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Microfabricated Pd and Pd–25Ag alloy membranes

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Abstract

Defect-free Pd membrane with the thickness of 2.5 μm and Pd–25Ag alloy membranes with the thickness of 1.2 and 3 μm were successfully prepared on 50 μm thick Ni layer with channel structure by micro-electro-mechanical systems (MEMS) technology. Hydrogen permeation experiment was performed in a conventional gas permeation apparatus within the temperature range of 473–673 K using high purity hydrogen. Hydrogen permeance of the 2.5 μm thick Pd membrane increased by 2.9–4.1 times after the annealing at 673 K owing to the enhanced surface reaction. However, the 1.2 and 3 μm thick Pd–25Ag alloy membrane had lower hydrogen permeance than the 2.5 μm thick Pd membrane because the surface reaction was rate limiting. The surface morphology of the Pd and Pd–25Ag alloy membranes were examined by scanning electron microscope (SEM) before and after the hydrogen permeation.

Keywords: Palladium; Palladium–silver alloy; Hydrogen permeation

1. Introduction

Palladium alloy membranes are important for hydrogen-separation applications because of high hydrogen permeability and excellent catalytic ability on atomic splitting and recombination of hydrogen molecular [1]. It is necessary to understand hydrogen permeation of Pd alloy membrane with the thickness of down to several μm for practical applications. There are numerous reports in the literature focused on the preparation of the thin Pd alloy membranes [2,3]. The thin Pd alloy membranes are usually supported by porous materials including ceramic and stainless steels [1–3]. The porous supports have high resistance to external hydrogen mass transfer so that it is difficult to know intrinsic hydrogen permeation behavior of the thin Pd alloy membranes [4], which is important not only for us to understand hydrogen permeation in metals but also for the development of low-cost composite membranes with high permeability [5–7].

Recently, micro-electro-mechanical system (MEMS) technology has been used for the preparation of thin Pd alloy membranes on silicon material with channel and microsieve structure [8,9]. The thin Pd alloy membranes prepared by the MEMS technology, i.e. the microfabricated membranes have much higher permeance than those supported by the porous materials because there is less resistance to hydrogen mass transfer. Hydrogen permeation of the microfabricated Pd alloy membranes has been examined in small packaged devices. The literature results, however, do not fit each other well because the mass transfer is significantly influenced by the structure of the small package devices [10].

In this work, nickel metal instead of silicon would be utilized as the mechanical support because it has excellent mechanical properties and much lower permeability than Pd alloys [11]. More importantly, it is possible to seal the Ni-supported membranes using metallic gaskets in conventional gas permeation apparatus. Therefore, the MEMS technology may make it possible for us to investigate the hydrogen permeation of thin Pd alloy membranes free from the significant external mass transfer resistance.

2. Experimental

Fig. 1 shows the MEMS-based fabrication route in details. We prepared the 2.5 μm thick Pd membrane, 1.2 and 3 μm thick Pd–25Ag alloy membrane on 4 in. Si wafer using multi-target sputtering at room temperature, the Ar

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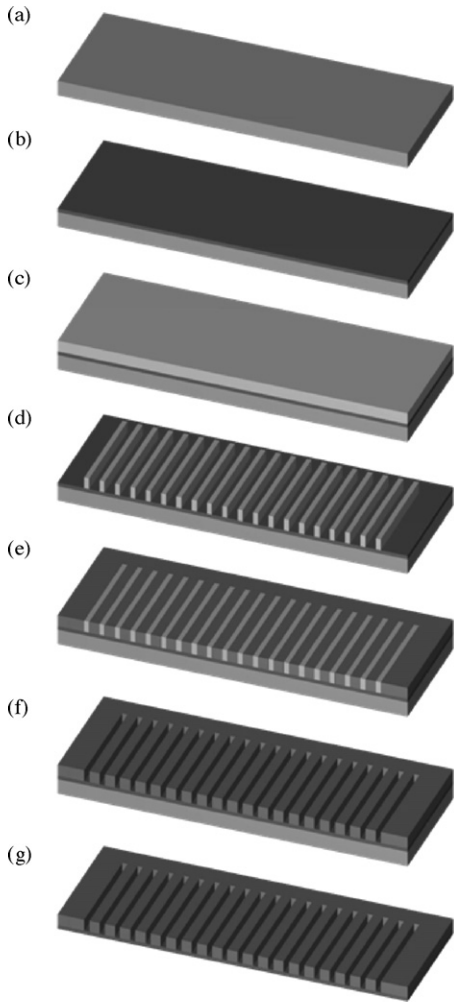

Fig. 1. Schematic sequence of MEMS fabrication: (a) Si wafer, (b) preparation of Pd alloy membranes by sputtering, (c) preparation of 60 μm thick negative resist layer by spin-coating, (d) patterning of the negative resist, (e) preparation of 50 μm thick Ni layer by electroplating, (f) remove the negative resist, and (g) remove the Si wafer in KOH solution.

pressure of 0.2 Pa and the gas flow rate of 25 sccm (Fig. 1(a) and (b)). Pure Pd (99.99%) and Ag (99.99%) target were used. 65 μm thick negative resist (XP-KMPR 1050, KAYAKU MICROCHEM) was spin-coated and patterned (Fig. 1(c) and (d)). Then 50 μm thick Ni layer was prepared by electroplating (Fig. 1(e)). After the negative resist was removed (Fig. 1(f)), Si wafer was etched away in KOH solution (Fig. 1(g)). The as-prepared Pd and Pd–25Ag alloy membranes were then cleaned by electron cyclotron resonance (ECR) method in order to remove contaminations possibly formed during the MEMS procedure.

Hydrogen permeation experiment was carried out in a homemade gas permeation apparatus [12] within the temperature range of 473–673 K. After membrane sample was sealed using aluminum gaskets, the gas permeation apparatus was evacuated to 10^{-4} Pa and heated up to 473 K. The gas-tightness of the membrane sample was examined by the procedure as follows: 20 kPa air was introduced into the upstream side of the membrane sample while the downstream side was kept in vacuum by continuous pumping. If there were holes and other defects in the membrane sample, there would be gas flow through a mass flow transducer in the downstream side accompanying with decreasing upstream pressure. Once passed the gas-tightness examination, 100 kPa air was introduced for the baking treatment [13]. Some membrane samples were annealed at 673 K for 30 min before the gas-tightness examination.

The as-prepared membrane samples were examined by X-ray diffraction (XRD) and scanning electron microscope (SEM).

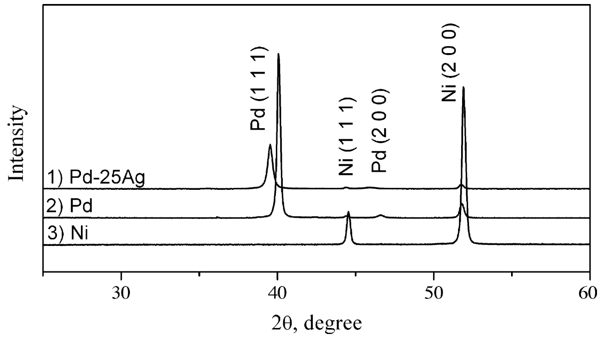

Fig. 2. XRD patterns of the Ni support layer, Pd and Pd–25Ag membranes.

3. Results and discussion

Fig. 2 is the XRD patterns of the Ni support, Pd and Pd–25Ag alloy membranes. The electroplated Ni layer was polycrystalline. The Pd and Pd–25Ag alloy membranes were fcc palladium structure with the (1 1 1) orientation. There were no peaks corresponding to Ag. The peaks of the Pd–25Ag membrane shifted to lower angle because of the lattice enlargement with the addition of Ag element. The measured concentration of Ag element in the Pd–25Ag alloy membrane ranged from 20 to 23 at.%.

Fig. 3 is representative SEM images of the microfabricated Pd and Pd–25Ag alloy membranes before and after hydrogen permeation. There was no visible grain boundary in the Pd membrane before the hydrogen permeation. After the hydrogen permeation, there were grains with different sizes in the Pd membrane (see Fig. 3(b)). Small grains were surrounded by large grains. This was in keeping with literature results that the grain growth has occurred in thin Pd membrane upon hydrogen permeation [14,15]. There were no noticeable surface morphology changes for the Pd–25Ag alloy membrane (Fig. 3(c) and (d)). We attributed it to that the sputtered Pd–25Ag alloy membrane had finer grains and higher resistance to grain growth [15].

Fig. 4 illustrates the temperature dependency of the hydrogen permeance of the microfabricated Pd and Pd–25Ag alloy membranes. The hydrogen permeance of the microfabricated Pd membrane increased by 2.9–4.1 times after it was annealed at 673 K for 30 min. The hydrogen permeance of the 1.2 μm thick Pd–25Ag alloy membrane increased slightly with increasing upstream pressure. The hydrogen permeance of the 3 μm thick Pd–25Ag alloy membrane was only plotted at 673 K while other measurements at lower temperature and higher pressures were failed because of leakage. The 3 μm thick Pd–25Ag alloy membrane had lower hydrogen permeance than the 1.2 μm thick one at 673 K. In comparisons to the annealed 2.5 μm thick Pd membrane, both the 1.2 and 3 μm thick Pd–25Ag alloy membrane had lower hydrogen permeance. It was different from the consensus that Pd–25Ag metal has higher hydrogen permeance than Pd metal within similar thickness range [1].

In Fig. 5 we plot the pressure dependency of the hydrogen permeation flux through the microfabricated membranes. The relationship between the pressure and the gas permeation flux through solids could be described using the equation as follows

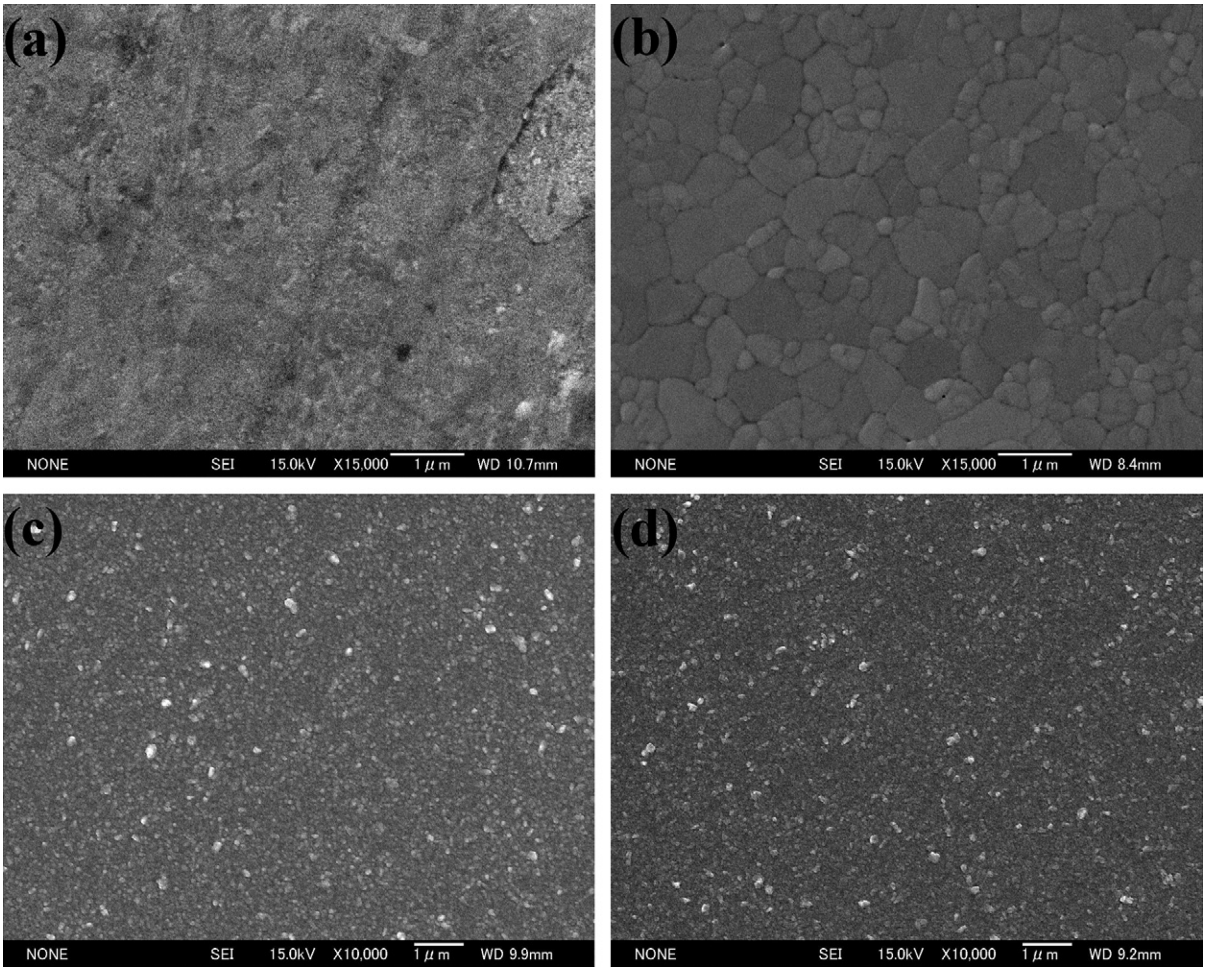

Fig. 3. SEM images of the microfabricated Pd membrane (a) before and (b) after the hydrogen permeation. SEM images of the microfabricated Pd–25Ag alloy membrane (c) before and (d) after the hydrogen permeation.

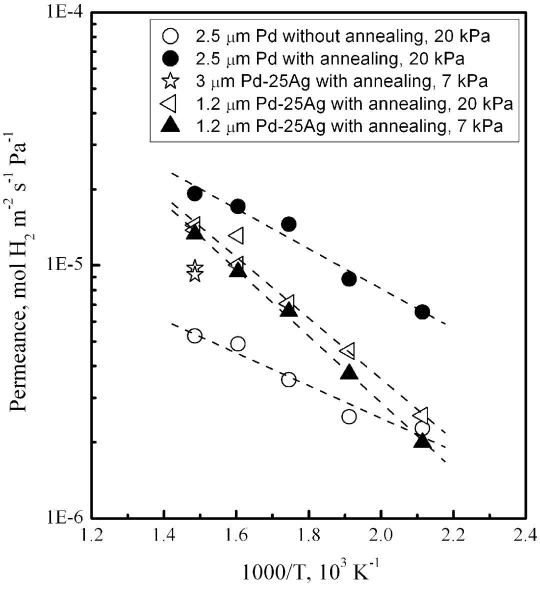

Fig. 4. Arrhenius plot of temperature dependency of hydrogen permeance of the microfabricated Pd and Pd–25Ag alloy membranes.

[16]:

$$J = \frac{\Phi \times (P_{\mathrm{u}}^{n} - P_{\mathrm{d}}^{n})}{L} \tag{1}$$

where J denote the permeation flux, Φ the hydrogen permeability, P the pressure, L the membrane thickness, and n is the pressure exponent. Fig. 5(a) shows that the pressure exponent of the 2.5 μm thick Pd membrane was 0.93 at initial state. The hydrogen permeation was mainly surface reaction limited. The pressure exponent decreased to 0.77 after the annealing treatment. The surface reaction was enhanced after the annealing. It indicated that the microfabricated Pd membrane had been effectively activated by the annealing and the following baking treatment.

Fig. 5(b) shows that the surface reaction was rate limiting for the hydrogen permeation of the microfabricated Pd–25Ag alloy membranes. It was thus understandable that they had lower permeance than the Pd membrane. The surface of the microfabricated Pd–25Ag alloy membrane was possibly in contaminated status even after the annealing and the baking treatment. There is little information on the surface state of microfabricated Pd alloy membranes in the literatures so that it was difficult for further discussion. The investigation on the hydrogen permeance ver-

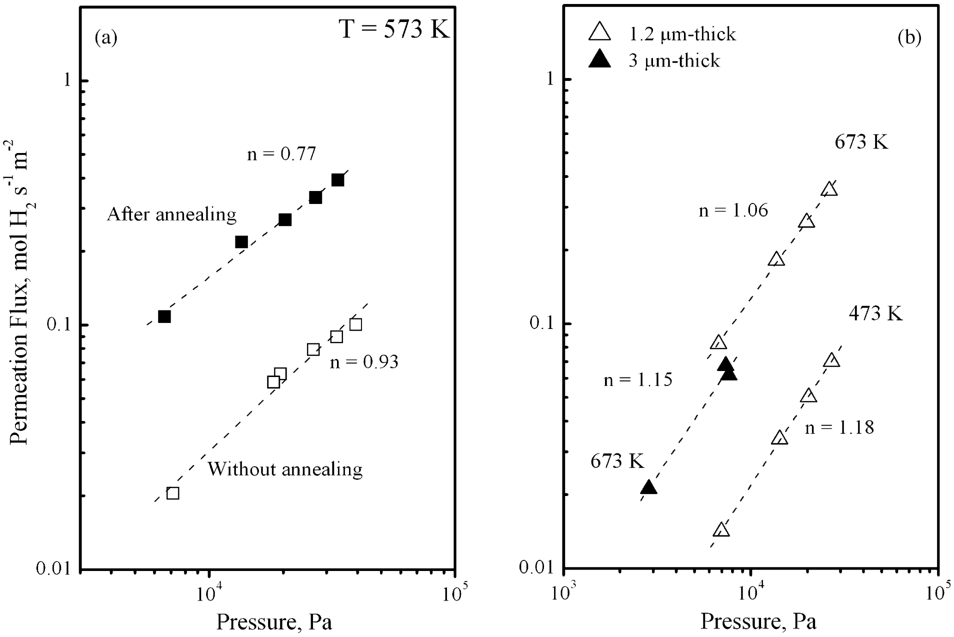

Fig. 5. (a) Pressure dependency of hydrogen permeation flux through the 2.5 μm thick Pd membranes at 573 K. (b) Pressure dependency of the hydrogen permeation flux through the 1.2 and 3 μm thick Pd–25Ag alloy membranes.

sus surface state is under way for the microfabricated palladium alloy membranes.

4. Conclusions

We successfully prepared the 2.5 μm thick Pd, 1.2 and 3 μm thick Pd–25Ag alloy membranes using MEMS technology. Their hydrogen permeation behavior was investigated using the gas permeation method within the temperature range of 473–673 K. The 2.5 μm thick Pd membrane showed similar permeation behavior to bulk Pd metal. The hydrogen permeance of the 1.2 and 3 μm thick Pd–25Ag alloy membranes was much lower than that of the 2.5 μm thick Pd membrane, suggesting that it was important to keep the membrane surface in clean state during the MEMS fabrication.

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