

Microfabrication of Palladium–Silver Alloy Membranes for Hydrogen Separation

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Abstract—In this paper, a process for the microfabrication of a wafer-scale palladium–silver alloy membrane (Pd–Ag) is presented. Pd–Ag alloy films containing 23 wt% Ag were prepared by co-sputtering from pure Pd and Ag targets. The films were deposited on the unetched side of a $\langle 110 \rangle$ -oriented silicon wafer in which deep grooves were etched in a concentrated KOH solution, leaving silicon membranes with a thickness of ca. 50 μm . After alloy deposition, the silicon membranes were removed by etching, leaving Pd–Ag membranes. Anodic bonding of thick glass plates (containing powder blasted flow channels) to both sides of the silicon substrate was used to package the membranes and create a robust module. The hydrogen permeability of the Pd–Ag membranes was determined to be typically 0.5 mol $\text{H}_2/\text{m}^2 \cdot \text{s}$ with a minimal selectivity of 550 for H_2 with respect to He. The mechanical strength of the membrane was found to be adequate, pressures of up to 4 bars at room temperature did not break the membrane. The results indicate that the membranes are suitable for application in hydrogen purification or in dehydrogenation reactors. The presented fabrication method allows the development of a module for industrial applications that consists of a stack of a large number of glass/membrane plates. [901]

Index Terms— $\langle 110 \rangle$ wafers, co-sputtering membrane module, hydrogen separation, microfabrication technology, palladium–silver (Pd–Ag) membrane.

I. INTRODUCTION

THE increased demand for hydrogen in recent years in many industrial applications, like petroleum refinement, petrochemical and semiconductor processing and sustainable energy (fuel cells) has led to a revival of interest in methods for separation and purification of hydrogen from gas mixtures [1]–[3]. In particular, palladium (Pd)-based membranes have been the subject of many studies, due largely to their unmatched potential as hydrogen-selective membranes for gas separation or purification. In most cases, palladium is alloyed with silver (Ag) to overcome the well-known problem of hydrogen embrittlement [4], [5]. Comprehensive reviews of Pd-based membranes and their applications have recently been provided by Shu *et al.* [6] and Dittmeyer *et al.* [7].

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However, conventional technology is limited by the high cost of palladium combined with fabrication methods resulting in thick Pd films. For instance, relatively expensive Pd–Ag multitubular assemblies with a membrane thickness of 50 μm or more have been used for many years in the laboratory for the purification of hydrogen [8], [9]. The wall thickness of these tubes incorporated in such assemblies reduces the hydrogen flux and inhibits their application for large-scale chemical production.

During the last decade it was attempted to achieve higher hydrogen fluxes by depositing thin Pd or Pd–Ag films on porous supports [10]–[12]. However, the selectivity of such membranes is often poor due to the fact that the used deposition method render insufficient step coverage, i.e., the inner walls of the pores of the support are not well covered by the film [10]–[12], leading to pin-holes in the membranes that give rise to gas leakage.

Recently it was demonstrated that methods originating from the field of microfabrication technology offer a novel approach for the fabrication of very thin, pin-hole free Pd-composite membranes [13], [14]. Such thin films dramatically increase the achievable hydrogen flux as well as the selectivity of the membrane, and possibly decreasing the costs, if the batch fabrication possibilities of microfabrication technology can be exploited. For example, a microfabricated Pd membrane reported by Frank *et al.* [13] achieved a high flux and high selectivity and is suitable for hydrogen purification in the laboratory, where normally a small, high quality amount of hydrogen is required.

However, most of the microfabricated Pd membranes reported up to now only have a limited size. Such *micro units* [13], [14] are unsuitable for the separation of high volumes of hydrogen. Furthermore, the reported micromachined Pd membranes were packaged with a PDMS polymer, which does not survive the high temperatures that are applied in industrial hydrogen separation, where hydrogen is normally extracted from a synthesis gas (a mixture of CO and H_2) at temperatures above about 400 $^\circ\text{C}$. The study presented in this paper focuses on the fabrication of a wafer-scale micromachined separation membrane module—*macro unit*, which is suitable for larger volume hydrogen separation in industry. The performance with respect to mechanical strength, hydrogen flux and selectivity of the Pd–Ag membranes in such a module was characterized and will be discussed in detail in this paper.

II. FABRICATION OF THE MEMBRANE MODULE

A. Pd–Ag Membranes on a Silicon Frame

A cross section of the Pd–Ag membrane module is shown in Fig. 1. It consists of a silicon wafer and two glass wafers. The

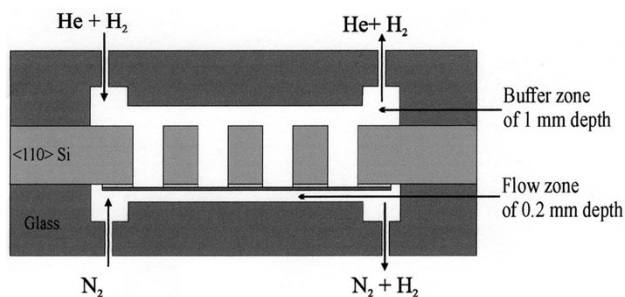


Fig. 1. Cross section of the separation membrane module.

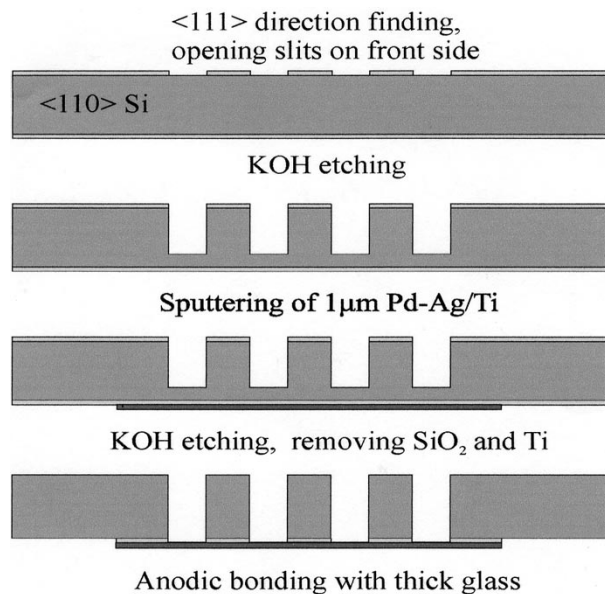


Fig. 2. Fabrication process of the Pd–Ag membrane.

sequence of process steps that was applied to achieve the membrane module is outlined in Fig. 2. In brief, the sequence runs as follows: A 3 inch double-side polished, $\langle 110 \rangle$ -oriented silicon wafer ($\langle 110 \rangle$ -Si) is coated with 1 μm of wet-thermally oxidized silicon dioxide (SiO_2), which is used as a protective layer during subsequent etching steps. To fabricate high-aspect-ratio features by anisotropic etching of $\langle 110 \rangle$ -Si, precise alignment of the features to the $\{111\}$ planes is of critical importance. To reveal the $\{111\}$ planes in the $\langle 110 \rangle$ -Si, fan-shaped structures are first imprinted on the silicon wafer by standard photolithography, followed by removal of SiO_2 in a commercial buffered oxide etch (BOE), and a short etch in a concentrated KOH solution. More details can be found in refs. [15], [16]. Next, long narrow slits of 23 by 1500 μm are aligned to the revealed $\{111\}$ planes and lithographically patterned using the steps mentioned above. The design consists of 1000 of such slits, which are divided into 8 ranges on a square area of 18 by 18 mm. The wafer is immersed in 25% KOH solution at 75°C to etch the silicon until about 50 μm of silicon is left at the bottom of the etched slits. As a result, etched structure or a silicon frame is created and shown in Fig. 3.

At this stage, an alloy film of Pd77–Ag23 at wt% with a thickness of 1 μm is deposited by co-sputtering [17] through a shadow mask on the flat side of the etched silicon frame, using titanium (Ti) as an adhesion layer. The co-sputtering pro-

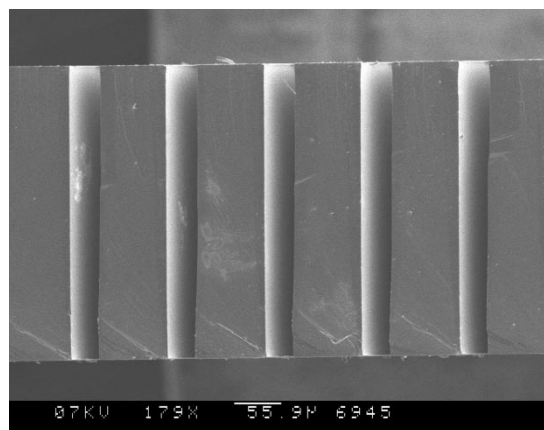


Fig. 3. SEM pictures of the silicon frame, narrow slits were etched in the $\langle 110 \rangle$ -oriented silicon wafer.

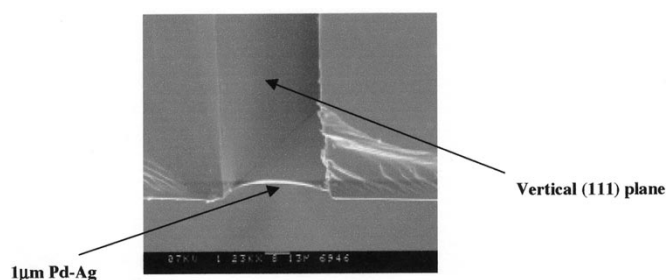


Fig. 4. Close-up of the Pd–Ag membrane across one etched slit.

cedure to deposit a homogenous Pd–Ag alloy film will be discussed in detail in Section II-B. Obviously, an advantage of this fabrication method is that Pd–Ag film is deposited onto a flat and smooth surface, therewith avoiding possible step coverage problems that may arise during deposition on a porous or patterned substrate. Thus, a very thin Pd–Ag film, potentially free of pin-holes will be obtained.

After alloy deposition, the concentrated KOH solution mentioned above is used to remove the remaining 50 μm of silicon in the trenches. Etching in KOH is continued until the SiO_2 layer is reached. Finally, this oxide layer and the Ti film are removed in BOE to uncover the back surface of the Pd–Ag membranes. It should be mentioned here that the BOE removes Ti, but does not affect Pd, Ag or Pd–Ag. A close up of the Pd–Ag membrane across one etched slit is depicted in Fig. 4, while Fig. 5 shows a top view of an array of long narrow etched slits on the silicon wafer. In Fig. 5, the gray parts are unpatterned silicon, the black areas are oblique $\{111\}$ planes appearing inside the etched slits, and the whitish parts are free Pd–Ag areas as seen through the etched slits.

B. Deposition of Pd–Ag Alloy Film by DC Co-Sputtering

Due to the high accuracy of the deposition rate, sputtering has frequently been used to fabricate micron-thick Pd–Ag alloy layers [11], [12]. Mostly, such layers are obtained by sputtering from a single composite target of Pd–Ag. However, it was found that the sputtered layers have a significantly lower Ag content than the original target, due to short target equilibration times [12], [18]. For instance, Xomeritakis and Lin [18] found a silver concentration of 15% for a film sputtered from a Pd75–Ag25 at wt% target. To avoid this compositional control problem, we

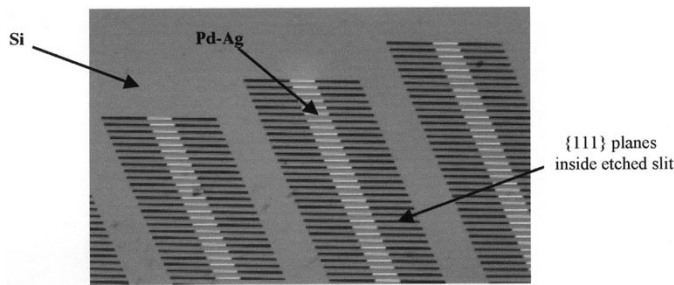


Fig. 5. Top view picture of long narrow etched slits and free areas of Pd-Ag on the silicon wafer. The Pd-Ag layer is deposited on the other side of the silicon wafer.

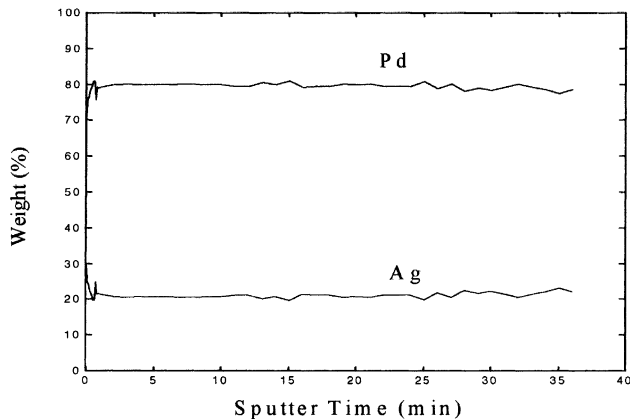


Fig. 6. XPS depth profile of the co-sputtering Pd-Ag film. Ti was detected but it was not show in the graph.

have deposited Pd-Ag alloy films by a co-sputtering method using two pure metal targets.

Experiments have been carried out in a dc sputtering system that accommodates three targets, of pure Pd, Ag, and Ti (Ti is used as an adhesion material), each target having its own controllable power source. Films were deposited at temperatures between 300 K and 700 K at an Ar pressure of $5 \cdot 10^{-4}$ mbar. To know the individual sputtered rate of Pd and Ag at certain sputtering conditions, 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. From these data, the sputter rate of each metal can be calculated determined. Pd-Ag alloy films were achieved by simultaneously sputtering from pure targets of Pd and Ag on the silicon structure described in the previous section, which contained a 20 nm thick adhesion layer of Ti sputtered just before. By controlling the power supplied to each target, the sputtered rates were adjusted at 50 and 17 nm/min for Pd and Ag, respectively. If these numbers are converted to weight concentrations, using (bulk) densities of the metals, an alloy composition of Pd77-Ag23 at wt% is expected. The sputtering time was used to get the desired film thickness, e.g., 15 min are needed to achieve a 1- μ m-thick alloy film.

The compositions of the Pd-Ag alloy films were checked by X-ray Photoelectron Spectroscopy (XPS). A representative example is shown in Fig. 6. It can be seen that the compositions are constant throughout the alloy film, and that the Ag content is just a little lower than expected, which might be due to the fact that the deposition rates of the metals in the co-sputtering

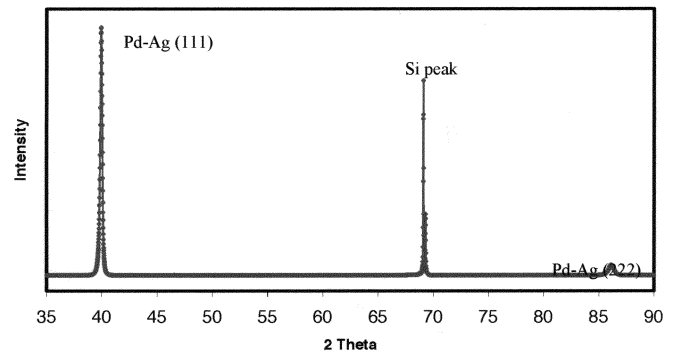


Fig. 7. XRD pattern of the deposited Pd-Ag layer on a thin layer of SiO₂ on a silicon wafer. The substrate temperature was 400 °C during sputtering.

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 co-sputtering). Furthermore, 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 lower than that of bulk material [17].

The crystalline properties of the deposited Pd-Ag layer were investigated by X-Ray Diffraction (XRD) (Philips, CuK α radiation). The results are shown in Fig. 7. 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 [18], respectively. The results indicate that the deposited Pd-Ag layer 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.* [18]. A more detailed XRD study of our sputtered Pd-Ag alloy films will be reported shortly [19].

In conclusion, it was found that an alloy of composition Pd77-Ag 23 at wt% can be deposited by co-sputtering from separate pure metal targets, which is a powerful method that can be used to fabricate many other types of alloy films with highly accurate compositional control, see also [20].

C. Flow Channels in Glass by Powder Blasting

Powder blasting was used to create a flow channel in a 5 mm thick borosilicate glass wafer. The method consists in directing particles with a high velocity toward a substrate, from which material will be removed by mechanical corrosion. Advantages of the method are: simplicity, low-cost and high etch rate [21]. The process steps used in powder blasting of thick glass plates are outlined in Fig. 8. In brief, two glass wafers were covered with an Ordyl BF 410 photosensitive foil, which acts as a protective layer during powder blasting. After a photolithography process as described in [21], powder blasting was applied to obtain a 1-mm-deep gas buffer zone on each of two glass wafers (see Fig. 1). These buffer zones are used to distribute the flow uniformly over the membrane surface. Without them, most of the gas would flow along the center of the membrane, thereby limiting the effective working area of the membrane. A

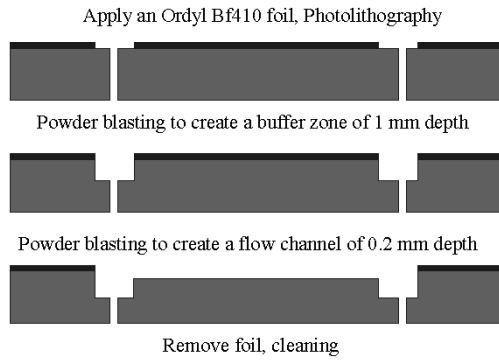


Fig. 8. Process-outline of fabrication of flow channels by powder blasting.

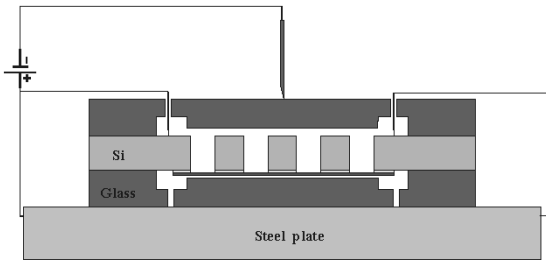


Fig. 9. Four electrode anodic bonding setup for glass-silicon-glass packaging.

second powder blasting step is performed in order to create a 0.2-mm-deep flow channel, which is connected to the peripheral equipment via holes previously drilled in the glass wafers.

D. Assembly of the Membrane

In the last process step, the silicon wafer is bonded between the two thick glass wafers by a four-electrode anodic bonding technique (see Fig. 9). This process is performed in two steps, because adequate bonding requires that a positive electrical voltage has to be applied to the silicon and a negative voltage to the glass. The process resulted in a tight seal between each glass wafer and the silicon wafer. Furthermore, the bonding process as it was performed here creates a membrane module which is robust enough for practical use, e.g., in this form it could be integrated in a stainless steel membrane holder (see Fig. 10) to have connections to a gas manifold and analysis equipment. In the used membrane holder, high forces, exerted by screws, are needed to press membrane module and stainless steel plates tightly together, without leakage. In our set-up, flexible graphite rings were applied in between the holder and the membrane module to make a gas-tight connection.

Although not tested here, the bonding method discussed above would allow the construction of a stack that consists of a large number of silicon wafers separated by glass plates. Such a stack would be suitable for industrial applications where a high volume of hydrogen needs to be extracted from a gas mixture.

III. RESULTS AND DISCUSSION

A. Etching of $\langle 110 \rangle$ Silicon

Fig. 4 shows a SEM micrograph of the cross-section of several narrow parallel slits, etched in a $350 \mu\text{m}$ thick $\langle 110 \rangle$ -Si and having a periodicity of $90 \mu\text{m}$. A similar pattern might also be obtained with Deep Reactive Ion Etching (DRIE) [22], however, with that method only one wafer at the time can be pro-

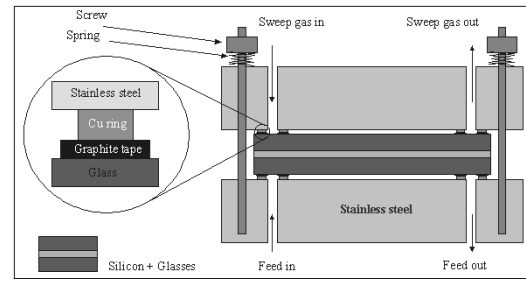


Fig. 10. Membrane holder, the upper part can move up and down and is pressed to the lower part by screws and springs.

cessed, while KOH etching allows a large number of wafers to be etched simultaneously. More details on high-aspect-ratio etching in $\langle 110 \rangle$ -Si wafers can be found elsewhere [23]–[26].

From Fig. 4 the width (l) of the etched slit is estimated to be about $28 \mu\text{m}$, while its initial width was defined by lithography to be $23 \mu\text{m}$. This widening of the etched slit should be characterized exactly and taken into account during the design, for two main reasons: 1) a wider slit would imply a wider membrane, which would have a lower mechanical strength (membrane strength strongly depends on membrane width [27]) and 2) unexpected widening of the slits would make the determination of the total free membrane area, i.e., the separation area, difficult. Slit widening is due to a nonzero etch rate of the vertical $\{111\}$ formula planes, which depends on the accuracy of alignment of the mask patterns to the $\{111\}$ planes (this factor was reduced to a minimum in our work by using the previously described fan-shaped pattern to find the exact $\{111\}$ planes), but also on etching conditions [25], [26]. In our work, the ratio of the etch rates of the $\{110\}$ to the $\{111\}$ planes is estimated to be about 140, which is comparable to data reported by Holke and Henderson [26].

These data can be used to calculate the substrate porosity, defined here as the relative area of the substrate that is available for hydrogen permeation. To define the hydrogen separation membrane area, the length of the free area (L_m) created by KOH etching of one slit through a $\langle 110 \rangle$ silicon substrate should be known (see Fig. 3). Using simple geometrical considerations, this length L_m is given by [23]

$$L_m = L_s - 2\sqrt{3}D + \frac{3\sqrt{2}}{4}l \quad (1)$$

with L_s the length and l the width of the opening slit, and D the thickness of silicon wafer. Applying (1) with $L_s = 1500 \mu\text{m}$, $D = 350 \mu\text{m}$ and $l = 28 \mu\text{m}$, gives a length L_m of $317 \mu\text{m}$. As a result, etching one slit per area of $1500 \mu\text{m}$ by $90 \mu\text{m}$ through a $\langle 110 \rangle$ -Si creates an effective separation area of $317 \mu\text{m}$ by $28 \mu\text{m}$.

In the first study, much attention was directed to exploring the microfabrication technology as a novel method to fabricate thin, strong and pin-hole free membranes to gain high hydrogen permeation and high selectivity, a membrane porosity (an area percentage to allow hydrogen permeation) has not been studied in detail. In the following paragraph, the membrane porosity aspect is discussed.

By making the slit broader (increasing l) or longer (increasing L_s) or using a thinner wafer [see (1)] will give a larger effective area for hydrogen separation and will increase the porosity.

However, as will be shown in the next section, the mechanical strength of the membranes strongly depends on their shortest dimension [27], therefore increasing their width (l) will result in weaker membranes. An alternative way to increase the porosity is to decrease the pitch of the slits. Taking all the above into account, the optimized design of the separation module will consist of slits of $3000 \mu\text{m}$ by $23 \mu\text{m}$ with a periodicity of $50 \mu\text{m}$, giving a porosity of about 20%.

The porosity can be increased even further, by using deep-reactive ion etching (DRIE) [22]. DRIE of silicon is not restricted by silicon $\{111\}$ planes and therefore it is possible to achieve slits with $L_m = L_s$. However, the drawback of using the reactive ion etching method is that wafer throughput is much lower than that obtainable with KOH etching.

B. Mechanical Strength of the Membranes

The mechanical strength of the membranes is an important aspect, as the hydrogen flux is driven by a (partial) pressure difference across the membrane. Predicting the mechanical strength of the membranes is however quite complicated, as it depends on various factors like membrane construction, thickness and material properties (which for thin films may be difficult to estimate or measure). Therefore, the strength of membranes is normally determined experimentally. Nevertheless, a rough estimation of the strength is very valuable during the design phase, and therefore we started our work with an estimation of the strength of our microfabricated membranes based on the originally chosen design parameters width and length (defined by the lithographic process), thickness and (bulk) material properties.

As can be seen in Figs. 1 and 5, the microfabricated membrane module is composed of many smaller Pd–Ag membranes acting in parallel, of which a single one is formed by a Pd–Ag membrane spanning across one etched slit. It can safely be assumed that the mechanical strength of the silicon support that surrounds the Pd–Ag membranes is much higher than that of a single Pd–Ag membrane, therefore the strength of the whole membrane module will be mainly determined by that of a single membrane. Van Rijn *et al.* [27] derived an equation that can be used to estimate the maximum transmembrane pressure P_{max} for a thin membrane of composed of a ductile material

$$P_{\text{max}} = 6.4 \frac{h\sigma_{\text{yield}}^{3/2}}{lE^{1/2}} \quad (2)$$

where h is the thickness of the membrane, l the length of the shortest side of the membrane, σ_{yield} the yield stress and E the Young's modulus of the membrane material. Several values of E and σ_{yield} for thick foils of Pd and Ag are given in Table I [28]. However, the values of E and σ_{yield} for sputtered Pd77–Ag23 wt% alloy film have not been reported yet. Besides that, the mechanical properties of thin may differ for different deposition methods and conditions [17], so that film property data obtained from literature cannot be taken for granted. Very critical is the temperature at which the membrane will have to operate. In general, both E and σ_{yield} are temperature dependent and typically a higher temperature will lower σ_{yield} . If it is assumed that the material properties of an alloy can be interpolated from the properties of the individual metal elements, we arrive at a yield strength of 80 MPa and a Young's modulus of 150 GPa

TABLE I
MECHANICAL PROPERTIES OF Pd, Ag, AND THE POSTULATED DATA FOR THE SPUTTERED Pd–Ag ALLOY

Material	σ_{yield} (MPa)	E (GPa)	σ_{ultimate} (Mpa)
Pd	35-205	121	175-325
Ag	172-330	83	172-330
Pd-Ag	80*	150*	Non estimate

* Postulated data for the sputtered Pd–Ag in this work

for the deposited Pd–Ag alloy film. Applying (2) for a single $1 \mu\text{m}$ thick Pd–Ag membrane spanning across a $28 \mu\text{m}$ wide slit, we find a P_{max} of 4.1 bars.

The rupture strength P_{break} of the Pd–Ag membrane was measured at room temperature in the setup described by van Rijn *et al.* [27]. It was found that the Pd–Ag membranes did not break at a pressure difference of 4 bars over the membrane, but some of the membranes broke at a pressure difference of about 5 bars. Tests at higher pressure could not be carried out with the setup used. Nevertheless, as was expected, the membranes that broke ruptured on the Pd–Ag membranes and not on the silicon support. Although the rupture strength of the membranes was not measured at higher temperatures, the room temperature tests show that the microfabricated membrane is mechanically strong enough to operate under the desired pressure gradient.

C. Hydrogen Permeation and Selectivity of the Membranes

To determine the hydrogen permeation and selectivity of the membranes, they were positioned in the previously described stainless steel membrane holder and heated up to the desired temperature. Membrane permeabilities and selectivities for hydrogen were determined as a function of hydrogen partial pressure (0–0.3 bars) and temperature (350–450 °C).

Although the mechanical strength tests at room temperature have shown that the membranes can withstand a pressure of at least 4 bars, up to this point no experiments had been carried out at high temperatures in the presence of hydrogen gas. It has to be taken into account that under such conditions the yield strength of the Pd–Ag film may be completely different and perhaps drops to lower values. In addition, the yield strength of the materials may decrease after repetitive loading cycles. Therefore, for safety reasons the membranes were only tested at hydrogen pressures of up to 0.3 bars.

During these experiments the retentate and permeate sides of the membrane were continuously flushed at atmospheric pressure, the retentate side with a mixture of hydrogen and helium, the permeate side with pure nitrogen. The flux and selectivity were determined by measuring the hydrogen and helium concentration in the nitrogen stream with a gas chromatograph, equipped with a thermal conductivity detector (TCD). Details of the measurement set-up have been reported by Gielens *et al.* [31].

The hydrogen flow rate through the membrane versus the duration of the experiment is given in Fig. 11. It should be noted

TABLE II
COMPARISON OF THE PERMEATION RESULT TO THE LITERATURE DATA OF THIN SPUTTERED Pd- AND Pd-ALLOY MEMBRANES ON POROUS SUBSTRATES

Membrane	Thickness (μm)	Measuring temperature ($^{\circ}\text{C}$)	Driving force $\Delta P(\text{H}_2)$ (Bar)	Flux ($\text{mol.H}_2/\text{m}^2.\text{s}$)	Selectivity	References
					H_2/N_2 or H_2/He	
Pd-Ag/ γ - Al_2O_3	0.35	250	1	0.015	5.7*	[11]
Pd-Ag/ γ - Al_2O_3	0.16-0.52	300	Not given	0.01	Up to 116**	[12]
Pd and Pd-Ag/ γ - α Al_2O_3	0.1-1.5	300	1	0.01-0.02	30-200	[18]
Pd-Ag/ α - Al_2O_3	0.7-1.1	350	2-5	0.05	4-80*	[31]
Pd-Ru-In/SS	1.5	370	1	0.03	Infinite	[32]
Pd-Ag	1	450	0.3	0.15-0.5	Minimal of 550	This work

* Selectivity for H_2/N_2

** Only one membrane had an exceptional selectivity of 3845

SS: stainless steel

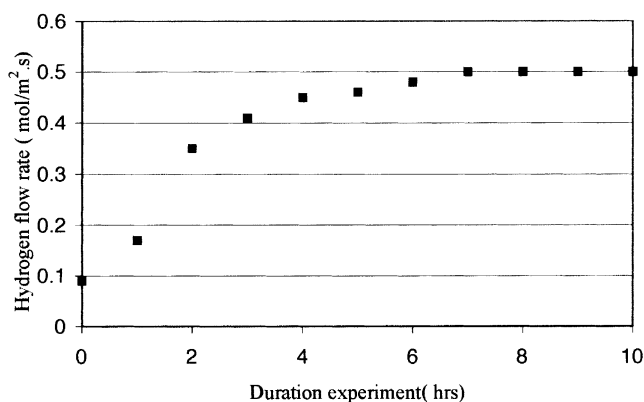


Fig. 11. Hydrogen flow rate through the membrane as a function of time at temperature of 450°C . The measurement started, when the membrane temperature was at 350°C in hydrogen environment.

that the measurement started when the membrane temperature was 350°C . At a membrane temperature of 450°C and a hydrogen partial pressure of 0.2 bar at the retentate side, a hydrogen flux of $0.5 \text{ mol H}_2/\text{m}^2.\text{s}$ was achieved. Testing the membranes at higher hydrogen pressure will probably give higher hydrogen fluxes through the membranes, this will be carried out in a next study.

The dependence of hydrogen flux on temperature was also investigated. Fig. 12 shows the hydrogen flow rates through the membrane at different temperatures from 350°C to 450°C . It can be seen that the hydrogen flow rate increases with increasing

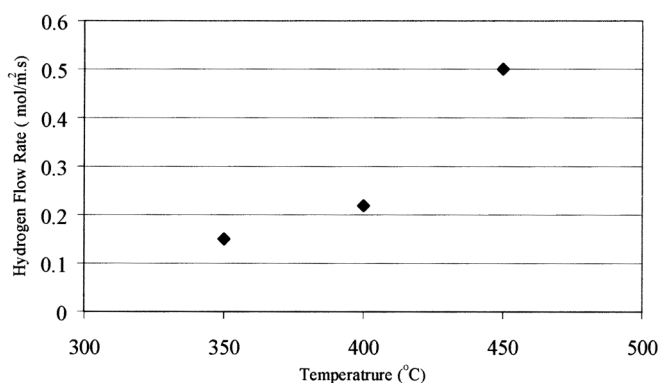


Fig. 12. Dependence of hydrogen flow rate through the microfabricated Pd–Ag membrane on temperature.

temperature, however, the dependence is larger than expected from theory [32]. More experiments are currently being carried out in our laboratory to elucidate this effect and have a better understanding of membrane performance. Nevertheless it can be said that in the temperature range considered here the obtained fluxes are high in comparison with reported values for thin sputter-deposited Pd–Ag membranes on porous substrates (see Table II).

For each of the samples that were investigated, we measured the helium concentration at the permeate side during the permeation experiment. A significant helium concentration would indicate a leak or pin-holes in the Pd–Ag membranes, but in none

of the cases helium was detected. Based on the helium detection limit of the gas chromatograph, a minimal separation selectivity of 550 for hydrogen to helium can be calculated. This selectivity is relatively high in comparison with that of conventional membranes fabricated by sputtering Pd–Ag on porous substrates (see Table II). The measurements thus indicate that the micromachined Pd–Ag membranes are virtually pin-hole free.

IV. CONCLUSION

Wafer-scale Pd–Ag alloy membrane modules were micro-machined and tested. KOH etching of $\langle 110 \rangle$ -Si was utilized to fabricate a supporting structure for a sputtered Pd–Ag film. This micron thick Pd–Ag layer was deposited by co-sputtering, which is a powerful method to make thin alloy film with highly homogeneous compositions. Anodic bonding of thick glass to silicon was used to package the membrane and create a robust module.

The membranes were found to have adequate mechanical strength and were capable of withstanding a pressure difference of 4 to 5 bars at room temperature. The microfabricated Pd–Ag membranes obtained a high permeation rate and high selectivity for hydrogen. Typical flow rates of $0.5 \text{ mol H}_2/\text{m}^2 \cdot \text{s}$ were measured at the hydrogen pressure of 0.2 bars at 450°C with a minimal selectivity of 550 for H_2 to He.

The reported membranes may be applied for hydrogen separation or purification from gas mixtures or in membrane reactors for dehydrogenation. The results indicate that an industrial module that consists of a stack of a number of glass/membrane plates with a higher throughput of hydrogen is feasible.

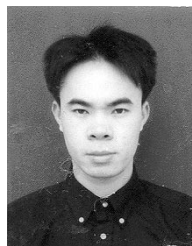
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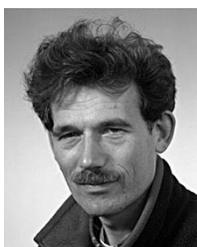
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