Thin Pd/Pt membranes supported in a porous silicon foil for H_2 separation in automotive reforming units

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Introduction The generation of highly pure hydrogen by the separation of the reforming gas using dense hydrogen permeable and selective („permselective") membranes in a microsteam reforming unit is one of the key issues for the automotive use of the fuel cell technology. The best candidate materials for development of these membranes are palladium and its alloys [1]. The problem with the Pd membranes are high cost and hydrogen embrittlement. However, a Pd-membrane tightly packed in the pores of a support may be resistant to hydrogen embrittlement which depends on grain size and grain boundaries of Pd films [2,3]. From the above consideration, a new design and technology of the preparation of thin Pd membranes supported in a porous silicon foil has been developed in this work. Thin palladium and platinum films were prepared by physical vacuum deposition and sputtering. Using this method a thin continuous film with thickness of several hundred nanometers up to one micron has been deposited on Si.

Fabrication of thin Pt/Pd membranes.

For our purpose, we used 200 - 525µm thick, (100) p-type Czochralski grown silicon substrates which are etched in electrolytes containing hydrofluoric acid (49%HF). First of all platinum (Pt) (or palladium) is evaporated on the backside of the wafer to provide an ohmic contact, and secondly, Pt was used as a stop-layer during deep anodic etching (DAE) of silicon. The samples were etched in a teflon cell at room temperature without illumination, a schematic illustration of the experimental setup is given in Fig.1. Etching was performed under galvanostatic condition with constant current and varying bias voltage in an electrolyte containing HF dissolved in an aqueous $(CH_3)_2COOH$ or DMF (Dimethylformamide) solution.

Large pore diameters have been obtained as a result of DAE with sample resistivities of 4000 Ocm (pore diameter 8-15 µm) and 1000 Ocm (pore diameter 5-7 µm). In this case the solution HF: H_2O : $(CH_3)_2COOH$ (5:25:9) has been used. Figure 2 shows a cross-sectional view taken from a 4000 Ocm sample prepared by randomly ordered DAE. The thickness of the porous foil is 212 µm, the thickness of platinum membrane on the top of the porous support equals to 200nm. Figure 3 shows a cross-sectional view of a platinum membrane supported in a porous silicon foil produced by ordered macropore formation process [4]. The thickness of the porous foil is 218 µm, the diameter of the pores range from 17 to 35 µm. The thickness of platinum membrane on the top of the porous support equals to 211nm. Although this process demands photolithographic technique it is possible to achieve larger pore sizes [4].

References

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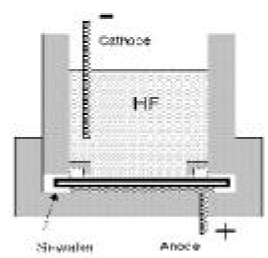

Fig. 1 : sketch of experimental setup

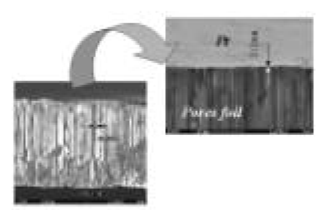

Fig.2. Randomly porous silicon foil as a support of Pt membrane

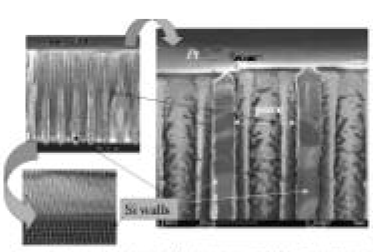

Fig.3. Ordered porous Si foil as a support of a Pt membrane