 2009, Qua J 2010] is usually used for kinetic studies. Similar range is used in our experiment so that the value of  $E_{\beta a}$  obtained is reliable.



Fig. 4.4 The trends of (a)  $\langle \rho \rangle$  and (b)  $\Pi$  against time in hydridation processes recorded at different temperatures. The change in (c)  $\langle \rho \rangle$  and (d)  $\Pi$  against time in hydridation processes recorded at different temperatures.



Fig. 4.5 The rate of the change of (a)  $\langle \rho \rangle$  and (b)  $\Pi$  against the time of reaction of hydridation processes performed at different temperatures.



Fig. 4.6 Plots of rate of change of (a)  $<\rho>$  and (b)  $\Pi$  against 1/T.



Fig. 4.7 Energy profile of  $\alpha$ - and  $\beta$ -phase formations in a Pd/Mg-Ni film.

# 4.1.5 Procedures of figuring out of the dependence of $\theta_{c}^{e}$ , $[M]_{\alpha}^{e}$ and $[M]_{\beta}^{e}$ from $P_{H_{2}}$ at constant T (isothermal)

To reproduce the main features of an OPT observed experimentally, we need to solve Eqs (4.24) to (4.27). This can be done by following the procedures described as follows.

(i) We start from initial  $P_{\text{H}_2}$  of 0 Pa at  $T = 60 \,^{\circ}\text{C}$ , and increase its value successively. With this setting, the initial values of other parameters are listed in Table 4.2:

Table 4.2 Initial values of the parameters used to solve Eqs (4.24) to (4.27).

Symbols	Values
$P_{\rm H_2}$	0
Kp	0
$K_{eta}$	0
$\theta^{e}_{p}$	0
$\theta^{\rm e}{}_{\rm c}$	0
$[M]^{e}_{\alpha}$	0
$[M]^{e}_{\beta}$	0
ΔG	0

 $K_{\rm p}$  and  $K_{\beta}$  are functions of  $P_{\rm H_2}$  and they become zero when  $P_{\rm H_2}$  is zero. By using Eqs (4.24) to (4.27),  $\theta^{\rm e}_{\rm p}$ ,  $\theta^{\rm e}_{\rm c}$ ,  $[M]^{\rm e}_{\alpha}$  and  $[M]^{\rm e}_{\beta}$  become zero if  $K_{\rm p}$  and  $K_{\beta}$  are zero.  $\Delta G$  is also equal to zero when  $\theta^{\rm e}_{\rm c}$ ,  $[M]^{\rm e}_{\alpha}$  and  $[M]^{\rm e}_{\beta}$  are zero.

- (ii) Assigned the values of the second group of parameters in Table 4.1, named as*"Assigned parameters"* by trial and error.
- (iii) By setting a little higher of  $P_{\rm H_2}$  to 0.5 Pa. In addition, the values of group 1

data in Table 1, namely $\Delta H_{\rm p}$ ,  $\Delta H_{\rm c}$  and  $\Delta H_{\alpha}$ , listed in Table 4.1, are found from literature, and put into our equations. The values of parameters,  $K_{\rm p}$ ,  $K_{\rm c}$  and  $K_{\alpha}$  are determined.

- (iv) It is assumed that  $\Delta G$  at  $P_{H_2} = 0.5$  Pa is the same as  $P_{H_2} = 0$  Pa and plug the  $\Delta G$  at  $P_{H_2} = 0$  Pa into the equation of  $K_{\beta}$ .
- (v) Inserting  $K_{\rm p}$ ,  $K_{\rm c}$   $K_{\alpha}$  and  $K_{\beta}$  into Eqs. (4.24) to (4.27), the values of the variables  $\theta^{\rm e}_{\rm p}$ ,  $\theta^{\rm e}_{\rm c}$ ,  $[M]^{\rm e}_{\alpha}$  and  $[M]^{\rm e}_{\beta}$  are obtained.
- (vi) Steps (iii) to (vi) are iterated by increasing  $P_{\rm H_2}$  by 0.5 Pa per step until  $P_{\rm H_2}$  reaches 4000 Pa.  $\theta^{\rm e}_{\rm p}$ ,  $\theta^{\rm e}_{\rm c}$ ,  $[M]^{\rm e}_{\alpha}$  and  $[M]^{\rm e}_{\beta}$  are functions of pressure only and are derived.
- (vii) The derived relationship of  $[M]^{e}_{\beta} \sim P_{H_2}$  and the TPI obtained from experiment are compared. Deviation are further diminished by readjusting the third group of parameters listed in Table 4.1, namely "Assigned parameters", until the calculated curve is closest to the experimental one. The fourth group of parameters, namely the concentration of the reactants, are derived which see to show similar trends as those of RPI and TPI.

# 4.1.6 Procedures of figuring out of the dependence of $\theta_{c}^{e}$ , $[M]_{\alpha}^{e}$ and $[M]_{\beta}^{e}$ from T at constant $P_{H_{2}}$ (isobaric)

Based on the procedures discussed in the previous section, we have obtained the values of variables ( $\Delta G$ ,  $\theta_{p}^{e}$ ,  $\theta_{c}^{e}$ ,  $[M]_{\alpha}^{e}$  and  $[M]_{\beta}^{e}$ ) and assigned parameters ( $K_{p}$ ,  $K_{c}$ ,  $K_{\alpha}$  and  $K_{\beta}$ ) at  $P_{H_{2}}$  of 4000 Pa at T = 60 °C. Following the steps shown below, the dependence of  $[M]_{\beta}^{e}$  from T at constant  $P_{H_{2}}$  is then obtained.

- (i) Starting from this set of initial values, *T* is increased to 60.5 °C. In addition, the values of group 1 data in Table 1, namely  $\Delta H_p$ ,  $\Delta H_c$  and  $\Delta H_a$ , listed in Table 4.1, are found from literature, and put into our equations (4.24) to (4.27).
- (ii) The values of parameters,  $K_p$ ,  $K_c$  and  $K_{\alpha}$  are determined. It is assumed that  $\Delta G$  at T = 60.5 °C is the same as T = 60 °C and plug the  $\Delta G$  at 60 °C into the equation of  $K_{\beta}$ .
- (iii) Inserting  $K_{\rm p}$ ,  $K_{\rm c}$   $K_{\alpha}$  and  $K_{\beta}$  into Eqs. (4.24) to (4.27), the values of the variables  $\theta^{\rm e}_{\rm p}$ ,  $\theta^{\rm e}_{\rm c}$ ,  $[M]^{\rm e}_{\alpha}$  and  $[M]^{\rm e}_{\beta}$  are obtained.
- (iv) Steps (i) to (iii) are repeated with T range from -10 to 300°C.



4.1.7 Procedures of figuring out of the dependence of  $\theta_c$ ,  $[M]_{\alpha}$  and  $[M]_{\beta}$  from hydrogen loading time at constant T and  $P_{H_2}$  (isothermal-isobaric)

To reproduce the main features of an  $\langle p \rangle$  and  $\Pi$  as a function of hydrogen loading time observed experimentally, we need to solve Eqs (4.11) to (4.18). This can be done by following the procedures described as follows.

- (i) It is assumed that the kinetic study of this system has only a small deviation from equilibrium [Boris S 2005] (i.e.  $\Delta G$  is kept constant as its equilibrium value throughout the whole period of hydrogen loading time). Therefore, we start from the value of  $\Delta G$  at  $P_{\rm H_2}$  of 4000 Pa at T = 60 °C which is obtained from the procedures of section 4.15. With this setting, the initial values of other unknown variables  $\theta_{\rm p}$ ,  $\theta_{\rm c}$ ,  $[M]_{\alpha}$  and  $[M]_{\beta}$  are set as zero.
- (ii) Assigned the values of the second group of parameters in Table 4.1, named as "Assigned parameters" by trial and error. In addition, the values of group 1 data in Table 1, namely  $\Delta H_p$ ,  $\Delta H_c$  and  $\Delta H_{\alpha}$ , listed in Table 4.1, are found from literature, and put into our equations.
- (iii) The derived relationship of the concentration  $[M]_{\alpha}$  and  $[M]_{\beta}$  against the hydrogen loading time and Fig 4.4 (a), (b) and Fig 4.5 (a), (b) obtained from experiment are compared. Deviation are further diminished by readjusting the third group of parameters listed in Table 4.1, namely "Assigned parameters", until the calculated curve is closest to the experimental one. The fourth group of parameters, namely the concentration of the reactants, are derived which see to show similar trends as those of Fig 4.4 (a), (b) and Fig 4.5 (a), (b).

## 4.2 Analysis of the changes of phase compositions in quasi and dynamic $\alpha$ -to- $\beta$ hydridation processes based on the model

#### Analysis of quasi (isothermal) $\alpha$ -to- $\beta$ hydridation process

In this section, we aim at deriving the main features of the  $P_{\text{H}_2}$  dependence of  $\theta^{\text{s}}_{\text{c}}$ ,  $[M]_{\alpha}$  and  $[M]_{\beta}$  of a quasi  $\alpha$ -to- $\beta$  hydridation process at a specific temperature T (isothermal). Meanwhile, equilibrium constants  $K_{\text{p}}$ ,  $K_{\text{c}}$ ,  $K_{\alpha}$  and  $K_{\beta}$  will be calculated. They are the ratios of products and reactants at steady state, and are determined by the ratios of rate constants of forward and reverse reactions. Referring to Eqs. (4.24-26),  $\theta^{\text{s}}_{\text{c}}$  increases with  $K_{\text{p}}$  and  $K_{\text{c}}$ ;  $[M]_{\alpha}^{\text{s}}$  increases with  $K_{\text{p}}$ ,  $K_{\text{c}}$  and  $K_{\alpha}$  but decreases with increasing  $K_{\beta}$ ;  $[M]_{\beta}^{\text{s}}$  increases with  $K_{\text{p}}$ ,  $K_{\text{c}}$  and  $K_{\alpha}$  but is a more complicated function of  $K_{\beta}$ .

Fig. 4.8 (a) shows the calculated results of  $\theta_c$ ,  $[M]_{\alpha}$  and  $[M]_{\beta}$  at isothermal condition with  $T = 30^{\circ}$ C.  $\theta_c$  and  $[M]_{\alpha}$  increases with  $P_{H_2}$  at the beginning of the loading of H<sub>2</sub>. When  $\theta_c$  and  $[M]_{\alpha}$  are high enough, formation of  $\beta$ -phase is initiated. Then,  $[M]_{\alpha}$  decreases because some  $\alpha$ -phase is converted into the  $\beta$ -phase. Results show that with increasing *T*, less products of the reactions, i.e. chemisorbed species,  $\alpha$ -phase and  $\beta$ -phase components are formed. Therefore, the values of  $\theta_c$  and  $[M]_{\beta}$ decrease in general [Fig. 4.8 (b) and (d)]. A plot of  $[M]_{\alpha}$  of the intermediate  $\alpha$ -phase (Fig. 4.8 (c)) with a higher *T* has a higher value at a higher hydrogen pressure. In addition, the hydrogen pressure corresponding to the maximum value of the plot of  $[M]_{\alpha}$  increases with increasing temperature due to the decrease of  $\theta_c$ .

Fig. 4.9 is an alternative presentation of Fig. 4.8 (d) by exchanging the roles of the two axes. Its shape reproduces the main features of the experimental RPI and TPI plots as shown in Fig. 4.2 (a) and (b), indicating that this model is valid in describing



the physical processes involved in the quasi-static hydridation process of a Pd/Mg-Ni film.



Fig. 4.8 (a) Plots of the calculated  $\theta_{c}^{s}$ ,  $[M]_{\alpha}^{s}$  and  $[M]_{\beta}^{s}$  values against  $P_{H_{2}}$  at temperature 30°C. (b)-(d) Plots of the calculated  $\theta_{c}^{s}$ ,  $[M]_{\alpha}^{s}$  and  $[M]_{\beta}^{s}$  values versus  $P_{H_{2}}$  at various temperatures.



Fig. 4.9 A plot of hydrogen pressure versus  $[M]^{s}_{\beta}$  at various temperatures.

#### Analysis of quasi (isobaric) $\alpha$ -to- $\beta$ hydridation process

Fig. 4.10 gives the key features by showing the plots of temperature dependences of the saturated  $\theta_c$ ,  $[M]_{\alpha}$  and  $[M]_{\beta}$  values evaluated at  $P_{H_2}$  = 4000 Pa. At low temperature, the material mainly exists in the  $\beta$ -phase. When temperature is increased to 40°C,  $[M]_{\beta}$  decreases substantially. Hence the reverse reaction resulting in the formation of more  $\alpha$ -phase dominates. On the contrary, if temperature increases continuously,  $[M]_{\alpha}$  decreases because  $\theta_c$  decreases with increasing temperature. Hence, there are little chemisorbed H atoms to maintain the growth of the  $\alpha$ -phase.



Fig. 4.10 A plot of temperature dependences of calculated  $\theta_c$ ,  $[M]_{\alpha}$  and  $[M]_{\beta}$  evaluated at  $P_{\text{H}_2}$  = 4000 Pa.

#### Analysis of dynamic $\alpha$ -to- $\beta$ hydridation (isothermal-isobaric) process

A dynamic  $\alpha$ -to- $\beta$  hydridation process is conducted by applied a fixed hydrogen pressure to a film sample maintained at a fixed temperature, while the concentrations of the constituents, and hence the electrical and optical properties of the film material vary through a non-equilibrium process to approach to the final state. As such, we need to apply the isothermal-isobaric condition in solving the equations in order to obtain the time dependences of the concentrations of the constituents in this process.

As a primary approach, we assume that  $\langle \rho \rangle$  of the film is proportional to  $[M]_{\alpha}$ and  $[M]_{\beta}$ ; and the optical transmittance  $\Pi$  of the film is directly proportional to  $[M]_{\beta}$ . By using the initial value of  $\langle \rho \rangle$  and  $\Pi$ , and the peak values of  $d\langle \rho \rangle/dt$  and  $d\Pi/dt$ measured at 30°C as shown in Figs. 4.4-5, the calculated values of  $\langle \rho \rangle$  and  $\Pi$  are obtained as functions of  $[M]_{\alpha}$  and  $[M]_{\beta}$ .

Fig. 4.11 (a) and (b) show calculated  $\langle \rho \rangle$  and Π with increasing time of reaction in hydridation processes at various temperatures. Figs. 4.12 (a) and (b) further show the rate of the changes of  $\langle \rho \rangle$  and Π with increasing reaction time in the hydridation processes performed at various temperatures. The calculated results reproduce the key features shown in Fig. 4.5 (a) and (b). The 1<sup>st</sup> and 2<sup>nd</sup> peaks in Fig. 4.5 (a) correspond to the nucleation of α- and β-phase respectively. The position and height of the 1<sup>st</sup> peak change slightly with temperature. The peak position for the 2<sup>nd</sup> peak decreases when temperature increases from 30°C to 60°C and then increases again for temperatures above 60°C. The peak disappears above 75°C. This phenomenon can be explained by using this model. As  $k_{\beta b}$  can be neglected at low temperature, forward reaction for β-formation is more favored. If temperature

increases,  $k_{\beta b}$  is increased by order of magnitude due to the increase  $\Delta G$  included in the exponent of the expression of  $k_{\beta b}$ . Therefore, the reverse reaction of  $\beta$ -formation becomes significant and hence peak position increases, peak height decreases and finally the 2<sup>nd</sup> peak disappears.



Fig. 4.11 Calculated (a)  $\langle \rho \rangle$  and (b)  $\Pi$  with increasing reaction time hydridation at various temperatures.



Fig. 4.12 Calculated rates of the changes of (a)  $\langle \rho \rangle$  and (b)  $\Pi$  with increasing reaction time in hydridation processes at various temperatures.

#### Analysis of the results of cyclic tests

Fig. 4.13 shows the H-sensing response of  $\langle \rho \rangle$ , response time and sensitivity S =  $\Delta \langle \rho \rangle / \langle \rho \rangle \times 100\%$  of Sample Pd(5)/MN(30)\_RT performed at 60°C. It is shown that the H<sub>2</sub> sensing properties degrade with increasing numbers of switching cycles, in the sense that response time is prolonged and sensitivity of detection decreases. We try to argue that these features are results of the decrease of  $\Delta H_{\beta}$  and increase of  $E_{\beta a}$ . By the use of Van't Hoff plot, the values of  $\Delta H_{\beta}$  of the film at the as-deposited state and after cyclic test are obtained. In addition, the values of  $E_{\beta a}$  of the film at the as-deposited state and after cyclic test can be found from the kinetic study. Fig. 4.14 shows a plot of  $E_{\beta a}$  and  $\Delta H_{\beta}$  of the two states.



Fig. 4.13 H-sensing response of  $\langle \rho \rangle$ , response time and sensitivity  $S = \Delta \langle \rho \rangle / \langle \rho \rangle \times 100\%$  of Sample Pd(5)/MN(30)\_RT performed at 60°C.





Fig. 4.14 Energy levels of the film involving the formation of  $\beta$ -phase before and after cyclic test.

Furthermore, the value of the metallic alloy phase concentration  $[M]_o$  of the as-deposited state and after cyclic test can be approximated according to the results of XPS analysis given in Chapter 3. By assuming that  $\Delta H_\beta$ ,  $E_{\beta a}$  and  $[M]_o$  are proportional to number of cycles n, the following equations can be obtained:

$$\Delta S = 0.193n + 40 \tag{4.32}$$

$$E_{\beta a} = 25.08n + 23700 \tag{4.33}$$

$$[M]_{o} = -0.0027n + 1 \tag{4.34}$$

By solving the differential equations, Fig. 4.15 (a) shows the calculated values of the rate of the change of  $<\rho>$ . It is found that the plot of  $d<\rho>/dt$  against reaction time reproduces some features of the experimental results as shown in Fig. 4.16 (b).



Fig. 4.15 The rate of change of  $< \rho >$  obtained by (a) calculation and (b) experiment.

It is noticed that the position and height of the peaks of the calculated curves do not completely match with the experimental ones, possibly because  $\Delta H_{\beta}$ ,  $E_{\beta a}$  and  $[M]_{o}$  are not completely proportional to number of switching cycles n. Firstly, the dependency of  $[M]_0$  on number of cycles should be better expressed with an exponential function rather than a linear one, because the decrease of the metallic alloy phase  $[M]_0$  is dominated by diffusion of atoms and should be affected by an exponential factor in the formulation. Secondly, the exact values of  $\Delta H_{\beta}$  and  $E_{\beta a}$  at the intermediate stages of the switching process are not easily obtained. Only those of the as-deposited state and after the cyclic test are found. Therefore, we claim that the model can be improved to suit the use in analyzing the results of a cyclic test if one can know: (i) how  $[M]_{o}$  depends on number of cycles; and (ii) how  $\Delta H_{\beta}$  and  $E_{\beta a}$ vary as the elemental composition become non-uniform with increasing switching cycles as observed from the XPS data. These information could be found by using ab initio calculation. However, at the present stage, we can just apply a simple linear relationship of  $\Delta S$ ,  $E_{\beta a}$  and  $[M]_{o}$  as functions of the number of switching cycles, all to perform the analysis. Our intention is to demonstrate that the switching processes can alter the elemental distribution in a Pd/Mg-Ni film, such that the values of  $\Delta H_{\beta}$ ,  $E_{\beta a}$ and  $[M]_{o}$  are affected as a consequence. Then, response time and recovery time are prolonged as a consequence. The H<sub>2</sub> detection sensitivity is also degraded.

#### 4.3 Summary

We have the following findings from this chapter

- A model based on physisorption, chemisorption, α-and β-formation was developed to investigate the hydridation effect of Pd/Mg-Ni film.
- Based on this model, the trends of quasi-isothermal and dynamic hydridation process are reproduced and they are matched with the data obtained experimentally.
- The model reflects that the sensitivity of the H-induced response would be increased by lowering operation temperature. α to β transition, is more ready to occur at *T* below 60°C, gives large response and sensitivity in and Π. However, the α to β transition rate is much decreased at low temperature (say below 60°C). Therefore, there exist anoptimum *T* which perform high sensitivity with acceptable response time.
- Result also shows that the increases of number of cycles in cyclic test give rise to increase of entropy of α to β transition ΔS, activation energy of α to β transition E<sub>βa</sub> and the concentration of Mg-Ni [M]<sub>o</sub>, hence the β concentration [M]<sub>β</sub> and the sensitivity of and Π decrease.

#### **Chapter 5**

# Improvement of stability of $H_2$ sensing response of Pd/Mg-Ni films by suppressing $\alpha$ -to- $\beta$ transition or using a thicker Pd cover layer

It has been concluded in Chapter 3 that a Pd/Mg-Ni film would experience a volume expansion when it is hydrogenated. The degree of expansion is relatively mild when the hydrogen concentration  $[H_2]$  is low, such that the film remains in the  $\alpha$ -phase. However, volume expansion is more pronounced when the film is exposed to an environment of a higher [H<sub>2</sub>], such that  $\alpha$ -to- $\beta$  transition occurs. As a consequence, stresses are built up in the bi-layered film structure, which can cause cracking of the Pd overcoat as well as the Mg-Ni alloy layer. Deformation occurs more readily in repeated hydrogenation-dehydrogenation cycles, and the corresponding fluctuation of film volume is termed as breathing effect. Oxygen molecules from the environment can then pass through the cracks and oxidize Mg atoms to generate an Mg-O layer on the alloy film surface. The Mg-O layer can slow down the motion of H atoms in the film. In addition, Mg and Ni atoms in the H<sub>2</sub>-senstive layer segregate, with the Mg atoms migrating towards the film surface. Moreover, Pd and Mg atoms from two adjacent layers inter-diffuse to form an alloy phase. The overall result of these phenomena is to degrade the H<sub>2</sub> sensing efficiency of the film.

Based on these findings, we conceived and carried out two strategies to aim at modifying the stability of the H<sub>2</sub> sensing properties of the films. The first is based on the intention of diminishing  $\alpha$ -to- $\beta$  transition. Two methods were tried, namely by (i) limiting the hydrogen pressure [H<sub>2</sub>] at a low level so as to keep the alloy film in the  $\alpha$ -phase; or (ii) by doping Pd atoms into the alloy film to accelerate the "pre-aging" of initial stability of the H<sub>2</sub> sensing properties of the alloy film. Results of this part of study are presented in Section 5.1.

The next strategy is to optimize the thickness of the Pd cover layer, such that it is thick enough to provide stronger resist against premature cracking of the structure due to H-induced volume change (especially volume breathing encountered in a cyclic testing), without causing significant electrical shorting the Mg-Ni layer when it is hydrogenated. Results of this part of study are presented in Section 5.2.

#### 5.1 Strategy I: Prevention of α-to-β transition

From the view point of kinetic theory of reaction, the formation rate of the  $\beta$ -Mg<sub>2</sub>NiH<sub>x</sub> phase is described by:

$$\frac{d[M]_{\beta}}{dt} = k_{\beta a} \theta_c^x [M]_{\alpha} - k_{\beta b} [M]_{\beta}$$
(5.1)

where  $[M]_{\alpha}$  and  $[M]_{\beta}$  are the concentration of the respective phases, and  $\theta_{c}$  is the coverage of chemisorbed hydrogen species. At equilibrium,  $\frac{d[M]_{\beta}}{dt} = 0$ , the equilibrium constant  $K_{\beta}$  can be written as:

$$K_{\beta} = \frac{k_{\beta a}}{k_{\beta b}} = \frac{[M]_{\beta}}{\theta_c^x [M]_{\alpha}}$$

To minimize the  $\beta$ -phase formation, the operation condition of the sensor should be set for  $K_{\beta}$  to be small. One method is to use the sensor in a low hydrogen concentration [H<sub>2</sub>] environment, which is set at 5400 ppm in our test. A low value of [H<sub>2</sub>] leads to a low coverage of surface sorbed hydrogen species,  $\theta_c$ , such that  $K_{\beta}$  can be kept at a small value.

Another method examined in this part of study aiming at suppressing the formation of  $\beta$ -phase is to introduce Pd doping in Mg-Ni layer (in addition to the Pd cover layer). The approach is inspired by the conception that inter-diffusion, and subsequent alloying of Pd and Mg atoms can torpify the H<sub>2</sub> sensing properties of a Pd/Mg-Ni film. In particular, results of a cyclic test indicate that deterioration is particularly pronounced in the initial stage of use. One may thus expect that introduction of Pd doping into the Mg-Ni layer could lead to pre-aging of the Mg-Ni layer, such that the stability to some extent over the term of use. However, the sensitivity of detection could be lowered a bit. We describe the results of the two methods in the following.

#### 5.1.1 Method 1: operating the film sensor at low $[H_2]$ to prevent $\alpha$ -to- $\beta$ transition

We employed a cyclic test (at 60°C) with hydrogen partial pressure  $P_{H_2}$  varying between 0 ppm, namely the background, and a relatively low level of 540 Pa. A  $P_{H_2}$ value of 540 Pa is equivalent to a nominal hydrogen concentration of  $C_{H_2} = 5400$ ppm in one atmospheric pressure, which falls in Region I of the Resistivity-Pressure Isotherm (RPI) plot as shown in Fig. 3.2. This value of  $C_{H_2}$  is so low that the Mg-Ni layer would mainly be in the  $\alpha$ -phase throughout the test. The alloy containing H

atoms is referred to as a solid solution of hydrogen, with the atoms located interstitially in a random atomic network.

Results are shown in Fig. 5.1. The number of repeatable switching cycles is over 900 without obvious sign of degradation. The figure also contains insets showing exaggerated features of sensing response of two segments. The cyclic response in respective regions appears to be highly reproducible. In particular, the response and recovery times, denoted as  $t_{90}$  and  $t_{10}$ , are found to vary in narrow ranges of 34 - 40 s and 60 - 65 s respectively, which seem to be rather suitable in practical use. Both the baseline and upper bound of the plot only shift mildly, and the variation of the detection sensitivity is under 14% throughout the test. The validity of the method for getting more stable sensing response by using the sensor at a low [H<sub>2</sub>] environment is justified.

According to the discussion in Chapter 4, it is confirmed that a plot of the rate of change of  $\langle \rho \rangle$  versus time observed in a hydrogenation process may contain two peaks. The first is associated with the incorporation of H atoms into the  $\alpha$ -phase, and the next corresponds to the  $\alpha$ -to- $\beta$  transition when more H atoms are added. Fig. 5.2 shows clearly that in this test each plot of the selected cycles (i.e. 1<sup>st</sup>, 51<sup>st</sup>, 101<sup>st</sup>, 301<sup>st</sup> and 701<sup>st</sup> cycles) shows one peak only, confirming that only  $\alpha$ -phase is involved. Under such a low [H<sub>2</sub>] working condition, the range of volume change is limited, such that H<sub>2</sub> sensing response is more stable, and the film if used as a H<sub>2</sub> sensor could be more durable. We further note that the peak changing rate of  $\langle \rho \rangle$ decreases substantially from 8.2  $\mu\Omega$  m s<sup>-1</sup> of the 1<sup>st</sup> cycle to 1.5  $\mu\Omega$  m s<sup>-1</sup> of the 51<sup>th</sup>

performed thereafter. The observed initial drop of the rate could be attributed to inter-diffusion of Pd and Mg atoms, or initial stabilization of the film structure.

From a practical point of view, the range of  $[H_2]$  for a Pd/Mg-Ni hydrogen film sensor can be adjusted by varying the operation temperature *T*. The working range of  $[H_2]$  for different value of *T* can be identified by referring to the respective isotherms. Moreover, the sensing response of the film confined in the  $\alpha$ -phase appears to be rather linear, facilitating simple conversion to obtain an accurate readout of  $[H_2]$ .



Fig. 5.1 Cyclic response of  $<\rho>$ , sensitivity *S*, response time  $t_{90}$  and recovery time  $t_{10}$  of Sample Pd(10)/MN(30) measured at 60°C with  $P_{H_2} = 540$  Pa.



Fig. 5.2 Plots of the changing rate of  $\langle \rho \rangle$  of the hydrogenation processes of selected cycles of Sample Pd(10)/MN(30) measured with  $P_{\rm H_2} = 540$  Pa and  $T = 60^{\circ}$ C.

#### 5.1.2 Method 2: introduce Pd doping to Mg-Ni layer

Another method is to add Pd atoms into the Mg-Ni layer (the preparation condition of the sample is given in Chapter 2). There are two main purposes for doping Pd atoms into an Mg-Ni layer. The first is to form Mg-Pd alloy in the Mg-Ni layer. As a consequence, the content of Mg-Ni becomes smaller. This change diminishes volume expansion in hydrogenation process to reduce damage of the sample's structure. The second reason is that the gradient of the concentration of Pd along the depth of the Mg-Ni layer decreases if Pd atoms are doped into Mg-Ni layer. Therefore, the tendency of inter-diffusion between Pd and Mg becomes less significant. The test was performed at 60°C, but a H<sub>2</sub> partial pressure  $P_{H_2}$  of 4000 Pa was used, equivalent to a  $C_{H_2}$  of 40000 ppm (= 4%). Normally, a Pd/M-Ni film operating at this high  $C_{H_2}$  would experience  $\alpha$ -to- $\beta$  transition accompanied by great volume change, such that the sensing stability is very poor.

However, with Pd doping (5.6% Pd in Mg-Ni layer) in this case, Fig. 5.3 shows that except for the first few tens of cycles, the sensing response is very stable over 900 cycles without showing any sign of degradation. After the first 50 switching cycles, both the base and saturated values of  $\langle \rho \rangle$  do not have significant change, and the variation of the detection sensitivity is stabilized within at 30% throughout the test.

Fig. 5.4 shows the changing rate of  $\langle \rho \rangle$  of the hydrogenation processes of selected cycles. Each curve only contains one peak, indicating that the Pd doped Mg-Ni films remains in the  $\alpha$ -phase in the hydrogenation process. The peak height decreases from 13.7 to 6.7  $\mu\Omega$  m s<sup>-1</sup> after the first 50 cycles, and is then stabilized at a value around 6.5  $\mu\Omega$  m s<sup>-1</sup>. The shape of the curve remains almost unchanged



afterwards, indicating that the stability of the  $H_2$  sensing properties of the film is fairly good.





Fig. 5.3 Cyclic response of  $\langle \rho \rangle$  and sensitivity *S* of Sample Pd(5)/PMN(30) measured at 60°C with  $P_{\rm H_2} = 4000$  Pa.


Fig. 5.4 Plots of the changing rate of  $<\rho>$  of selected cycles of Sample Pd(5)/PMN(30) measured at 60°C with  $P_{\rm H_2} = 4000$  Pa.

#### 5.2 Strategy II: Use a Pd cover layer with an appropriate thickness

Although Method 1 of Strategy I described in Section 5.2 is shown to be successful in improving the stability of the H<sub>2</sub> sensing properties of a Pd/Mg-Ni film sensor, the methods are only applicable at low [H<sub>2</sub>] condition. Method 2 of the Strategy 1 is also successful, but the sensitivity is relatively low. The Strategy II is thereby proposed, based on the concept that a thicker overcoat can provide better protection to the Mg-Ni layer.

The thickness of the Pd cover layer of the sample used in previous test is 5 nm. In this part of study, we used a sample with a thicker Pd cover layer of 10 nm to examine the idea. The preparation condition of the sample is shown in Chapter 2.

Fig. 5.5 shows the results of H-induced cyclic response of  $\langle \rho \rangle$  of the sample. It was set to react with  $P_{H_2} = 4000$  Pa (or  $C_{H_2} = 40000$  ppm) at 60°C. The cyclic sensitivity shows an initial drop and is stabilized at around 150% after 50 cycles. The number of repeatable switching cycles exceeds 400 without showing any sign of deterioration. With the use of this  $C_{H_2}$  value, one expects that  $\alpha$ -to- $\beta$  transition and substantial volumetric breathing of the Mg-Ni layer would occur (evidence to be shown). The observed excellent stability of the resistive response of the film strongly supports the idea that a thicker Pd layer can withstand larger internal stresses and provide stronger protection to Mg-Ni layer from being cracked and oxidized. The background value of  $\langle \rho \rangle$  of the film at metallic state can be recovered very well, showing that the film is particularly suitable to be used for H leakage monitoring.

From application point of view, a Mg-Ni film  $H_2$  sensor involving transitions between  $\alpha$ - and  $\beta$ -phase has an advantage that it exhibits great change in optical transmittance ( $\Pi$ ), which can be used as a signal for detecting  $H_2$ . A film sensor

working in such an optical mode consumes little electrical power, and does not have a risk of, generating sparks by an electrical circuit like that required by the sensor working in electrical mode. Fig. 5.6 shows the H-induced cyclic response of the optical transmittance ( $\Pi$ ) of a sample with a 10-nm Pd cover layer. The number of repeatable switching cycles was determined to be not less than 400. Meanwhile, no sign of degradation was observed, except for the initial drop of the sensitivity.



Fig. 5.5 H-induced cyclic electrical response, sensitivity *S* (percentage change in  $\langle \rho \rangle$ ) and the corresponding rising and dropping time ( $t_{90}$  and  $t_{10}$ ) of the sample Pd(10)/MN(30) measured at 60°C and  $P_{H_2} = 4000$  Pa. Insets: Details of the change of  $\langle \rho \rangle$  of selected cycles.





Fig. 5.6 H-induced cyclic optical transmission response, sensitivity *S* (percentage change in  $\Pi$ ) and the corresponding rising and dropping time ( $t_{90}$  and  $t_{10}$ ) of the sample Pd(10)/MN(30) measured at 60°C and  $P_{H_2}$  = 4000 Pa. Insets: Details of the change of  $\Pi$  of selected cycles.



Fig. 5.7 and 5.8 show the changing rate of  $\langle \rho \rangle$  of selected switching cycles of Sample Pd(5)/MN(30) and Pd(10)/MN(30). General speaking, two peaks are identified in each curve. The appearance of the second peak implies that  $\beta$ -phase is generated during hydrogenation. Also shown in the figures is that the peak rate drops very fast in the first 50 cycles. The insets shown in Fig. 5.7 illustrate that the amplitude of the second peak of the samples with a 5-nm Pd cover layer further decreases beyond 50<sup>th</sup> cycles. On the other hand, for the sample with a 10-nm cover layer, the second peak stops decreasing and is stabilized at around 0.04  $\mu\Omega$  m s<sup>-1</sup> after the 50<sup>th</sup> cycles. This verifies that the use of a 10-nm Pd cover layer has a stronger resist against cracking. Consequently, the alloy layer is better protected from being oxidized.



Fig. 5.7 Plots of the changing rate of  $\langle \rho \rangle$  of Sample Pd(5)/MN(30)\_RT measured at 60°C with  $P_{\rm H_2}$  = 4000 Pa with different number of switching cycles.



Fig. 5.8 Plots of the changing rate of  $<\rho>$  of Sample Pd(10)/MN(30) measured at 60°C with  $P_{\rm H_2} = 4000$  Pa with different number of switching cycles.

Fig. 5.9 shows the results of a film sensor having a even thicker (20 nm) Pd cover layer. The saturated  $\langle \rho \rangle$  and sensitivity would drop significantly though the sensing response behaves much more repeatable. This illustrates that the Pd layer is thick enough to electrically short the film material, which dominates significantly the resistance of the sample and the appearance H<sub>2</sub> sensing response is relatively low.





Fig. 5.9 H-induced cyclic electrical response, sensitivity *S* (percentage change in  $\langle \rho \rangle$ ) and the corresponding rising and dropping time ( $t_{90}$  and  $t_{10}$ ) of the sample Pd(20)/MN(30) measured at 60°C and  $P_{H_2} = 4000$  Pa. Insets: Details of the change of  $\langle \rho \rangle$  of selected cycles.

Considering the changing rate of  $\langle \rho \rangle$  of Sample Pd(20)/MN(30) as shown in Fig. 5.10, it is found that formation rate of the  $\beta$ -phase is faster than those of a sample with a thinner Pd layers. It should be attributed to the increase of coverage of chemisorbed hydrogen species,  $\theta_c$ . Since Pd is a catalyst for H<sub>2</sub> dissociation, the rate constant  $k_{ca}$  would increase if more Pd atoms exist. Therefore,  $\alpha$ - and  $\beta$ -phase can be formed with a faster rate.



Fig. 5.10 A plot of rate of change of  $<\rho>$  of Sample Pd(20)/MN(30) measured at 60°C with  $P_{\rm H_2} = 4000$  Pa with different number of switching cycles.

## **Chapter 6**

#### Durability improvement by adding Ni interfacial layer

From the studies and results presented in previous chapters, one may claim that the degradation of  $H_2$  sensing properties is due to two reasons. The first is the significant volume expansion associated with the  $\alpha$ -to- $\beta$  transition, which leads to cracking and/or fragmentation of the Pd cover layer, such that oxygen atoms from the surrounding invade into the alloy layer and oxidize the alloy layer. This factor could be alleviated to some extent by properly adjusting the thickness of the Pd cover layer to strengthen the oxidation resistance of the alloy film. The second factor leading to the degradation of  $H_2$  detection sensitivity is inter-diffusion of Pd and Mg atoms as described in Section 5.2. In chapter 6 this chapter, we report the effect of adding a Ni buffer layer between the Pd cover layer and the Mg-Ni layer, with an intention to obstruct inter-diffusion of Pd and Mg atoms across the boundary of the cover and alloy layers.

#### 6.1 Hydrogen-induced changes of the properties of Pd/Ni/Mg-Ni films

In this part of study, each film sample is made to have a Ni interfacial layer between the Pd cover layer and the alloy layer. It does not block H diffusion by referring to the diffusivity of H atoms in Ni is  $3.2 \times 10^{-13}$  m<sup>2</sup>s<sup>-1</sup> at 60°C (diffusivity of H atoms in Pd is  $10^{-10}$  m<sup>2</sup>s<sup>-1</sup>) [D.J. Fisher 1999], such that the response rate of the film to H<sub>2</sub> should not be affected. In addition, the process of adding a Ni layer is



technologically simple, because a Ni target has been set at one of the three sputtering guns in the system.

Figs. 6.1 and 6.2 show the H-induced cyclic response of  $\langle \rho \rangle$  of two Sample Pd(5)/Ni(3)/MN(30) and Sample Pd(5)/Ni(6)/MN(30) measured at  $P_{H_2} = 4000$  Pa and 60°C. The numbers inside the blankets of the sample code represent the thicknesses of the respective layers in nanometers. From the figures, it is seen that the saturated values of  $\langle \rho \rangle$  after hydrogenation and H<sub>2</sub> detection sensitivities S (defined as the fractional change of  $\langle \rho \rangle$ ) of the two samples remain high up to 100<sup>th</sup> and 150<sup>th</sup> cycles respectively, but start to drop significantly beyond these two limits. Referring to Fig. 6.3 shows the results of a sample without a Ni interfacial layer for comparison. Its saturated  $\langle \rho \rangle$  and S are not stable but keep dropping from the beginning of the test, and become stabilized gradually beyond around 50<sup>th</sup> cycle. This result suggests that the insertion of a Ni interfacial layer helps to stabilize the S value at the initial stage of a cyclic test. The degree of stabilization can is enhanced by increasing the thickness of Ni interfacial layer.

In addition, the response time  $t_{90}$  (the time required for  $\langle \rho \rangle$  to increase to 90% of the successive saturated  $\langle \rho \rangle$  level of the hydrogenation state) show slight increase from 10 to 30 s for the two Ni-buffered samples. However, the recovery time  $t_{10}$  (the time required for  $\langle \rho \rangle$  to drop to 10% of the successive dehydrogenated  $\langle \rho \rangle$  value) increase from 40 to 110 s and 30 to 260s for Sample Pd(5)/Ni(3)/MN(30) and Pd(5)/Ni(6)/MN(30), respectively. In general,  $t_{10}$  increases with the thickness of Ni layer and  $t_{90}$  is insensitive to the thickness of the Ni layer. It is noted that the background level of  $\langle \rho \rangle$  corresponding to the metallic state does not drift for the cyclic tests performed on the Ni-buffered samples.





Fig. 6.1 H<sub>2</sub>-induced response of  $\langle \rho \rangle$ , detection sensitivity *S*, and response and recovery times ( $t_{90}$  and  $t_{10}$ ) of Sample Pd(5)/Ni(3)/MN(30) measured at 60°C and  $P_{H_2}$  = 4000 Pa. Insets: Details of selected cycles.





Fig. 6.2 H<sub>2</sub>-induced electrical response, sensitivity *S*, response and recovery times ( $t_{90}$  and  $t_{10}$ ) of the sample Pd(5)/Ni(6)/MN(30) measured at 60°C and  $P_{H_2}$  = 4000 Pa. Insets: Details of selected cycles.



Fig. 6.3 H<sub>2</sub>-induced resistive response, detection sensitivity S, and response and recovery times of Sample Pd(5)/MN(30)\_RT performed at  $60^{\circ}$ C.



Fig. 6.4 and 6.5 shows the rate of change of  $\langle \rho \rangle$  of the Sample Pd(5)/Ni(3)/MN(30) and Pd(5)/Ni(6)/MN(30) recorded after different numbers of switching cycles. In general, two peaks could be observed in a curve before the start of substantial drop of the saturated  $\langle \rho \rangle$  of the hydrogenated state (namely 100<sup>th</sup> cycle in Fig. 6.4 and 151<sup>th</sup> cycle in Fig. 6.5). This result implies that  $\beta$ -phase can be formed in this stage of the tests. Beyond this stage, only one peak is observed in a curve. It is therefore suggested that the film ceases to undergo  $\alpha$ -to- $\beta$  transition.

In addition, the position of the peak associated with the  $\alpha$ -to- $\beta$  transition for Sample Pd(5)/Ni(3)/MN(30) almost does not shift in the course of the switching process (Fig. 6.4), but that of Sample Pd(5)/Ni(6)/MN(30) continuously shifts towards the side of long time (Fig. 6.5) with increasing number of switching cycles. This is possibly because the addition of a thicker Ni interfacial layer would prolong the time of H diffusion to enter the alloy layer.



Fig. 6.4 A plot of the rate of change of  $<\rho>$  of Sample Pd(5)/Ni(3)/MN(30) measured at 60°C with  $P_{\rm H_2} = 4000$  Pa after different numbers of switching cycles.



Fig. 6.5 A plot of the rate of change of  $<\rho>$  of Sample Pd(5)/Ni(6)/MN(30) measured at 60°C with  $P_{\rm H_2} = 4000$  Pa after different numbers of switching cycles.

#### 6.2 Results of XPS analysis

Referring to Fig. 6.6 (a), at the as-deposited stage, Pd atoms are mainly located in a depth of 5 nm below the film surface. Ni concentration is high in the range of depth from 5 to 10 nm, and remains constant in deeper region. The concentration of Mg first increases with depth and stabilized at 10 nm. A representative Mg-to-Ni ratio is 1.7, which is detected at a certain depth from the surface, consistent with the sample Pd(5)/MN(30)\_RT without addition of a Ni layer. No oxide phase is found throughout the depth to the substrate.

Fig. 6.6 (b) shows that after 370 switching cycles, Pd atoms are still found to penetrate into the film. However, the amount is much less than that detected in Sample Pd(5)/MN(30)\_RT after the similar switching processes. Most Pd atoms the film sample investigated in the present study still remain at the surface region, implying that the Ni interfacial layer is very effective in blocking inter-diffusion between Pd and Mg atoms.

It is noted that even addition of the Ni layer can delay the occurrence of degradation of the H<sub>2</sub> detection sensitivity, Fig. 6.6 (b) illustrates that an Mg-O phase is eventually formed after 370 switching cycles. AFM images reflect that the cracking of the Pd cover layer is still observed. The film thickness is increased by 10 nm after the switching cycles, suggesting that mechanical deformation due to volume breathing effect is not avoidable, which eventually damages the H<sub>2</sub> sensing effect of the film.



Fig. 6.6 Depth profiles of elemental contents and chemical states of Sample Pd(5)MN(30)\_RT(a) at as-deposited state and (b) after 40 switching cycles.



The effects of adding a Ni interfacial layer between the Pd and Mg-Ni layer are summarized in the following. The presence of the Ni interfacial layer can obstruct inter-diffusion between Pd and Mg atoms. This helps to maintain a high saturated  $\langle \rho \rangle$  value of the hydrogenation state for more number of switching cycles. However, XPS results reflect that Pd atoms can still be able to diffuse deeply in the film. The main reason is that alloying between Pd and Ni atoms would also occur [Hughes R. C 1992, Ted B 1999], based on the fact that the heat of formation of Pd-Ni alloy is smaller than that of Pd-Mg alloy. At last, we suggest to search for new interfacial material, which should have a high diffusivity for H atoms, and small heat of formation when forming alloys with Pd, Mg and Ni.



### **Chapter 7**

#### Durability improvement by Fe doping in Mg-Ni layer

One of the major causes of the degradation of the H<sub>2</sub> sensing properties of a Pd/Mg-Ni film in a cyclic switching test is inter-diffusion between Pd and Mg atoms. It has been demonstrated that if a Ni interfacial layer is inserted between the Pd cover layer and the Mg-Ni layer, inter-diffusion between Pd and Mg can be obstructed to some extent. Degradation of H<sub>2</sub> sensing properties can be partly suppressed. However, further improvement may not be obtained by continuously increasing the thicker the Ni interfacial layer, because diffusion of H from in the Mg-Ni layer would be slowed down, such that the response time becomes longer. In this chapter, we report the results of another approach by doping iron (Fe) atoms (5.2%) into the Mg-Ni layer. It is expected that Mg-Fe bonds may be formed which could be stronger than the Pd-Mg bonds, such that with the formation of Mg-Fe bonds, inter-diffusion between Pd and Mg atoms could be suppressed. In other words, the structure of Pd coated Fe-doped Mg-Ni film (denoted as Pd/Mg-Ni:Fe) is more stable than the Pd-Mg alloy.

#### 7.1 H<sub>2</sub> sensing properties of Pd/Mg-Ni:Fe films

Fig. 7.1 shows the change of  $\langle \rho \rangle$  of Sample Pd(5)/MN:Fe(30) observed in a cyclic switching test performed at  $P_{\rm H_2}$  = 4000 Pa and 60°C. The saturated  $\langle \rho \rangle$  value of the film at hydrogenated state decreases from 1.6  $\mu\Omega$  m in the first 50 cycles and is stabilized at 1.2  $\mu\Omega$  m. The background level of  $\langle \rho \rangle$  of the metallic state remains almost unchanged.

The results are compared with that of Sample Pd(5)/MN(30)\_RT with the same thickness of Pd but without Fe doping. For Sample Pd(5)/MN:Fe(30), the initial *S* is smaller (262 %) compared with that of Pd(5)/MN(30)\_RT (427%); the response time of the 1<sup>st</sup> cycles  $t_{90}$  (10.8 s) is longer compared with that of Pd(5)/MN(30)\_RT (8.6 s); and the recovery time  $t_{10}$  (43.1 s) is approximately the same as that of the Pd(5)/MN(30)\_RT film (46.4 s). However, after 300 switching cycles, Sample Pd(5)/MN:Fe(30) has a sensitivity of (121%) which is higher than 64% of Sample Pd(5)/MN(30)\_RT; and  $t_{90}$  and  $t_{10}$  of Pd(5)/MN:Fe(30) films are 29.2 and 179 s, prominently shorter than 41.0 and 269 s of Sample Pd(5)/MN(30)\_RT. This result implies that Sample Pd(5)/MN:Fe(30) is still under the influence of inter-diffusion of Pd and Mg atoms.



Fig. 7.1 H<sub>2</sub>-induced cyclic electrical response, sensitivity S (percentage change in  $\langle \rho \rangle$ ) and hydrogenation and dehydrogenation times ( $t_{90}$  and  $t_{10}$ ) of Sample Pd(5)/MFN(30) measured at 60°C and  $P_{H_2}$  = 4000 Pa. Insets: Details of  $\langle \rho \rangle$  of selected cycles.



Fig. 4.14 H<sub>2</sub>-sensing response of  $<\rho>$ , response time and sensitivity S of Sample Pd(5)/MN(30)\_RT performed at 60°C.



Fig. 7.2 shows the rate of change of  $\langle \rho \rangle$  of Sample Pd(5)/MN:Fe(30) after different numbers of switching cycles. Two peaks are found in the curve of the 1<sup>st</sup> switching cycle, where the second peak should be associated with the  $\alpha$ -to- $\beta$ transition. The two peaks in a curve tend to merge as switching processes proceed. The peak heights drop concurrently. Compared with the results of Sample Pd(5)/MN(30)\_RT (without Fe doping) as shown in Fig. 5.7, the second peak associated with the  $\alpha$ -to- $\beta$  transition is still observed even at the 301<sup>th</sup> cycle, but that of Sample Pd(5)/MN(30)\_RT 7.2 diminishes. This indicates that Fe doping could maintain the ability of the film to perform  $\alpha$ -to- $\beta$  transition even after a larger number of switching circles, so as to give a better durability when used as a H<sub>2</sub> sensor.



Fig. 7.2 A plot of rate of change of  $<\rho>$  of Sample Pd(5)/MN:Fe(30) measured at 60°C with  $P_{\rm H_2} = 4000$  Pa with different number of switching cycles.

#### 7.2 AFM analysis of a Pd/MN:Fe Sample

AFM images show that the film surface is roughened markedly after 360 switching cycles (Fig. 7.3 (a) and (b)), and the root mean square roughness is increased from 2.75 to 3.64 nm. The image taken after the test shows that some clusters are formed on the film surface.



Fig. 7.3 AFM images of Sample Pd(5)/MN:Fe(30) captioned (a) at as-deposited stage and (b) after 360 switching cycles performed with  $C_{\rm H_2}$  = 40000 ppm for hydrogenation.

#### 7.3 Results of XPS analysis

Referring to depth profiles of the elements of Sample Pd(5)/MN:Fe(30) shown in Fig. 7.4 (a), the concentration of Pd is 27 % at the surface and drops to zero at a depth of 5 nm below the film surface. After cyclic test (Fig. 7.4 (b)), the concentration of Pd at the surface still remains high, namely at a level of 25 %. Compared with the result of Sample Pd(5)/MN(30)\_RT as shown in Fig. 3.6, without Fe doping, Pd atoms can diffuse deeply into the alloy layer.

In addition, though an Mg-O phase is found in the interior of Sample Pd(5)/MN:Fe(30), a rather substantial amount of Mg atoms are found to remain in the metallic alloy phase, which are effective in contributing to the H<sub>2</sub>-induced switching of the film properties. On the contrary, after the same number of switching cycles, all the Mg atoms in Sample Pd(5)/MN(30)\_RT with no Fe doping have reacted with oxygen and stay in the Mg-O phase. Therefore, the H<sub>2</sub>-induced switching of the film properties is greatly jeopardized.



Fig. 7.4 Depth profiles of elemental contents and chemical states of Sample Pd(5)/MN:Fe(30) (a) at as-deposited state and (b) after 40 switching cycles.



Fig. 3.6 Depth profiles of elemental contents and chemical states of Sample Pd(5)MN(30)\_25C\_0m (a) at as-deposited state and (b) after 40 switching cycles.

In conclusion, adding Fe to Mg-Ni film help to maintain the stability of the elemental composition and uniformity when the film undergoes cyclic switching by reacting with hydrogen and air alternatively.

Hence, the  $H_2$  detection sensitivity is kept higher after a certain number of switching cycles. Because less Mg-O phase is formed, the response time remains short in the switching processes.

#### **Chapter 8**

# $\rm H_2$ sensing properties of Pd/Mg-Ni films in humid environment and the effects adding SiO\_2 or SiN\_x protection layer

It is known that the  $H_2$  sensing properties of a sensor may be significantly affected by the presence of moisture. It is found that addition of a thin SiO<sub>2</sub> [David. H 2005, Tournier. G. 2005, Weh T 2000] and SiN<sub>x</sub> [Tao F 2002, Toshiharu M 2006, Santana G 2005] overcoat on the surface of a gas sensing element can enhance the selectivity of  $H_2$  sensing as the pores size of SiO<sub>2</sub> or SiN<sub>x</sub> is comparable to the size of a  $H_2$  molecule. According to literatures [Feng CD 1994], the selectivity enhancement became more pronounced when the pore size decreased. A SiO<sub>2</sub> or SiN<sub>x</sub> film can act as a filter to limit permeation of water molecules into the film structure.

This technique is still frequently used in recent research. [Katsuki A 1998, Wada K 1998, Feng CD 1994] In this chapter, we report the effects of adding a 3 nm  $SiO_2$  or  $SiN_x$  layer on the surface of a Pd/Mg-Ni film on resisting the influence from moisture.

#### 8.1 H<sub>2</sub> sensing properties of Pd/Mg-Ni films in humid environment

Fig. 8.1 shows the H-induced response of  $\langle \rho \rangle$  of Sample Pd(10)/MN(30) with the presence of moisture. The saturated  $\langle \rho \rangle$  at hydrogenation state drops continuously in the first 25 cycles. This feature is similar as that measured in dry environment (Fig. 5.5). The background level of  $\langle \rho \rangle$  of the metallic state drifts

gradually at the beginning, and accelerates after 50 cycles. This is possibly a result of recovery time of dehydrogenation  $t_{10}$  is prolonged with increasing number of switching cycle, such that the setting of the period for dehydrogenation in a cycle, i.e. 300 s, becomes too short of for the film to return to the metallic state.

Furthermore, Fig. 8.1 shows that the H<sub>2</sub> sensing sensitivity, S, drops from 532% to 31.7 % after 225 cycles, which deteriorates very much faster than that detected at a dry environment, i.e. relative humidity RH = 0%, where S remains at a high level of 89.4% after 400 switching cycles. In addition, the response and recovery times  $t_{90}$  and  $t_{10}$  are prolonged as switching processes proceed.  $t_{90}$  and  $t_{10}$  increase from 25 to 51 s and 38 to 257 s respectively after the test, similar to that observed in a dry environment (Fig. 5.5).



Fig. 8.1 H<sub>2</sub>-induced response of  $\langle \rho \rangle$ , detection sensitivity *S* and response/recovery times  $t_{90}$  and  $t_{10}$  of the sample Pd(10)/MN(30) measured at 60°C, *RH* = 80% and  $P_{H_2}$  = 4000 Pa for hydrogenation. Insets: Details of selected cycles.



Fig. 8.2 shows the rate of the change of  $\langle \rho \rangle$  of Sample Pd(10)/MN(30) measured in a humid environment. Initially, the second peak associated with the  $\alpha$ -to- $\beta$  transition is very strong, but it decays very fast as shown in the inset of the figure. Compared with Fig. 7 for the same sample investigated in a dry environment, this peak seem to diminish much faster when measured in a humid environment, indicating that moisture could react with Mg atoms to weaken  $\alpha$ -to- $\beta$  transition of the alloy phase.



Fig. 8.2 A plot of the changing rate of  $<\rho>$  of Sample Pd(10)/MN(30) measured at 60°C, RH = 80% and  $P_{H_2} = 4000$  Pa after different numbers of switching cycles.
#### 8.2 AFM analysis

AFM images of Sample Pd(10)/MN(30) taken before and after the cyclic test are shown in Fig. 8.3 (a) - (b). The film surface is roughened markedly after 360 switching cycles, and the root mean square roughness is increased. The images show that clusters are formed on the films surface by cyclic switching processes.



Fig. 8.3 AFM images of Sample Pd(10)/MN(30) in an area of (a) 10x10  $\mu$ m<sup>2</sup>; and (b)-(c) 2x2  $\mu$ m<sup>2</sup> captured after 320 cycles at *RH* = 80% and *P*<sub>H2</sub> = 40000 ppm.

# 8.3 H<sub>2</sub> sensing properties of Pd/SiO<sub>2</sub>/Pd/Mg-Ni films in dry and humid environment

To protect the Pd/Mg-Ni films from the influence of moisture,  $SiO_2$  or  $SiN_x$  are added in the preparation of film samples. A film is made to have four layers. A  $SiO_2$ or  $SiN_x$  layer is added on the top surface of a Pd/Mg-Ni film. Finally, an additional Pd layer is added on top of the  $SiO_2$  or  $SiN_x$  layer for activating dissociation of H<sub>2</sub> molecules (otherwise the detection sensitivity would be small as  $SiO_2$  or  $SiN_x$  layer cannot dissociate H<sub>2</sub> molecules).

For Sample Pd(10)/MN(30) without a dielectric layer, the detection sensitivity *S* decreases from 457 to 89% in a dry environment after 200 cycles. In a humid environment, S decreases more prominently, namely from 532 to 32%. This result strongly proves that moisture can damage the H<sub>2</sub> sensing properties of a Mg-Ni film. For Sample Pd(5)/SiO<sub>2</sub>(3)/Pd(5)/MN(30) having a dielectric layer, *S* decreases from 195 to 95% in a dry environment after 320 cycles (Fig. 8.4 (a)). In a humid environment, *S* decreases from 248 to 61% (Fig. 8.4 (b)), which is much less severe compared with the case with no dielectric layer, showing the effectiveness of the dielectric in protecting the Mg-Ni layer from the influence of moisture.

In addition, it is noted that the value of  $t_{90}$  and  $t_{10}$  of the 1<sup>st</sup> cycle measured in dry environment are 10 and 93 s, which are close to those of Pd(10)/MN(30) without a dielectric layer in dry environment, namely 14 and 86 s. This implies that the addition of a Pd/SiO<sub>2</sub> bi-layer does not generate any delay on response and recovery time.



Fig. 8.4 H<sub>2</sub>-induced electrical response, sensitivity *S*, response and recovery times ( $t_{90}$  and  $t_{10}$ ) of Sample Pd(5)/SiO<sub>2</sub>(3)/Pd(5)/MN(30) measured at (a) *RH* = 0% and (b) *RH* = 80%, and *T* = 60°C by using  $P_{\rm H_2}$  = 4000 Pa in hydrogenation processes. Insets: Details of selected cycles.



Fig. 8.5 (a) and (b) show the rate of change of  $\langle \rho \rangle$  of Sample Pd(5)/SiO<sub>2</sub>(3)/Pd(5)/MN(30) measured in dry and humid environments. It is noticed that the second peak related to  $\alpha$ -to- $\beta$  transition still observable in a humid environment. Since  $\alpha$ -to- $\beta$  transition gives larger changes in the physical properties of a Mg-Ni film, its presence means that the detection sensitivity is still strong in the presence of moisture, such that the addition of the dielectric layer is proved to be effective in protecting the Mg-Ni layer. On the contrary, for Sample Pd(10)/MN(30) without a dielectric layer, the peak related to  $\alpha$ -to- $\beta$  transition in the plot of the rate of  $\langle \rho \rangle$  disappears very fast with increasing number of switching cycles. Finally, we note that for the curves in Fig. 8.5 (a) and (b), the peak related to  $\alpha$ -to- $\beta$  transition shifts towards the longer time region and the magnitude decreases with increasing number of switching cycles, suggesting that further improvement is still needed even a dielectric layer is added.



Fig. 8.5 Changing rate of  $<\rho>$  of Sample Pd(5)/SiO<sub>2</sub>(3)/Pd(5)/MN(30) measured at (a) RH = 0% and (b) RH = 80% with T = 60°C and  $P_{H_2} = 4000$  Pa with different numbers of switching cycles.

# 8.4 $H_2$ sensing properties of Pd/SiN<sub>x</sub>/Pd/Mg-Ni films in dry and humid environment

Fig. 8.6 (a) and (b) show the H<sub>2</sub>-induced change of  $\langle \rho \rangle$  of Sample Pd(5)/SiN<sub>x</sub>(3)/Pd(5)/MN(30) in dry and humid environments.

In a dry environment, the detection sensitivity *S* of the sample decreases from 324 to 83% after 320 switching cycles. This behavior is close to that of Sample Pd(10)/MN(30) without a dielectric layer. In a humid environment (Fig. 8.6 (b)), after 320 cycles, Sample Pd(5)/SiN<sub>x</sub>(3)/Pd(5)/MN(30) can keep a larger value of S of 69%, which is larger than that of Sample Pd(10)/MN(30) and Sample Pd(5)/SiO<sub>2</sub>(3)/Pd(5)/MN(30) of a value of S of 61%.

Consider the response rate. The value of  $t_{90}$  of the 1<sup>st</sup> cycle of Sample Pd(5)/SiN<sub>x</sub>(3)/Pd(5)/MN(30) as shown in Fig. 8.6 (a) is 30 s, which is double of 14 s that of Pd(10)/MN(30) as shown in Fig. 5.5. This implies that the addition a Pd/SiN<sub>x</sub> bi-layer to Mg-Ni causes some delay of H<sub>2</sub>-induced response. However,  $t_{90}$  of Pd(5)/SiN<sub>x</sub>(3)/Pd(5)/MN(30) is found to reduce from 30 to 18 s after 320 cycles, indicating that the delay on H<sub>2</sub>-induced response can diminish after several numbers of switching cycles.

Consider the recovery rate. The initial value of  $t_{10}$  of Sample Pd(5)/SiN<sub>x</sub>(3)/Pd(5)/MN(30) is 90 s, which is comparable with 86.3 s of Sample Pd(10)/MN(30). After 320 switching cycles, the value of  $t_{10}$  of Sample Pd(5)/SiN<sub>x</sub>(3)/Pd(5)/MN(30) keeps relatively short, i.e. 142 s, which is smaller than that of Sample Pd(5)/SiO<sub>2</sub>(3)/Pd(5)/MN(30).



Fig. 8.6 H<sub>2</sub>-induced  $\langle \rho \rangle$  response, detection sensitivity *S*, response and recovery times  $(t_{90} \text{ and } t_{10})$  of Sample Pd(5)/SiN<sub>x</sub>(3)/Pd(5)/MN(30) measured at (a) *RH* = 0% and (b) *RH* = 80% at *T* = 60°C and by using  $P_{\text{H}_2}$  = 4000 Pa for hydrogenation. Insets: Details of selected cycles.



The changing rate of  $\langle \rho \rangle$  of Sample Pd(5)/SiN<sub>x</sub>(3)/Pd(5)/MN(30) measured in dry and wet environment are shown in Fig. 8.7 (a) and (b). Similar to the sample Pd(5)/SiO<sub>2</sub>(3)/Pd(5)/MN(30), the second peak associated with the  $\alpha$ -to- $\beta$  transition shifts towards the longer time period, and the magnitude drops with increasing number of switching cycles in the dry and humid measurement conditions. The magnitude of this peak is in general larger than that of Sample Pd(5)/SiO<sub>2</sub>(3)/Pd(5)/MN(30) in dry and wet environment compared after the same number of switching cycles, indicating that the use of SiN<sub>x</sub> layer gives a better result in resisting the influence of moisture.



Fig. 8.7 Sample Pd(5)/SiN(3)/Pd(5)/MN(30) measured at (a) RH = 0% and (b) RH = 80% with T = 60°C and  $P_{H_2} = 4000$  Pa for hydrogenation after different numbers of switching cycles.

In this chapter, we reported the results of degradation of Pd/Mg-Ni films under the influence of moisture. It is found that moisture accelerates oxidation of the Mg-Ni layer in a cyclic test. Degradation of the H<sub>2</sub> sensing properties of a Pd/Mg-Ni film can be alleviated by adding a Pd/SiO<sub>2</sub> or a Pd/SiN<sub>x</sub> bi-layer on top. Results show that both methods can make the detection sensitivity *S* to drop with a slower rate and to maintain fast response.

### **Chapter 9**

### Conclusions

In this study, the resistive and optical H-sensing responses of an amorphous Pd/Mg-Ni film in a quasi-static process performing at 60°C exhibit three well defined stages. At low hydrogen content, the film is first in an amorphous  $\alpha$ -phase where hydrogen atoms are incorporated "interstitially" in the atomic network. Increase in hydrogen content initiates a transition to an amorphous  $\beta$ -phase where the volume of the alloy layer expands drastically in the direction perpendicular to the substrate surface. Finally, the film remains in the amorphous  $\beta$ -phase, with all the hydrogen atoms added afterwards to be located interstitially in the atomic network. This is only accompanied with a minor expansion in the volume. The rise of the effective electrical resistivity  $<\rho>$  and optical transmittance  $\Pi$  are most significant and fast in the second stage.

Results of the cyclic response of  $\langle \rho \rangle$  and  $\Pi$  and structural analysis indicate that repeated exposures to hydrogen and air cause volume breathing of the Mg-Ni layer, which results in successively cracking and slackening of the Pd and Mg-Ni layer. At the same time, Mg atoms tend to migrate towards the film surface, and oxygen atoms invade readily to the alloy layer and react with Mg atoms to form an oxide phase. This is accompanied with the depletion of Mg atoms in the alloy phase. All these features lead to a drop of the H-sensing response.

A model based on physisorption, chemisorption,  $\alpha$ -and  $\beta$ -formation was developed to investigate the hydridation effect of Pd/Mg-Ni film. Based on this model, the trends of quasi-isothermal and dynamic hydridation process are reproduced and match with experimental results. The model reflects that the sensitivity of the H-induced response would be increased by lowering operation temperature.  $\alpha$ -to- $\beta$  transition is occurs more readily at *T* below 60°C, giving larger response of  $\langle \rho \rangle$  and  $\Pi$ . However, the rate of  $\alpha$ -to- $\beta$  transition decreases more significantly at low temperature (e.g. below 60°C). Therefore, there exists an optimum *T* at which the magnitude of detection of sensitivity and response time reach the best compromise. Result also shows that with increasing number of cycles, the entropy  $\Delta S$  and activation energy  $E_{\beta a}$  are changed, such that the concentration of the Mg-Ni metallic alloy phase  $[M]_{o}$ , and hence the molar concentration of the  $\beta$ -phase  $[M]_{\beta}$  are also changed. All the changes lead to the reduction of sensitivity of  $\langle \rho \rangle$  and  $\Pi$  decreases.

Different approaches are tried to improve the durability of a Pd/Mg-Ni H<sub>2</sub> film sensor. The first is to limit the film to work within the  $\alpha$ -phase. This can be realized by operating the film at a low H<sub>2</sub> partial pressure. This method gives the film H<sub>2</sub> sensor to have a nearly linear response, fast response rate and high durability. We claim that his sensor is of practical use. For a Pd/Mg-Ni H<sub>2</sub> film sensor involving  $\beta$ -phase formation, a higher sensitivity is obtained, but the detection sensitivity would degrade with increasing number of switching cycles. In another approach, the thickness of Pd was adjusted to have an optimum value, such that cracking of the Pd layer can be diminshed. The H<sub>2</sub> sensing properties seem to be more durable in a cyclic test. In some applications, a H<sub>2</sub> sensor is required to display H<sub>2</sub> concentration

precisely and reproducibly. The first approach is better for this situation. For the use of H<sub>2</sub> leakage monitoring, the second approach is more preferred.

To suppress inter-diffusion between Pd and Mg atoms, Ni interfacial layer is inserted in between Pd and Mg-Ni layer. The consequences of adding Ni interfacial layer in Pd/Mg-Ni film can be concluded in the following. We first consider a Pd/Mg-Ni film with no Ni interfacial layer. Pd atoms start diffuse into the film at the beginning of a test. Mixing and interaction between Pd and Mg atoms are basically completed after 50 cycles. In the 1<sup>st</sup> cycle,  $\beta$ -phase can be formed to give a great detection sensitivity (several hundred percentage change). As switching process proceeds, elemental segregation occurs. The entropy  $\Delta S$  of associated with the  $\alpha$ -to- $\beta$ transition increases, and hence the equilibrium constant  $K_{\beta}$  decreases. As a result, the formation of the  $\beta$ -phase is suppressed and the formation of the  $\alpha$ -phase is favoured. A study on Sample Pd(5)/MN:Pd(30) shows that if Pd atoms are doped into the Mg-Ni layer, only  $\alpha$ -phase can be formed and  $\langle \rho \rangle$  in that phase is much smaller than that of the  $\beta$ -phase. If Ni interfacial layer is added, inter-diffusion of Pd and Mg is blocked. Therefore, a large upper bound and S can be lasted for more number of switching cycles. XPS results show that Pd atoms can diffuse deeply into the Mg-Ni layer, implying that the Ni layer cannot completely block Pd diffusion. The main reason should be due to tendency of alloying between Pd and Ni atoms. Since the heat of formation of Pd-Ni alloy is smaller than that of Pd-Mg, the diffusion tendency of Pd into the film interior is smaller if a Ni layer is inserted. Therefore, we suggest the criteria for choosing the element of interfacial layer as following: 1. The element should have a relatively high diffusivity for H atoms; 2. The element should have a small heat of formation of alloying when reacting with Pd, Mg and Ni.

We also tried to suppress the inter-diffusion of Pd and Mg by doping Fe atoms into the Mg-Ni layer. The presence of Fe atoms hinders the elements to segregate in a cyclic test. Therefore, the sensitivity can be kept at a higher value. Oxidation of Mg is less significant, and the response time remains fast.

Finally, we investigated the degradation of Pd/Mg-Ni films under the influence of moisture. It is found that water vapour accelerates oxidation of Mg atoms during the switching cycles. The change in  $\langle \rho \rangle$  and the changing rate of  $\langle \rho \rangle$  indicate that the H<sub>2</sub> sensing response of such a film can degrade as if a Pd/Mg-Ni film with a thinner Pd cover layer. The degradation by moisture can partly be alleviated by adding a Pd/SiO<sub>2</sub> or Pd/SiN<sub>x</sub> bi-layer on top. Results show that both methods can keep the film to have a higher sensing response *S* and a faster response rate. The possible reason for this improvement is that dielectric layer can filter away moisture but allow H<sub>2</sub> molecules to pass through.



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