Preparation of palladium–silver alloy films by a dual-sputtering technique and its application in hydrogen separation membrane

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Abstract

Submicron thick palladium–silver alloy films with 23 wt.% of silver (Pd–Ag23) have been synthesized by simultaneous sputtering from pure targets of Pd and Ag. Full characterization of the deposited films was performed by using X-ray photoelectron spectroscopy, high-resolution scanning electron microscopy, high-resolution transmission electron microscopy, and X-ray diffraction. The analytical results revealed that the deposited Pd–Ag alloy had a Ag content of about 21–22 wt.%, very close to and within measurement error of the expected Ag content of 23 wt.%. The as-deposited Pd–Ag alloy had a fine microstructure. The characterized Pd–Ag alloy films were then deposited on a supporting microsieve to form Pd–Ag membranes for hydrogen separation. The submicron thick Pd–Ag membranes obtained high separation fluxes up to 4 mol H_2/m^2 s with a selectivity higher than 1500 for hydrogen over helium.
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1. Introduction

Pd-based membranes have been studied extensively in the last several decades [1–9], largely because of their unique properties with hydrogen. For example, Pd has very high hydrogen solubility, it absorbs 600 to 900 times its gaseous volume at room temperature, and its various alloys absorb comparable quantities [5]. This high solubility is coupled with its high diffusivity for hydrogen and chemical inertness with oxygen at elevated temperature [4], thus Pd has an unmatched potential as a hydrogen-selective membrane for separation or purification and in membrane reactors for hydrogenation/dehydrogenation reactions [1–9]. Today it is well known that hydrogen permeates with an infinite selectivity via a solution-diffusion mechanism through Pd and its alloys: it adsorbs on the top surface of the Pd surface, dissociates, diffuses through the bulk metal, and then recombines at the back surface to form hydrogen molecules [1–5].

The use of pure Pd membranes is, however, restricted because of a transition from the α-phase (hydrogen-poor) to the β-phase (hydrogen-rich) at temperatures below 300 °C and pressures below 2×10^6 Pa, which depends on the hydrogen concentration in the metal. Since the lattice constant of the β-phase is 3% larger than that of the α-phase this transition leads to lattice strain and, consequently, after a few cycles to a distortion of the metal lattice, i.e. embrittlement [3]. Alloying the Pd with group 1B metals, especially with silver (Ag), reduces the problem of embrittlement and leads to an increase of the hydrogen permeability. The increased resistance to embrittlement by face centered cubic lattice (f.c.c.) alloys is attributed to the low diffusivity and high solubility of hydrogen in these alloys compared to f.c.c. structured Pd [10]. Among its alloys, Pd–Ag23 at wt.% has been the most commonly used, as it possesses both high hydrogen

permeation and high resistance to hydrogen embrittlement [1,2].

Up to now many methods have been developed to deposit Pd or Pd alloy films on porous supports to form membranes, including physical vapor deposition, electroless plating, electrodeposition, chemical vapor deposition (CVD), micro-emulsion, pyrolysis, pore-plugging by liquid impregnation and sputtering [1–7]. Among the mentioned techniques, the most often used methods are electroless plating, CVD and sputtering. Under properly controlled conditions all three methods produce good quality thin Pd/Ag membranes, with hydrogen to nitrogen selectivity over 3000 at temperatures above 300 °C [11]. The two chemical methods (electroless plating and CVD) have the advantage of easy scale-up and the flexibility to coat the metal film on supports of different geometry. However, the main disadvantage is the difficulty to control the composition of the alloy [5,9]. Sputtering has several advantages like: (a) synthesis of ultrathin films with minimal impurity; (b) easily controllable process parameters; (c) flexibility for synthesizing alloys; and (d) the ability to generate nanostructured films [12–15]. The last two points are very important in membrane preparation for hydrogen separation because fabricating membrane alloys helps to overcome the problem of hydrogen embrittlement, while the nanostructured films may have unique size-dependent properties, e.g., a high hydrogen permeation [12,13].

Due to the mentioned advantages, sputtering has frequently been used to fabricate (sub) micron thick Pd–Ag alloy layers. Mostly, such layers are obtained by sputtering from a single alloy target of Pd–Ag. However, it was found that the sputtered layers have a significantly lower Ag content than the original target, due to a short target equilibration times [16,17]. For instance, Xomeritakis and Lin found a silver concentration of 15 wt.% for a film sputtered from a Pd–Ag25 wt.% target [17]. To avoid this compositional control problem, this paper focuses on the preparation of submicron thick Pd–Ag23 wt.% alloy films with a high compositional control, using a dual-sputtering technique. In addition, different techniques are used to characterize microstructures of the deposited Pd–Ag film. Finally, the well-characterized dual-sputtered Pd–Ag alloy film is deposited on microfabricated support structures to realize Pd–Ag membranes for hydrogen separation.

2. Dual-sputtering experiment

2.1. Experiment setup and sputtering conditions

Experiments have been carried out in a DC magnetron sputtering system (Balzers Cryo, 2 diameter targets) that accommodates three targets, of pure Pd, Ag and Ti (99.99%; Engelhard-Clal), each target having its own controllable power source. The sputter guns are arranged in a convergent manner, with the substrate rotating about its center with a speed of ca. 15–20 rpm. The metal films (Pd, Ag, or alloys) were sputtered onto 4 in., (100) silicon substrate with 500 nm of a wet-thermally grown SiO_2 film as an anti-diffusion layer, mounted a distance of 13 cm from the metallic targets. Before sputtering, the system was pumped down to a base pressure of 10^{-5} Pa.

The main object of this paper is the fabrication of a Pd–Ag alloy membrane, which is used for high temperature hydrogen separation. The deposited film therefore should be a film with accurate composition, high-density (non-porous), crack-free, and fine grain size. Although films with these properties may be realized by systematically varying the important experimental parameters like sputtering pressure, substrate temperature, and sputter rate etc., these procedures will consume a lot of time. To reduce the experimental procedure to realize the desired films, the well-known principle of the so-called 'Thornton model for sputtered films' [16,17] in combination with the work of Ying et al. for sputtered Pd membranes [10,11] were consulted in choosing sputtering pressure and sputtering temperature. For instance, Ying et al. reported that they obtained thin Pd films with a high-density, no cracks and fine grain size at an Ar sputtering pressure of ca. 0.1 and 7 Pa [12,13]. Their claim agrees with a sputtering pressure deduced from the Thornton model. The same authors [12,13] explained that at high sputtering pressures (10–100 Pa) the metal atoms collide with argon atoms and loose energy. This cooling leads to a high supersaturation of metal atoms, which can cause homogeneous nucleation to form nanocrystalline particles in the gas phase. As the gas pressure is lowered, thermalization decreases, and the thermal atoms are likely to deposit directly onto the substrate, forming granular thin films with grain sizes in the nanometer range. Therefore, most of our experiments have been carried out at an Ar pressure between 0.1 and 1 Pa.

Additionally, the work of Thornton [18] and others [14,15] was consulted to choose substrate temperatures during sputtering. As the melting points (Tm) of Pd and Ag are 1828 and 1234 K, respectively, sputtering the films at a substrate temperature (Ts) between 700 and 800 K so that Ts/Tm ~0.4 would yield high-density films with fine grain sizes. However, as Xomeritakis et al. reported that beyond a substrate temperature of about 700 K, tensile stresses develop in the sputtered films and may generate defects during cooling to the ambient [17], we mostly sputtered the films at temperatures between 673 and 700 K. In addition, these temperatures are close to the temperature that membranes will be operated in a separation experiment (673–723 K), and therefore may minimize a thermal stress in the deposited film [14]. The pressure and the temperature during sputtering are given in Table 1. By using this set of process parameters, the realized Pd–Ag films may have microstructures that fall in a zone T in the Thornton model for sputtered films.

Table 1
Dual sputtering parameters for the Pd–Ag 23 wt.%

Alloy	Metal	Sputtering pressure (Pa)	Substrate temperature (K)	Single sputtering power (W)	Single sputter rate (nm/min)	Density (kg/m^3)	Dual sputtering power (W)	Expected compositions (wt.%)
Pd–Ag	Pd	0.1–1	673–700	135	25	12 000	135	Pd77–Ag23
	Ag			26	8.5	10 500	26	

2.2. Individual sputter rates of Pd and Ag

Before performing a dual-sputtering procedure, it is important to determine the individual sputter rates of Pd and Ag at relevant sputtering conditions. Therefore, several single sputtering runs of Pd and Ag were done on silicon wafers with photoresist patterns. After sputtering, the resist was removed by acetone in an ultrasonic bath, leaving a patterned metal layer of which the thickness was measured with a Dektak Surface Profiler (Veeco Dektak 8; 0.1 nm resolution). From these data, the sputter rate of each metal is calculated and given in Table 1.

2.3. Dual sputtering

After determining the individual sputter rates of Pd and Ag, the Pd–Ag films were synthesized by simultaneously sputtering from pure targets of Pd and Ag on the silicon substrate described in the previous section, which contained a 20-nm-thick adhesion layer of Ti sputtered just before. During sputtering, the powers supplied for Pd and Ag targets were 135 W and 26 W, respectively, corresponding to sputter rates of 25 nm/min for Pd and 8.5 nm/min for Ag. If these numbers are converted to weight concentrations, using (bulk) densities of the metals, an alloy composition of Pd–Ag23 at wt.% is expected. We deposited materials at these relatively low sputter rates, as this may help to yield films with fine (nano) structures [12,13]. Monitoring the sputtering time was used to get the desired film thickness, e.g. 15 min are needed to achieve a 500-nm-thick Pd–Ag film. Additionally, the thickness of several sputtered films was checked by a Dektak Surface Profiler and by high-resolution scanning electron microscopy (SEM). The results of these three methods were in agreement.

3. Characterization of the dual-sputtered Pd–Ag film

3.1. Composition

The XPS analysis were performed in the Quantum 2000 Scanning X-ray Multiprobe of Physical Electronics. This system is equipped with a monochromated Al Ka source. An X-ray beam with a diameter of 100 μm and 125 W power was used for XPS analysis and scanned over an area of 700 μm×500 μm. Ar ion sputtering was used for depth profiling. Ar ions with energy of 3 keV scanned over an area of 3 mm×3mm with an etch rate of 5.4 nm min^{-1}. The etch rate was calibrated on a layer of 100 nm SiO$_2$ on a silicon

substrate. We then used Physical Electronics software package MultiPak for data processing.

The Quantum 2000 sensitivity factors (SF) of 5.637 for Pd3d and 6.277 for Ag3d were used for a calculation of the Pd and Ag atomic concentrations, respectively. Because the SF are related to a transmission function, we therefore checked the transmission function of the system on a Cu sample by measuring the Cu2p, CuLMM and Cu3p peaks at different pass energies (PE). Normally, the Physical Electronics software package MultiPak reads out the contents of elements in atomic concentrations. However, in the literature data of the Pd–Ag membrane technology, the contents of Pd and Ag are often reported in weight percentages (wt.%) [2–9]. We therefore converted the obtained atomic concentrations to weight concentrations by using (bulk) densities of 12000 kg/m^3 and 10500 kg/m^3 for Pd and Ag, respectively.

A representative XPS result of the deposited Pd–Ag films is shown in Fig. 1. It can be seen that the compositions are constant throughout the alloy film, and that the Ag content in the deposited film of about 21–22 wt.% is just a little lower than expected. This might be due to the fact that the deposition rates of the metals in the dual-sputtering state are slightly different from those in the calibration runs in which only one target was used (perhaps due to a slight interference of the plasma fields on the two targets during dual-sputtering). In addition, using bulk metal densities to calculate the composition of the thin film could also be a reason for the lower Ag concentration. It has often been reported that, depending on the deposition conditions, the density of sputtered films is different with that of bulk material [15].
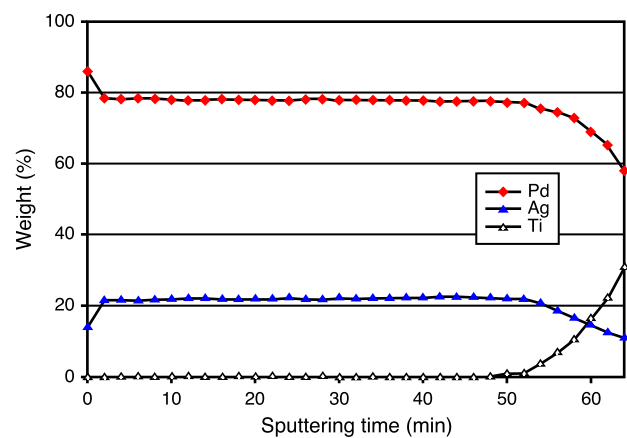

Fig. 1. Evolution of dual-sputtered Pd–Ag film weight composition calculated from XPS depth profile analysis.
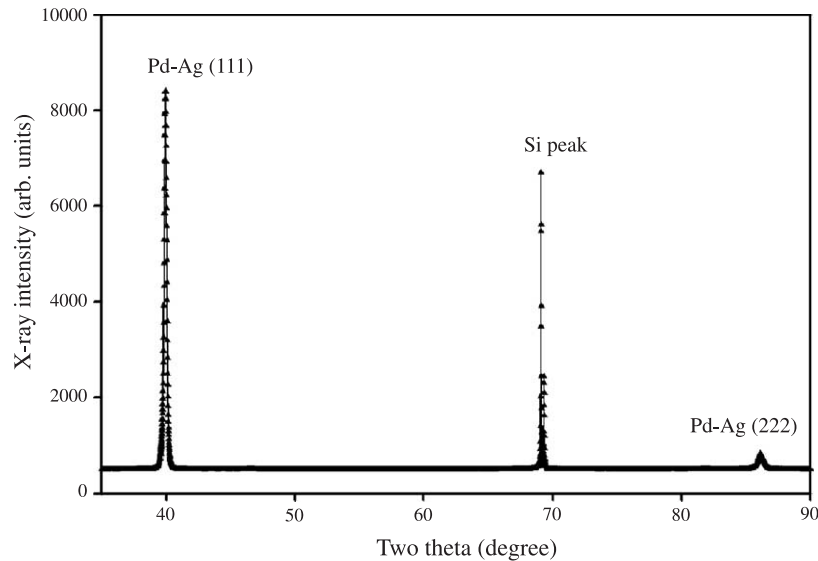
Fig. 2. XRD pattern of the deposited Pd–Ag layer on a thin layer of SiO$_2$ on a silicon wafer.

3.2. Phase and microstructures

The crystalline properties of the deposited Pd–Ag layer were investigated by X-ray Diffraction (XRD) (Philips, CuKα radiation). The results are shown in Fig. 2. The XRD pattern consists of (111) and (222) diffraction peaks, where the (111) peak corresponds to a lattice spacing of 2.268 Å, to be compared with the corresponding {111} lattice spacing of pure Pd and pure Ag of 2.246 Å and 2.359 Å [17], respectively. The results indicate that the deposited Pd–Ag layer was an alloy of pure Pd and pure Ag, and exhibits a preferential orientation in the [111] direction.

The average crystallite size was calculated by applying Scherrer's equation to the (111) peak and found to be about 35 nm, which is quite consistent with the grain size of sputtered Pd–Ag layer reported by Xomeritakis et al. [17]. However, this grain size was about 2 times higher than that reported for the nanostructured Pd films [12,13], probably due to the fact that our films were synthesized at higher substrate temperature than in [12,13]. Although the substrate heater is turned-off after sputtering, the substrate cools down only very slowly due to the vacuum in which it is kept, and therefore is still at a high temperature for several hours, which makes the grains in the film grow.

Additionally, the microstructure of the deposited Pd–Ag film was studied by transmission electron microscopy (TEM) (Philips CM30 Twin STEM). A typical result is presented in Fig. 3. It can be seen that the layer is a non-porous film with fine polycrystalline structure.

Furthermore, the surface morphology of the layer was investigated by a high-resolution scanning electron microscope (SEM) (LEO Gemini 1550 FEG-SEM). The result is shown in Fig. 4. As shown, the Pd–Ag film has a uniformly smooth surface.
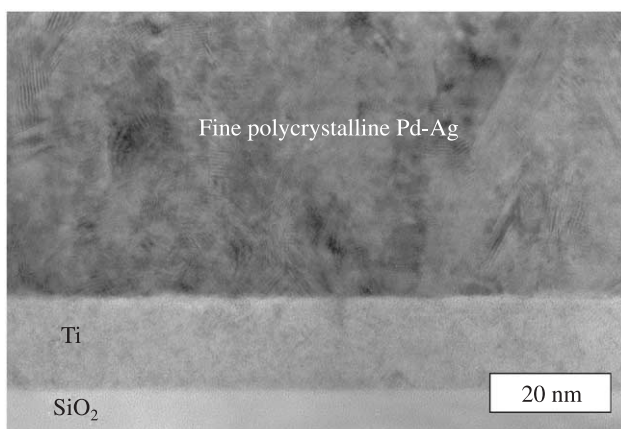

Fig. 3. Cross-sectional TEM image of the Pd–Ag film shows a non-porous film with fine polycrystalline structures.
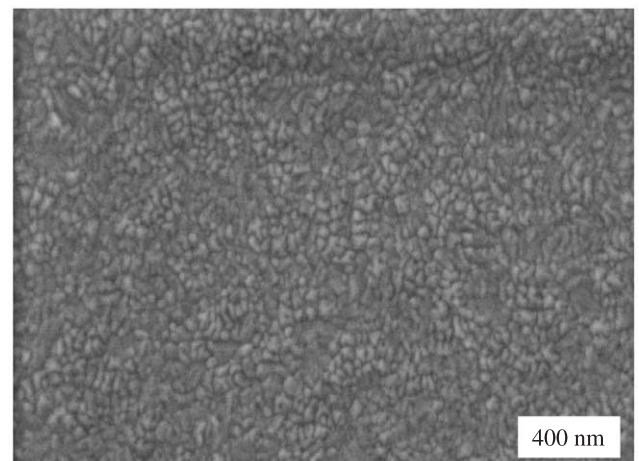

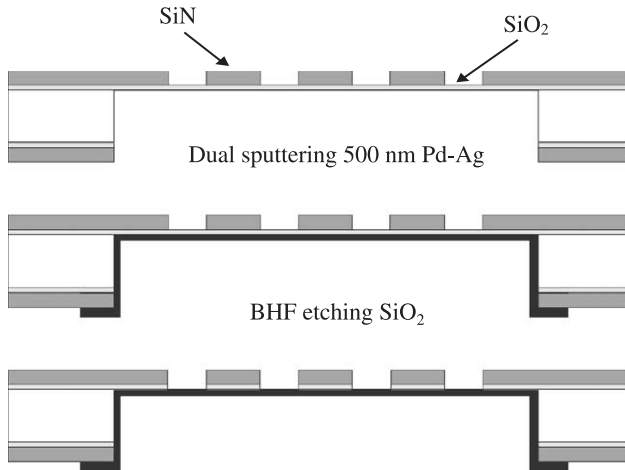Fig. 4. SEM image of the dual Pd–Ag film, deposited at a substrate temperature of 673 K.

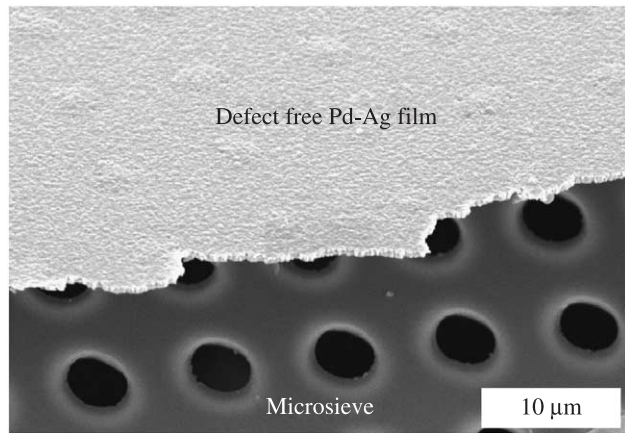Fig. 5. Fabrication process of the Pd–Ag membrane on the supporting microsieve.

Fig. 6. Pd–Ag membrane on the supporting microsieve.

4. Pd–Ag membrane fabrication and hydrogen separation

Fig. 5 shows a sequence of fabrication steps to realize Pd–Ag alloy membranes on a supporting microsieve, which in more detail has been reported earlier [19]. In brief, alloy films of Pd–Ag are dual sputtered on the flat side of a supporting SiO_2/SiN microsieve, using 20 nm of titanium (Ti) as an adhesion layer. Then, the SiO_2 and the Ti are removed in a buffered oxide etch (BHF) through the opening of the sieves to partially reveal the back surface of the deposited Pd–Ag film, thus forming a Pd–Ag membrane.

By using the technology described above, we have successfully fabricated Pd–Ag alloy membranes with various thicknesses in the range of 200–1000 nm [19,20]. Fig. 6 is a SEM image of ca. 500-nm-thick Pd–Ag membrane on a supporting microsieve with a pore size of 5 μm. As shown, the fabricated Pd–Ag membrane is uniform in thickness, has a smooth surface, and is crack-free.

The permeability of the membrane was determined for hydrogen (H_2) and helium (He) with the experimental setup described by Gielens et al. [21]. The hydrogen flow rate through the 500 nm Pd–Ag membrane versus the duration of the experiment is given in Fig. 7. The flux is defined as the molecular hydrogen flow through the membrane divided by the free Pd–Ag area (mol H_2/m^2 s). At a membrane temperature of 723 K and a hydrogen partial pressure of 83 kPa at the feed side, a high hydrogen flux of ca. 4 mol H_2/m^2 s was measured. This flux is ca. a few times higher than the fluxes reported in literature [1–9].

The reasons for obtaining such high fluxes may be that a thin Pd–Ag membrane (500 nm) with high composition control and nanostructures was used. Moreover, such a
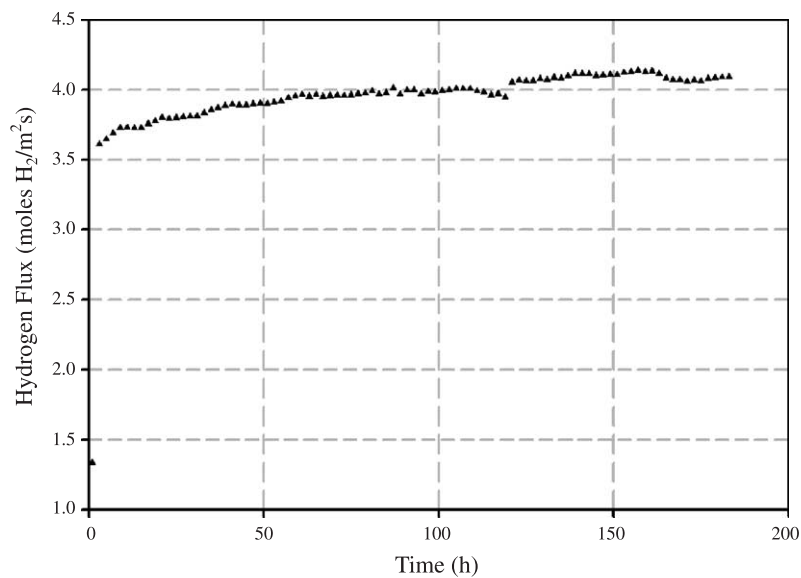

Fig. 7. Hydrogen flow rate through the membrane as a function of time at 723 K and a hydrogen pressure of 83 kPa in the feed. Note that after measuring for ca. 125 h, the feed flow rate was increased from 600 to 900 ml/min, corresponding with the increasing of the hydrogen separation flux from ca. 4 to 4.2 mol H_2/m^2 s.

membrane has a very low resistance to mass transfer, because virtually no support layer is present [19].

Fig. 7 also shows that the flux is rather stable; it first increased from ca. 3.6 mol H_2/m^2 s to 4 mol H_2/m^2 s over a period of about 50 h, then became stable. The increase of the flux in the first measuring period may be explained by an increase in Pd grain size, as was suggested by Lin [11]. However, the increase of flux in the current report is much less than that observed by Lin. After measuring for a period of ca. 120 h, the feed flow rate was increased about 50% from 600 to 900 ml min^{-1} to investigate the flux change. However, there was only a very small increase of the separation flux, suggesting that the previous separation flux of about 4 mol H_2/m^2 s is a stable value under these measurement conditions.

Possible membrane leaks during the permeation experiment can be detected by measuring the He concentration at the permeate side. However, no He was found during the experiments. Therefore, in order to calculate a minimum selectivity of H_2 over He, the detection limit of the gas chromatograph for He is used as the maximum He concentration. In this way, a minimal separation factor of 1500 for H_2 to He is calculated. This high selectivity indicates that the Pd–Ag membrane is most likely non-porous and crack-free.

Considering the high hydrogen separation flux as well as high selectivity, the present membrane seems to be suited for small-scale purification units that supply high quality hydrogen for applications like fuel-cells, semiconductor materials processing, or laboratory use [22]. Currently, more experiments like the influences of CO, CO_2 or steam on membrane performance are ongoing and the results will be reported soon.

5. Conclusions

A dual-sputtering procedure has been used to synthesize submicron thick Pd–Ag alloy films with high compositional control. By choosing the right sputtering parameters, Pd–Ag alloy films with high density (non-porous), crack-free, smooth surfaces, and fine polycrystalline microstructures, etc., were synthesized. The results for thin film fabrication suggest that the dual-sputtering method may be a powerful technique to synthesize alloys with accurate composition for many different applications [23,24].

The information from the fabrication and characterization of the dual-sputtering procedure helps to realize submicron thick Pd–Ag hydrogen separation membranes, which achieved high fluxes, high selectivity, and good stability.

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