Activation Energies of Hydrogen Absorption and Desorption in Pd Thin Films for the α phase

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팔라디움박막의 α 상영역 수소 활성화에너지

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Abstract

4-probe resistivity measurement technique was used to study hydrogen A-D(Absorption-Desorption)kinetics on Pd films(18 to 67nm thick) from 25 to 50℃, from 0 to 5 torr hydrogen pressure. Pd films were made on sapphire substrate by thermal evaporation technique under high vacuum at room temperature. Upto about 100 hydrogen A-D cyclings, no pulverization was observed, but film was detached partially from substrate. Forward reaction and backward reaction rate were analyzed separately. The activation energies of hydrogen A-D processes were obtained from the Arrhenius plot of the reaction rates. The activation energies of Pd films are not strongly dependent on the thickness of the film. But the activation energy of very thin film(18nm thick) was smaller than the others'.

조영신

초 록

팔라디움 박막시료들(두께 18 ~ 67nm)에 대한 수소 흡수-방출 동역학을 4-극 전기비저항 측정법을 이용하여 연구하였다. 실험온도와 수소압력은 25 ~ 50℃, 0 ~ 5 torr 범위였다. 팔라디움 박막은 고진공내에서 열증착 방법으로 사파이어 기판 위에 제작하였다. 수소 흡수-방출과정을 약 100회 반복할 때 까지 시료들의 분말화 현상은 관찰되지 않았으나 박막의 일부가 기판으로부터 분리되는 현상이 관찰되었다. 정방향 반응과 역방향 반응을 분리하여 분석하였다. 반응율에 대한 Arrhenius 그림에서 수소 흡수 방출 활성화 에너지를 얻었다. 팔라디움 박막의 활성화 에너지값들은 박막의 두께 변화에 강하게 의존하지 않았다. 그러나 매우 얇은 박막(두께18nm)의 활성화 에너지값은 다른 박막의 활성화 에너지 값들보다 작은 경향을 보였다.

1. INTRODUCTION

Most of bulk material of hydrogen absorption metal pulverize after several hydrogen absorption and desorption process(A-Dprocess). Hydrogen absorption kinetics changes due to the pulverizaton, which changes physical properties of samples, i.e. surface area of particle and contact area between particles. But it is not easy to see pulverization in thin film metal-hydrogen system[1]. We can observe size effect in hydrogen absorption kinetics due to the difference of film thickness[2-4]. Pd film was made by thermal evaporation for hydrogen absorption kinetics experiments. Hydrogen gas was introduced to the sample and measure hydrogen concentration change in time by using resistivity measurement technique at the temperature range between 25 and 50℃. Activation energy of hydrogen absorption-desorption process in the α phase were calculated by analyzing kinetics data of the sample.

2. THEORY

Most of previous articles of hydrogen absorption kinetics research did not deal forward reaction and backward reaction separately. In this work we analyze two reactions separately.

Reaction rate is given as v = 1/A dn_H/dt, where A is the surface area, n_H the number of moles of hydrogen, and t the time. The rate of the hydrogenation is given by the difference of the rates of the forward and backward reaction. The forward reaction rate is a function of the hydrogen pressure and of the hydrogen concentration, the backward reaction rate is only a function of the hydrogen

concentration[5].

$$v = \overrightarrow{v}(P_{H2}, X_H) - \overleftarrow{v}(X_H) \qquad (1)$$

In the hydrogenation the forward and the backward reaction occur simultaneously. In the dehydrogenation the hydrogen pressure is virtually zero and only the backward reaction occurs. Thus we can calculate the forward reaction contribution in the hydrogenation by using equation (1). In the α phase of Pd, the forward reaction and backward reaction rates are given as follows;

$$\overrightarrow{v} = k\,P_{H2}\,\frac{1}{1 + KX_H} \qquad (2)$$

$$\overleftarrow{v} = k'\,\frac{KX_H^2}{1 + KX_H} \qquad (3)$$

where X_H is the hydrogen concentration, P_{H2} the hydrogen pressure, k and k' the rate constants, and K the equilibrium constant for the adsorption equilibrium.

3. EXPERIMENTS

Pd films(1mm × 10mm) were evaporated thermally on the sapphire substrate in high vacuum (pressure= 1~20 ×

10^{-7}torr). The substrates were heated 300~350℃ for good adhesion of film to substrate. The evaporation rate is about 1 Å／sec and the distance between the substrate and Pd source(purity = 99.99%) is about 20 cm. The thickness of the sample was monitored by quartz crystal thickness monitor. Ultrasonic wedge bonder was used to make connection lead (25 μ m diameter Al wire) for resistivity measurement. Sample length for resistivity measurement is about 6mm long. Pd wire(0.127mm diameter, 88mm long) was prepared to see bulk properties.

Hydrogen gas (purity = 99.999%) was used for hydrogenation of the sample. The pressure was measured by pressure transducer (WIKA Model 1290). The 4-probe resistivity was measured by using DMM(Keithley Model 196) and temperature is measured by using PT-100 via DMM(Keithley Model 195A). All of the above data were collected by PC(IBM AT) via HP-IB interface card (HP Model 82335).

Films were hydrogenated upto 2 torr hydrogen pressure and dehydrogenated at 30℃ for activation. This process was repeated several times(18nm sample: 13 times, 31nm sample: 47 times, 67nm sample: 91 times) until the resistivity of the sample reaches the equilibrium value. The wire sample was charged and discharged hydrogen by electrolysis in

H$_2$SO$_4$ with 1~200mA, 3~60 minute 61 times for activation. The resistivity of sample were decreased about 1~2% during activation process. The sample was hydrogenated upto 5 torr hydrogen pressure and dehydrogenated to measure hydrogen absorption-desorption kinetics in the temperature range between 25 and 50℃ in the α phase.

4. RESULTS AND DISCUSSION

The change of the resistivity of the Pd sample is linear to the change of the hydrogen concentration in the α phase. Thus hydrogen concentration of the sample can be obtained by measuring the resistivity of the film. Hydrogen concentration $X_H \propto \triangle R/R_0$, where R_0 is initial resistance, $\triangle R$ is $R - R_0$, R is resistance of the sample during hydrogenation[6]. The rate of reaction v was calculated from hydrogen concentration vs. time plot. Fig. 1 shows typical hydrogen concentration vs. time plot. Fig. 2 shows reaction rate vs. time plot (data were obtained from Fig. 1).

To separate forward reaction part $\overrightarrow{v}$ during absorption process Eq. (1) was used. To get v_0 value, which is v value when $X_H = 0$, equation (2) was rewritten as
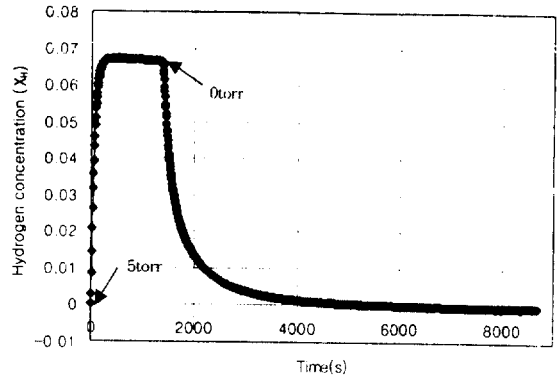

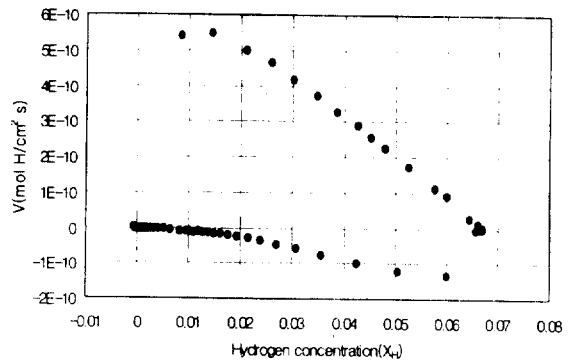Figure 1. Hydrogen concentraton vs. time plot of Pd film(67nm thick) at 35℃

Figure 2. Reaction rate vs. hydrogen concentration plot of Pd film(67nm thick) at 35℃

$$\frac{1}{\vec{v}} = \frac{K}{k\ P_{H2}}\ X_H + \frac{1}{k\ P_{H2}} \qquad (2)'$$

v_0 was determined by extrapolating curve in the $1/v$ vs. X_H plot. And initial forward reaction rate was given by $v_0 = k\ P_{H2}$. The slope of the best fitted line in v_0 vs. P_{H2} plot gives the k value. Plot of $\ln k$ vs. $1/T$ gives the activation energy of the forward reaction. Fig. 3 shows the activation energy vs. thickness of the sample.

Equation (3) was rewritten for the analysis of backward reaction as follows;

$$\frac{X_H}{\overset{\leftarrow}{v}} = \frac{1}{k'K}\ \frac{1}{X_H} + \frac{1}{k'} \qquad (3)'$$

k' was determined by extrapolating the line in the X_H/v vs. $1/X_H$ plot. The Arrhenius plot gives the activation energy of the backward reaction. The activation energy of the samples can be seen Fig. 4.

When we compare Fig. 3 and Fig. 4, the values of activation energy of backward reaction are larger than that of forward reaction. This property is very similar to the bulk's[5]. This can be seen directly from Fig. 1, i.e. absorption process is much faster than desorption process. Activation energies of Pd films are not strongly dependent on the thickness of the film. But activation

energy of very thin film(18nm thick) is rather smaller than the others'. Error in the activation energy of film is rather large. This might be due to geometry change or surface condition change during A-D process. In contrary to these results the thickness dependence of the pressure-resistivity change $(P-\Delta R/R_0)$ relation was observed[6,7]. More experiments will be needed for better understanding of this mechanism.
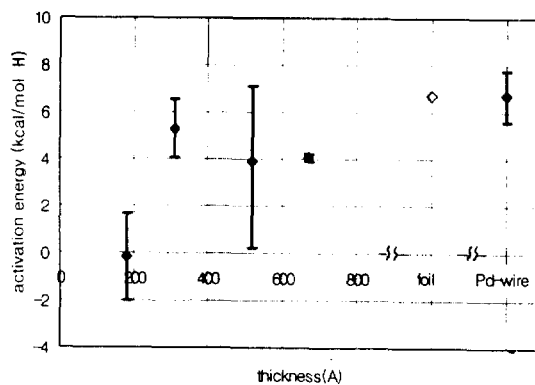

Figure 3. Activation energy of forward reaction vs. thickness of Pd film at $25\sim50\,℃$. ◆ is present work and ◇ is Auer and Grabke's work.
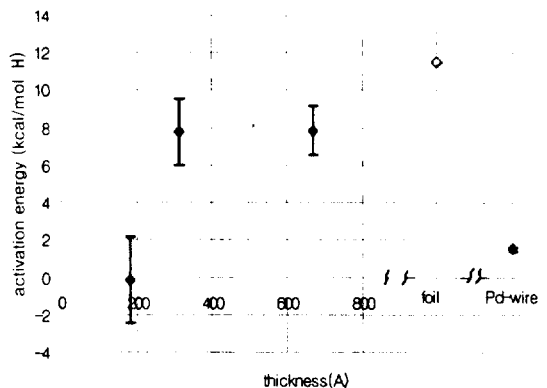
Figure 4. Activation energy of backward reaction vs. thickness of Pd film at $25\sim50℃$. ◆ is present work and ◇ is Auer and Grabke's work.

5. CONCLUSION

4-probe resistivity measurement technique was used to study hydrogen A-D kinetics on Pd films(18 to 67nm thick) from 25 to 50℃, from 0 to 5 torr hydrogen pressure. Forward reaction and backward reaction rate were analyzed separately. The values of activation energy of backward reaction were larger than that of forward reaction. But the activation energies of Pd films were not strongly dependent on the thickness of the film.

ACKNOWLEDGEMENTS

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