Fabrication of Porous Noble Metal Thin-Film Electrode by Reactive Magnetron Sputtering

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Porous platinum films have been fabricated by reactive sputtering combined with subsequent thermal annealing. Using the SEM, XRD, XPS, and polarization resistance measurement techniques, the microstructural development of the film and its resultant electrochemical properties have been characterized. Pore evolution was understood as a result of the thermal grooving of platinum during annealing process. We demonstrated that crystallization should be followed by agglomeration for the evolution of porous microstructures. Furthermore, reaction sputtering affected the adhesion enhancement between the film and substrate compared to the film deposited by non-reactive sputtering. The polarization resistance of the porous platinum film was five times lower than that of the dense platinum film. At 600 °C the resistance of the porous film was 5.67 Ω - cm², and that of the dense film was 38 Ω - cm².

Keywords: Porous Film, Platinum, Electrode, Electrochemical Cell, Sputtering.

1. INTRODUCTION

Porous platinum electrodes have attracted great attention owing to their high catalytic activity and high surface area. In particular, porous platinum electrodes of thin film configuration are applied in various types of electrochemical devices, such as fuel cells,¹ metal-air batteries,² and electrochemical sensors.³ Such porous electrodes should have the characteristics of being electrically conductive and contiguous in a microstructural regime at elevated temperature. Electrochemical reactions at the electrodes require not only high electrical conductivity but also large surface area because the reaction takes place near the interface which is composed of conducting phases and pores. An efficient supply of gas phase to electrochemical reaction sites is a key concern for electrode designs.

The recent growing demands for the integration of electrochemical devices, which is a viable solution for energy efficient devices and energy-sources, have led to the adaptation of a novel cell fabrication process such as vacuum deposition.⁴ Physical vapor deposition is, however, used for dense film fabrication compatible with metallization, which is a basic component of most semiconductor and magnetic devices.⁵ Therefore, the problem has arisen of identifying the most effective method to achieve a porous microstructure which is stable at elevated temperatures during electrochemical reaction in a vacuum processing regime. A typical example is the porous platinum electrode of high-temperature fuel cells.¹ Most fuel cell electrodes adapt the porous microstructures at both sides of the ion transport membrane. The well-known methods for fabricating porous electrodes are particulate-driven processes such as microfluidic lithography,⁶ photoresist molding,⁷ and so on. Even though these methods provide precise control of the cell size and pore-structure, contamination and poor reproducibility of the electrode microstructure is a remaining issue. Therefore, it is necessary to develop a vacuum deposition process for porous electrodes which is compatible with membrane fabrication techniques.

To make porous electrodes using vacuum deposition, template masking has been adapted to the electrode materials deposition process, which introduces the pore structure. Such an ideal structure suffers from the rearrangement of the microstructure towards local equilibrium at high temperature (> 500 °C), which leads to performance degradation during electrochemical operation. Furthermore, introduction of a template mask increases the complexity of the device fabrication process.⁸-¹⁰ Except for alloying-dealloying strategies,¹¹ only two possible methods of porous platinum thin film fabrication without template masks have been reported: one is in-situ physical vapor deposition at high pressure,¹ and the other is the post-annealing of dense polycrystalline film at high temperature.⁵ The porous microstructures induced by
post-annealing are a result of thermally activated agglomeration. This phenomenon has been reported for various metals\textsuperscript{12–15} and mechanisms.\textsuperscript{16–19} In a previous report,\textsuperscript{5} Au film was observed to agglomerate via nucleation of voids, followed by its fractal growth and propagation; however, the agglomeration of Pt film follows the grain boundary grooving process. The reason why Pt films only follow the grooving process for porous structure evolution is unknown.

Agglomeration of thin film is influenced by various variables such as the annealing time, temperature,\textsuperscript{20} thickness of film,\textsuperscript{21} roughness of substrates, and so on.\textsuperscript{22,23} We also confirmed that a porous thin-film microstructure could be achieved by controlling such parameters. In addition, when metal film is deposited on the membrane, delamination of the film takes place easily because of the residual stress induced by the mismatch between the film and substrate,\textsuperscript{5,21} which should be overcome by strengthening the adhesion of the films. Experimentally, we have suggested reactive sputtering is a viable method to enhance the adhesion of porous Pt-films.

We have fabricated porous platinum thin films using reactive magnetron sputtering in an oxygen atmosphere with subsequent post-annealing at high temperature. Agglomeration has been correlated with the crystallization of platinum thin films. And the influences of annealing time, temperature and film thickness have been examined. The electrochemical property of the porous Pt film has also been investigated using electrochemical impedance spectroscopy.

2. EXPERIMENTAL DETAILS

Platinum films were deposited on SiO\textsubscript{2}(1 \textmu m)/Si(100) substrates by DC reactive magnetron sputtering. The platinum target had a purity of 99.99\% and a diameter of 4 inches. To prevent unexpected oxidation and/or contamination during the sputtering processes, the target was pre-sputtered at a DC power of 100 W for 5 min in a pure Ar atmosphere. After that, the platinum thin film was deposited at room temperature and a working pressure of 5 mTorr. The deposition rate of the film was 20 nm/min at an O\textsubscript{2}/Ar gas ratio of 1, which was estimated by \textit{ex-situ} cross-sectional microstructure observation. The deposited thin film was post-annealed in a temperature range from 300 °C to 800 °C for 1 h in air.

The phase development and crystallinity of the films were examined by X-ray photoelectron spectroscopy (XPS, ULVAC-PHI, Inc., Japan) and X-ray diffraction (XRD, Cu K\alpha, PANalytical, Netherlands). The surface morphologies of the films were investigated by scanning electron microscopy (SEM, XL30, Philips, Netherlands). The electrochemical properties of the porous Pt films were probed by impedance spectroscopy. For impedance studies, Pt thin films were deposited on a polished YSZ single-crystal substrate, and silver paste and Pt wires were connected to them and heat treated at 600 °C for 1 h in air. AC impedance measurements were carried out at temperatures ranging from 400 °C to 600 °C in air over a frequency range of 0.005–5 MHz using a frequency response analyzer (Solartron1260, Solartron Inst., England) combined with a potentiostat (Solartron1287, Solartron Inst., England).

3. RESULTS AND DISCUSSION

The microstructure of the as-deposited platinum thin film is shown in Figure 1. The surface morphology was homogeneous and dense. There was no evidence of porous microstructure generation during deposition. The observed film thickness was 170 nm. After annealing in air, the films were transformed into porous morphologies, as shown in Figures 2(a) and (b). As the annealing temperature increased from 700 °C to 800 °C, the pore size and the porosity of the platinum film increased. The heat treatment must have generated the porous microstructure by rearrangement and agglomeration of the platinum film. However, in cases when the sample was annealed at a lower temperature (< 500 °C) for a prolonged period of time (> 20 h), no change in the microstructure was observed and it was similar to that of the as-deposited sample.

The agglomeration of the platinum thin films and resultant pore growth could be explained by thermal grooving,\textsuperscript{24} a thermally activated process by which the free energy of a system is reduced through atomic diffusion at the surface and/or interface. The driving force for the atomic diffusion on the thin-film surface is the chemical potential differences induced by curvature difference localized at three-grain junctions. The diffusion continues until the chemical potential difference is diminished around each localized junction point. Eventually, the thin film becomes a collection of interconnected-island shapes owing to the agglomeration. Therefore, the observed thermal grooving is a result of the surface diffusion of the...
Fig. 2. Surface microstructures of platinum thin films post-annealed at (a) 700 °C and (b) 800 °C for 1 h in air.

atoms that try to relocate at the local equilibrium position. Figure 3 shows XRD patterns of platinum thin films annealed at various temperatures. No peaks, except for the substrate itself, of the as-deposited film strongly suggest that the pristine film is amorphous. As the annealing temperature was increased, particularly above 600 °C, the (111) and (200) peaks of the platinum started to appear, which demonstrated that the amorphous platinum film transformed to a crystalline one.

At this point, we assumed that the crystallization of the films was followed by agglomeration because thermal grooving is always valid in the crystalline phase. We crystallized the amorphous platinum films at 650 °C for 5 min using RTA without pore structure generation, and further heat-treated them at 300 °C for 6 h. As shown in Figure 4(a), before the additional annealing, the platinum film showed a polycrystalline microstructure with well-developed grain boundaries as a result of crystallization during RTA annealing. By further annealing at 300 °C, however, the platinum thin films successfully transformed to porous microstructure.

Fig. 3. XRD patterns of the platinum thin films annealed at various temperatures for 1 h in an air atmosphere. Si peaks originated from substrate.

Fig. 4. Surface microstructure of (a) platinum thin films crystallized at 650 °C for 5 min using RTA and (b) subsequently post-annealed at 300 °C for 6 h in air. Inset of (a) shows the crystallization of platinum film during annealing.
Fig. 5. Surface microstructures of (a) 170 nm-thick platinum thin films annealed at 700 °C for 10 h in air, and (b) 100 nm-thick platinum films post-annealed at 800 °C for 1 h in air.

(see Fig. 4(b)). Therefore, we concluded that the crystallization of platinum film is a necessary condition for porous microstructure development when the thermally activated agglomeration mechanism is dominant.

High-temperature annealing promotes fast surface diffusion near the grain boundaries, and prolonged annealing signifies the depth and broadens the width of the grooves, eventually exposing substrate surfaces. Figure 5(a) shows the surface morphologies of 170 nm-thick platinum films that had been annealed at 700 °C for 10 h. The relative porosity of each film was measured as 33%, which corresponds to the double of porosity of the sample annealed for 1 h (see Fig. 2(a)). According to Mullins' work, the development of the grooves becomes limited because the grain of polycrystalline thin films should have an equilibrium shape with a uniform curvature. Moreover, Mullins reported that a certain critical thickness of the films exists at which groove growth is restricted, and the film does not undergo agglomeration into island forms. Such criteria were validated by changing the annealing temperature and film thickness. When the sample of 100 nm in thickness was annealed at 800 °C for 1 h, Pt film was agglomerated to separate islands, as shown in Figure 5(b). Disconnected Pt film is not a proper configuration for the effective current collection during electrochemical cell operation. The morphological figures of the porous films could be quantified by measuring the platinum-to-platinum bridge wall thickness, called ligament size, which is shown in Figure 6. The ligament size increased as the annealing temperature increased. However, thermal annealing during which no crystallization takes place (< 500 °C), introduced neither morphological nor porosity changes. On the other hand, the samples had been already crystallized by RTA annealing, the thermal agglomeration led to the development of porous structures during subsequent annealing. These results also demonstrate that crystallization is followed by agglomeration.

Figure 7 shows the XPS results of as-deposited and post-annealed platinum films. The binding energy of the annealed film is similar to that of the reference platinum,
which has two energy states of $4f_{5/2}$ at 71.3 eV and $4f_{7/2}$ at 74.7 eV. We concluded that the composition of the annealed-porous film corresponds to the pure platinum. In the case of an as-deposited film, however, the binding energy was not that of platinum itself, but of platinum suboxide, $\text{PtO}_x$. This result shows that the reactive sputtering of platinum in an oxygen atmosphere forced the incorporation of oxygen atoms into the deposited platinum followed by the release of oxygen during the post-annealing process. From the survey scan of sample, no existence of impurity phase was confirmed. An interesting aspect of this result is that the adhesion between the deposited film and the substrate was enhanced compared to the film deposited by non-reactive sputtering. Figure 8 shows the surface microstructure of Pt films deposited by non-reactive sputtering without oxygen, which clearly demonstrates the poor adhesion of Pt films by the peel-off test using 3M-tape. It has been reported that pure-metal films deposited by non-reactive sputtering are readily delaminated from SiO$_2$-coated substrate because of the poor adhesion between platinum and SiO$_2$-coated substrates. On the other hand, the Pt films deposited by reactive sputtering were not delaminated from SiO$_2$, even in the case of the thick film (> 800 nm), which corresponds to a highly stressed condition. We believe that the improved adhesion was due to residual oxygen at the interface between the Pt and SiO$_2$. Such strengthening of adhesion was also observed with the YSZ single-crystal surface.

To investigate the electrochemical properties of the fabricated porous platinum film, the polarization resistance of the symmetric porous platinum film cell was compared to dense films in the temperature range from 450 °C to 600 °C in air. Films were deposited on both sides of thin sliced YSZ single crystals. As shown in Figure 9, the polarization resistance of the porous film was five times lower than that of dense film. At 600 °C, the resistance of the porous film was $5.67 \, \Omega \cdot \text{cm}^2$, and that of the dense film was $38 \, \Omega \cdot \text{cm}^2$. The low polarization resistance of the porous Pt film is the result of easier diffusion of oxygen through the pores and increased density of three phase boundaries (TPBs). The polarization resistance is determined by TPB site density and ionic and electronic pathways. In particular, the marked increase of polarization resistance in the dense Pt electrode can be attributed to the reduction of TPB density and poor access of oxygen gas. The microstructure evolution and resultant reduction in polarization resistance of our porous platinum film allows the possibility of physical vapor deposition process adaptation to electrochemical electrode fabrication, especially for solid oxide fuel cells and batteries, which are comprised of porous/dense interface structures.

4. CONCLUSIONS

Porous platinum thin films have been fabricated by reactive sputtering combined with a subsequent thermal annealing process. The as-deposited amorphous and dense platinum films transformed into porous and crystalline phases. The porous structure evolution was carried out by a thermal grooving mechanism which required crystallization. Reaction sputtering in an oxygen atmosphere enhanced adhesion between the metal film and substrate. The platinum film with controlled porosity showed superior electrochemical properties, such as low polarization resistance compared to the dense film. The polarization resistance of the porous platinum film was five times lower than that of the dense platinum film in the temperature range from 450 °C to 600 °C.

Acknowledgment: This work was supported by a grant from the National Research Foundation of Korea funded by the Korean Government (MEST) (NRF-2010-C1AAA001-2010-0028971).

References and Notes


Received: 7 July 2012. Accepted: 2 August 2012.