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PREPARATION OF A DUAL SPUTTERING PD-CU ALLOY FILM AND ITS APPLICATION IN HYDROGEN SEPARATION

H.D. Tong a, H.T. Hoang a, F.C. Gielens b, H.V. Jansen a, M.C. Elwenspoek a

aTransducer Science Technology Group, MESA Research Institute, University of Twente, P.O. Box 217, 7500 AE, Enschede, The Netherlands
bDepartment of Chemical Engineering and Chemistry, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands
E-mail: T.Hien@el.utwente.nl; Tel.: X-31-53-4892805; Fax: X-31-53-4893343.

Abstract: Sub-micron thick Pd-Cu alloy films have been deposited by a dual sputtering, which allows a high composition control of the layer. The compositions, surface morphology and phase structure of the sputtered layers were investigated by energy dispersive spectrometer (EDS), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), transmission electron microscope (TEM) and X-ray diffraction (XRD), respectively. The results proved that the Pd-Cu layers were the alloy of pure Pd and pure Cu. The characterized Pd-Cu alloy layers were deposited on a silicon support structure to create Pd-Cu membrane for hydrogen separation. High fluxes of up to 1.6 mol H₂/m²s have been measured through a 750 nm Pd-Cu at 723 K with the minimal selectivity of about 500 for H₂ over He.

Keywords: Dual sputtering; Pd-Cu alloy layers; Support structures; Pd-Cu alloy membranes; Hydrogen separation.

I. INTRODUCTION

The increased demand for hydrogen in recent years in many sectors such as petroleum refining, petrochemical and semi-conductor processing, as well as in new energy-related applications such as clean fuel for fuel cells and vehicles has led to a revival of interest in methods for separation and purification of hydrogen from gas mixtures [1-3]. Metal membranes with high perm-selectivity for hydrogen and good thermal, chemical, mechanical properties are widely being used. Among most used metals, palladium (Pd) is predominant because of its high hydrogen permeation and compatibility with other gases in mixtures [4-6].

Pd, however suffers from the α- to β-phase transition during hydrogen absorption, a well-known problem of hydrogen embrittlement [7-9], which often causes a destruction of the membrane structure. Nevertheless, this problem can be reduced by alloying Pd with several elements such as silver (Ag), copper (Cu), gold (Au) or nickel (Ni) etc. For example, Pd-Ag alloy membrane was commonly used due to high permeability of hydrogen and reducing the palladium embrittlement [10-12], while, Pd-Cu membranes have been reported to have high resistance to hydrogen sulfide and sulfurous constituents in gas mixtures while maintaining a desirable set of properties [13-14].

Up to now many methods have been developed to fabricate palladium-copper composite membrane including electroless plating, electrodeposition, chemical vapor deposition (CVD) and sputtering etc [15-17]. Among these deposition methods, sputtering is a simple process with fast deposit rate and given high purity layers [9, 18].

This paper focuses on the preparation of palladium-copper alloy films with high composition control using the dual sputtering technique. Afterward, several techniques like the EDS, XPS, SEM, TEM, and XRD are used to investigate the surface morphology and microstructures of layers. The characterized dual sputtered Pd-Cu alloy is deposited on a micromachined support structure to realize a Pd-Cu membrane.

II. EXPERIMENTS

II.1. PREPARATION OF PD-CU

The experiments were carried out in DC sputtering machine with three single targets of Pd, Cu and Ti as adhesion layer. Each target has its own power supply so that the individual sputter rate can be independently adjusted. Before deposition, sputtering chamber was evacuated to 3.10⁻⁷ mbar.
and Ar gas is filled up to sputtering pressure of 5.10⁻⁴ mbar. In order to get uniform surface and to clean target surface, the pre-sputtering is carried out for a few minutes. Pd-Cu films are deposited by simultaneously sputtering from pure target of Pd and Cu, while a thin layer of Ti is used as an adhesion layer. During sputtering, the power supplies for Pd and Cu targets were 135W and 105W, respectively. By these sputtering conditions, we expected to realize the layer of 77% for Pd and 23% for Cu at weight.

II.2. CHARACTERIZATION OF THE DUAL SPUTTERING PD-CU

II.2.1. COMPOSITIONS

Compositions of the sputtered layer were checked by EDS and XPS. The EDS shows that the compositions of the layer were 77.15% of Pd and 22.85% of Cu in weight. In addition, the depth distribution of the Pd-Cu film with the composition of 77.19% for Pd and 22.81% for Cu was obtained by XPS (see Fig. 1). This proved that the compositions of deposited film were rather similar to the desired compositions of 77% Pd and 23% Cu. Moreover, the compositions are really homogeneous on the whole thickness of the layer.

II.2.2. PHASE AND MICROSTRUCTURES

The surface morphology of the layer was investigated by SEM. The SEM image revealed that Pd-Cu layer has very smooth and rather uniform surface. While the microstructures of the dual sputtering Pd-Cu film were observed by TEM (see Fig. 2). TEM study reveals that the layer with a fine polycrystalline structure was obtained.

Furthermore, the phase structures of the Pd-Cu film were studied by X-Ray Diffractometer (XRD) (Philips, CuKα radiation). Fig. 3(a) shows the XRD pattern of Pd-Cu film prepared at 300K and the pattern depicts the diffraction peaks of {111}, {200} planes with spacing lattice of 2.210Å, 1.921Å, respectively. XRD spectrum noticed that the intensity of reflection peaks was not much different from each other so it could not see the clear orientation of the crystalline planes at 300K. However, in the XRD pattern of the Pd-Cu layer at 400K (Fig. 3(b)) there was the predominance of intensity of the (111) peak, while the (200) peak was hardly seen. At 400K, the preferred orientation in the crystalline was [111] direction. This result suggests that the deposition temperature affected primarily on the microstructure of the layer.

From XRD data d-spacing values of sputtered films at different compositions were calculated and listed in Tab.1. The fact that d-spacing values of the deposited layer were between those of pure Pd and pure Cu proves the layer was an alloy of Pd and Cu. Furthermore, crystallite size of composite film may be obtained from the diffraction spectrums following the preferred direction based on Scherrer’s equation. Our results show that the grain size is strongly depended on substrate temperature during sputtering, it raises up very rapidly from 150Å at substrate of 300K to 2400Å when substrate was of 600K.
Table. 1. \(d\)-values depend on the compositions

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
<th>Peaks</th>
<th>(d_{\text{pd}}) (Å)</th>
<th>(d_{\text{Cu}}) (Å)</th>
<th>(d_{\text{Composite}}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd77Cu23</td>
<td>111</td>
<td>2.244</td>
<td>2.087</td>
<td>2.210</td>
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<tr>
<td>Pd60Cu40</td>
<td></td>
<td>2.172</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd48Cu52</td>
<td></td>
<td>2.151</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd77Cu23</td>
<td>200</td>
<td>1.944</td>
<td>1.807</td>
<td>1.933</td>
</tr>
<tr>
<td>Pd60Cu40</td>
<td></td>
<td>1.889</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pd48Cu52</td>
<td></td>
<td>1.864</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig 3(b). XRD of Pd-Cu alloy film deposited at 400 K

Fig 3(a). XRD of Pd-Cu alloy film deposited at 300 K

III. MEMBRANE MICROFABRICATION AND HYDROGEN SEPARATION

The investigated alloy layers were deposited on a micromachined silicon support structure to create the membranes with various thicknesses from 200nm to 750nm. The technology to fabricate the micromachined silicon support has been reported in our previous paper [19]. The microfabricated membranes were then tested by a measurement set up described by Frank et al. [20] to investigate the membrane separation properties and gave a positive result (Fig. 4). High fluxes of up to 1.6 mol H\(_2\)/m\(^2\).s have been measured through 750 nm Pd-Cu membrane at 723 K and hydrogen pressure of 0.95 bars in a retentate side. A minimal selectivity of hydrogen over helium for this membrane was about 500. Currently, more measurements have been carried out to attain more the results, which help us to understand better about membrane behaviors.

IV. CONCLUSIONS

Above results confirm that a dual sputter technique is the powerful method to deposit Pd-Cu alloy films with high composition controlling.

The dual sputtered Pd-Cu alloy has smooth surface, fine polycrystalline structures. The study also shows that the phase structures as well as the grain size of the film are strongly depended on the substrate temperatures during the sputtering process.

The dual deposited Pd-Cu membranes are fabricated and achieve high fluxes and reasonable selectivity.

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Fig. 4. Dependence of the hydrogen flux on hydrogen partial pressure in retentate

REFERENCES