Fabrication of Hole-Array Metal Membrane by Two-Step Replication

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Abstract: The nano-technology was recently regarded as a very important field to research. In this work, we build up a Cu metal hole-array membrane by using the nano-technology of two-step replication technique and electrochemical deposition. The negative-type structure can be obtained from poly(methyl methacrylate) (PMMA). PMMA with low molecular weight (15000 and 70000 g/mole) was difficult to fabricate the negative-type structure from PAA template. The increasing molecular weight of PMMA to 965000 g/mole was helpful for the fabrication of negative-type PMMA. The length of PMMA nano-array was about 30μm. The Cu metal hole-array membrane can be electrochemically deposited into the bottom part of the negative-type PMMA nano-array. The morphology of Cu metal hole-array membrane was similar to the feature of commercial PAA mother template.

Key-Words: porous anodic alumina, PMMA, two-step replication, electrochemical deposition, hole-array structure

1 Introduction

Nano-technology is in highly interesting in many field recently due to the nano-scale materials exhibit special and excellent properties. The precise control of the geometrical structure of materials at dimensions ranging of submicrometer to nanometer scale is a potential field for developing functional materials with nano-scale structure and large surface area. Template-assisted method is a conventional technique for the fabrication of nano-structure such as nanodots, nanowires and nanotubes. And the two-step replication was a technique based on the template-assisted method. The two-step modeling process can fabricate nanohole-array structure using the porous anodic alumina, which is a typical self-organized hole-array structure [1-5], as a template. The two-step replication of PAA can fabricated the nanohole-array membrane of metals [1-4] and semiconductors [5]. The two-step replication consists of two main parts: (I) the fabrication of negative-type PMMA of PAA porous structure and (II) the subsequently deposition of various materials into the cavity of the negative type to form a positive type by electrochemical deposition (ELD) or electrophoresis deposition (EPD). PMMA was used as the fill material due to its great chemical stabilization and easily fabricated process. The electrochemical deposition was used to deposit the Cu membrane from negative-type PMMA because of electroplating was a conventional technique to fill the template.

In this report, we build up a Cu hole-array membrane by using the two-step replication technique and electrochemical deposition. The two-step replication for fabrication of Cu hole-array membrane was including the negative-type structural replication from commercial porous anodic alumina (PAA) by poly(methyl methacrylate) and the electroplating of Cu metal from divalent copper solution. This two-step replication technique will be applied in many applications such as energy storage and the detail of the research will be discussed in the future.

2 Experimental procedure

An experimental process for fabrication a hole-array structure by two-step replication technique is shown schematically in Fig.1. The commercial porous anodic alumina (PAA) was used as the mother structure to build up a hole-array Cu membrane by two-step replication. The hole diameter of the PAA was 200nm and the thickness was 60μm. A thin Pt layer was deposited on the surface of the PAA template by evaporation, and the Pt layer was used as an electrode for the subsequent metal-plating process. Different molecular weight (Mw=15000, 70000, and 965000g/mole) of poly(methyl methacrylate) (PMMA) was dissolved in chlorbenzene with various concentration and was injected into the PAA template. After the evaporation of the chlorbenzene, the PAA template was removed by 5M NaOH and a replicated negative-type PMMA with a cylindrical structure was obtained. The Pt layer coated on PAA surface previously was transfer to the bottom of the PMMA cylindrical nano-array as a current collector for electroplating. The Cu metal membrane was electrochemically deposited from the solution that containing $CuSO_4 \cdot 5H_2O$ (238g/L) and H_2SO_4 (21g/L), and the deposition process was carried out in room temperature. The metal deposition started from the bottom part of the PMMA cylindrical nano-array and filled the cavity of the replicated negative-type PMMA structure gradually. After the removal of PMMA by acetone, a Cu hole-array membrane was obtained.

The morphologies of the replicated negative-type PMMA cylindrical structure and Cu hole-array membrane were observed by scanning electron microscope (Hitachi S4100).

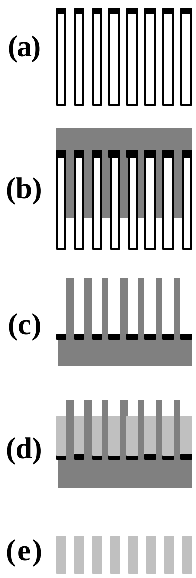

Fig. 1 Schematic diagram of the process for the fabrication of the metal nanohole array: (a) Pt deposition with vacuum evaporation on porous alumina, (b) injection of PMMA, (c) remove porous alumina by NaOH, (d) metal electroplating, and (e) metal hole array (remove PMMA by actone).

3 Results and discussion

3-1 Fabrication of PMMA cylindrical structure

The SEM observations of replicated negative-type PMMA (molecular weight of 15000 g/mole) that fabricated by template-assaited method were shown in Fig.2. The Fig.2(a) and 2(b) were PMMA concentration of 10wt% and 15wt% respectively. Because of the low molecular weight of PMMA, the replicated PMMA linked and showed a porous structure. The replicated negative-type PMMA didn't exhibit fine cylindrical structure.

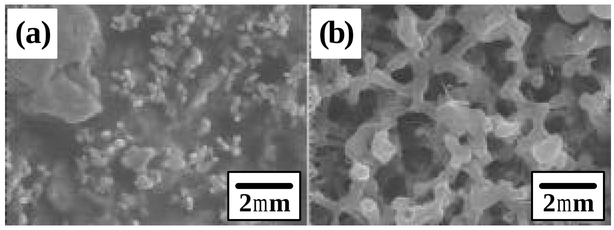

Fig.2 SEM top-views of replicated negative type of PMMA (molecular weight of 15000 g/mole) that fabricated with various concentrations: (a) 10wt% and (b) 15%

The SEM observations of replicated negative-type PMMA (molecular weight of 70000 g/mole) that fabricated by template-assaited method were shown in Fig.3. Fig.3(a) was PMMA concentration of 10wt% and 3(b) and 3(c) were PMMA concentration of 15wt%. From Fig.3(c), the structure of replicated negative-type PMMA array that obtained from 70000 g/mole PMMA possessed cylindrical structure. This feature was better than that obtained from 15000 g/mole PMMA. It is supposed that the interaction of high Mw PMMA molecules was helpful for the fabrication of PMMA replication. But the cylindrical structure was not good enough even though the molecular weight was increasing to 70000 g/mole.

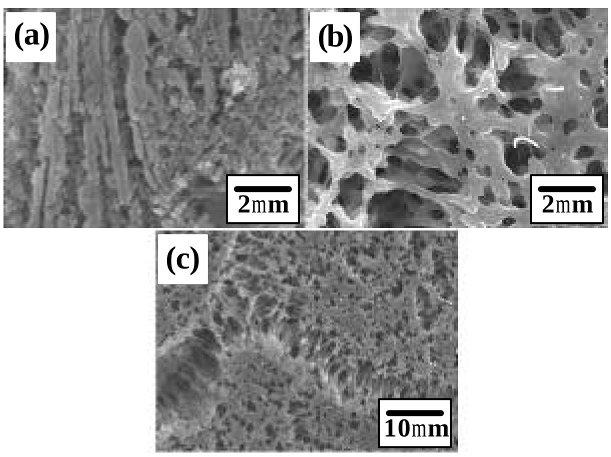

Fig.3 SEM top-views of replicated negative type of PMMA (molecular weight of 70000 g/mole) that fabricated with various concentrations: (a) 10wt%, (b) and (c) 15%

Because of the increasing molecular weight of PMMA was helpful to obtained fine cylindrical structure. The Mw of PMMA was increased to 965000 g/mole. The replicated negative-type PMMA nano-array that fabricated from molecular weight of 965000 g/mole PMMA was shown in Fig.4. The 4(a), 4(b), and 4(c) were top-view and 4(d), 4(e), and 4(f) were the cross-section images of PMMA nano-arrays that obtained from various PMMA concentrations of 10wt%, 13wt%, and 15wt%. From the top-view observations, the aggregation of the PMMA nanowires was observed, and it is due to the Van der Waals' force between the long length of PMMA nanowires. The cross-section images showed that the PMMA with 200nm diameter was successful obtained by injecting 965000 g/mole PMMA into the PAA template.

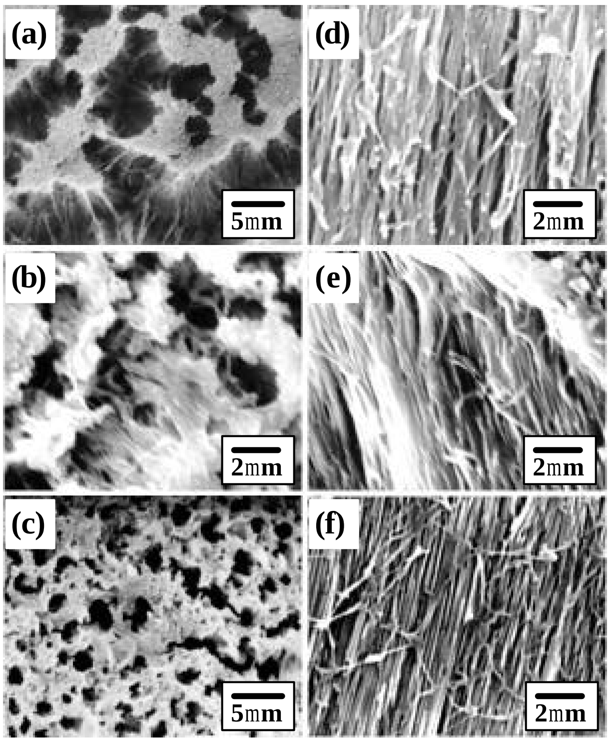

Fig.4 Top-view images of PMMA nano-arrays fabricated at PMMA concentration of (a) 10wt%, (b) 13wt%, and (c) 15wt%, and cross-section images (d) 10wt%, (e) 13wt%, and (f) 15wt% (Mw of PMMA was 965000 g/mole)

3-2 Cu hole-array membrane obtained by electroplating

Fig.5 shows the curve of current transient for the Cu metal electroplating into the negative-type PMMA. Fig.5(a) and 5(b) show the conventional curves for electroplating into a template [6-7]. In the short time (region I), the curve (Fig.5(a)) indicated that the Cu metal was continuously deposited into the cavity of the negative-type PMMA. In region II, the increasing current resulted from the increasing deposition area due to the cavity of the negative-type PMMA was filled with Cu metal and the Cu began to coalesce and formed a Cu layer over the negative-type PMMA. After the formation of a Cu layer covered on the negative-type PMMA, a metallic top layer grew continuously, as shown in region III. Therefore, based on the current transient of electrochemical deposition into the negative-type PMMA, the thickness of Cu hole-array membrane can be controlled.

Fig.6 shows the SEM top-view observation of Cu hole-array membrane that fabrication by electroplating. The morphology of Cu hole-array membrane was similar to the feature of commercial PAA template. Based on this work, Cu hole-array membrane was successful fabricated by the two-step replicated technique and the application for replication with various materials will be detailed in the future.

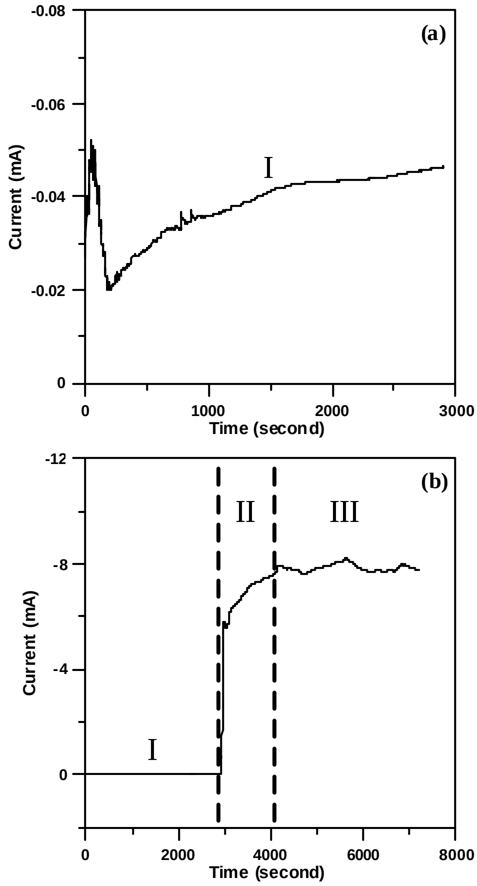

Fig.5 The current transient curves for the Cu metal electroplated into the negative-type PMMA: (a) short time (<3000 seconds) and (b) long time.

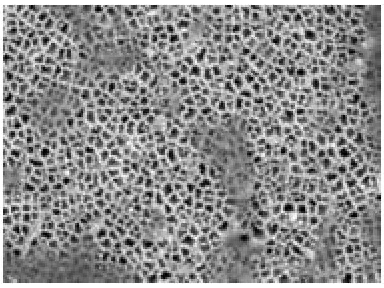

Fig.6 SEM top-view observation of Cu hole-array membrane that fabrication by electroplating

4 Conclusion

The PMMA with low Mw (15000 and 70000 g/mole) can't build up fine negative-type PMMA replication. The negative-type PMMA replicated structure was successful fabricated by increasing the molecular weight of PMMA to 965000 g/mole. Cu metal hole-array membrane was deposited by electrochemical deposition. The morphology of Cu hole-array membrane was similar to the feature of commercial porous anodic alumina (PAA). The thickness of Cu hole-array membrane can be controlled by the curve of current transient. This two-step modeling process was useful to build up a hole-array structure and the applications of this technique in fuel cells and batteries will be detailed in the future.

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