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Communication—Micro-Scale Columnar Architecture Composed of Copper Nano Sheets by Electrodeposition Technique

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Micro-scale columnar architectures composed of copper sheets with nanometer thickness were fabricated by electrodeposition using a photolithography technique. A copper sulfate solution containing a polyacrylic acid was used as the plating bath, and the electrodeposition was conducted under galvanostatic conditions. Patterned electrodeposits with a cylindrical shape and composed of thin copper sheets were formed. Every copper deposit had openings on the top and side regions and also had a porous interior. This novel three-dimensional (3D) copper architecture should provide functional copper electrodes with large effective surface areas.

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Since three-dimensional (3D) nanostructured metal architectures have large surface areas as well as high electrical conductivities, their application as electrodes for devices such as supercapacitors,¹ fuel cells,² and batteries³ has been intensively researched. In particular, the application of 3D copper nanostructured architectures in components such as tin-based lithium-ion battery anodes⁴⁻⁸ and glucose sensors⁹⁻¹¹ is currently one of the hottest areas of research. Various methods of forming 3D copper architectures have been examined, including de-alloying of copper from an Al-Cu alloy⁴ and electrodeposition of copper using templates such as hydrogen bubbles⁵⁻⁷ or porous alumina.⁸ Our group has developed a very simple template-free method for fabricating 3D copper nanostructured architectures by one-step electrodeposition in which an organic additive is introduced to the electrodeposition bath.¹² The 3D copper architecture formed by the one-step electrodeposition (3DC1) consists of thin copper sheets and has a porous interior. Although such 3D architectures have large surface areas and can therefore be expected to be useful as high-reaction-rate electrodes, the bottom region of the structures is often not fully functional due to an insufficient supply of electrochemically active species. If the electrode reaction rate is dominated by such transport limitations, then improvement in the supply rate of the active species toward the outer Helmholtz plane of the deep interior electrode surface should increase the reaction rate. In general, pattern plating using thick photoresists can provide fine metal structures with a high aspect ratio. If the patterned structures have a columnar shape, they can make contact with the surrounding media, such as the electrolyte, not only at the top surface but also at the side surface, improving the supply rate of active species to the deep interior surface. Therefore, patterned columnar 3DC1 is expected to exhibit high reaction rates.

In this study, patterned 3DC1 was formed by electrodeposition using a photolithography technique, and the microstructure of the electrodeposits was analyzed.

Experimental

A sulfuric plating solution composed of 0.85 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 0.55 M H_2SO_4 was used as the base plating bath. 3×10^{-4} M polyacrylic acid (mean molecular weight 5000: PA-5000) was added to the base plating bath, resulting in the 3DC1 plating bath. The process of fabricating a patterned 3DC1 is summarized in Fig. 1. A pure copper substrate was coated with a negative-type dry film photoresist (RY-3025, Hitachi Chemical Co., Ltd.) approximately 30 μm thick, and then patterned using a photomask with an arrangement of 50- μm -diameter circles at 50 μm intervals. A copper plate containing phosphorous was used as the anode. The electrodeposition of copper

onto the substrate (the exposed copper surface area, i.e., the total surface area of the circles, was approximately 2 cm^2) was carried out under galvanostatic conditions (20 mA) using the 3DC1 plating bath without agitation at 25°C. After the electrodeposition, the photoresist was removed using an alkaline solution, resulting in a patterned 3DC1. The morphology of the patterned 3DC1 was observed using field emission scanning electron microscopy (FE-SEM; SU8000, Hitachi High Technologies). Cross-sectional samples of the patterned 3DC1 were prepared using a focused ion beam system (JIB-4610F, JEOL) and observed by FE-SEM.

Results and Discussion

Exfoliation of the patterned photoresist from the copper substrate was not observed during any of the electrodeposition tests, and copper was perfectly deposited in the photoresist pattern in every electrodeposition test. Figure 2 shows SEM images of electrodeposits from the 3DC1 plating bath with 60 C (30 C cm^{-2}) of charge transferred. The deposits were regularly spaced on the substrate, and all of the deposits had almost the same volume (Fig. 2a). Each electrodeposit had a similar cylindrical appearance and was composed of thin copper sheets. Furthermore, openings into the interior of the deposits were observed not only on the top surface, but also on the side surface (Fig. 2b).

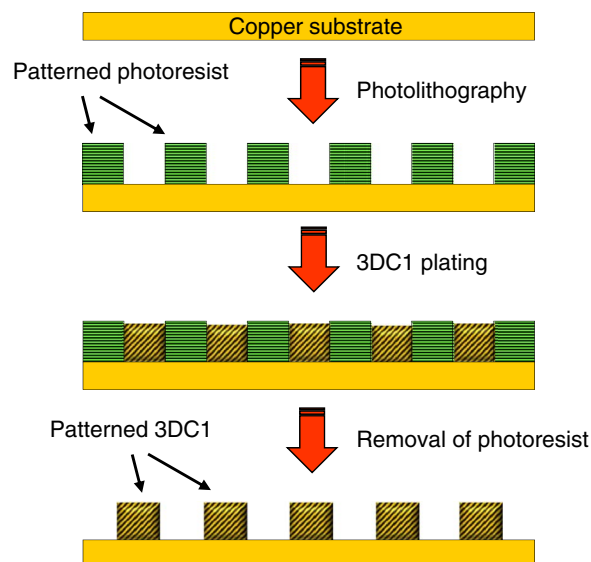


Figure 1. Schematic illustration of the fabrication process for the micro-scale columnar architecture composed of copper thin sheets.

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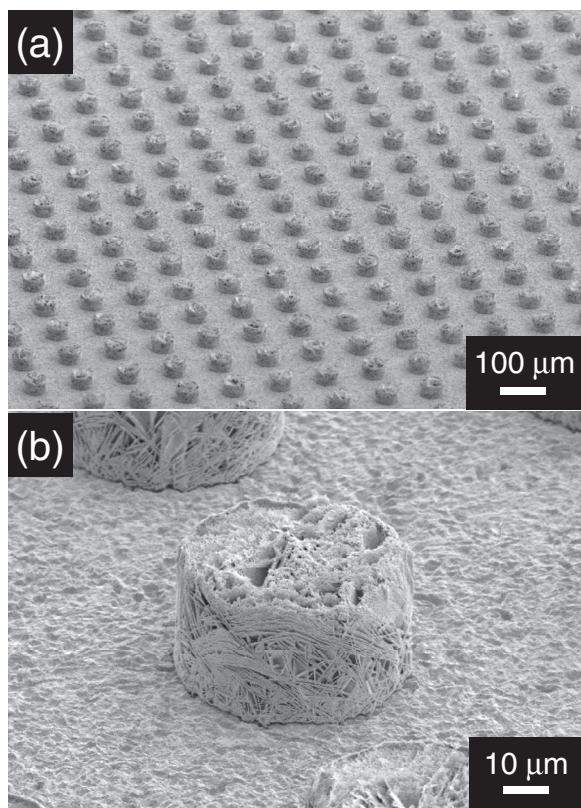


Figure 2. SEM images of patterned 3DC1: (a) low magnification and (b) high magnification. The amount of charge transferred is 60 C (30 C cm^{-2}). The observation angle is 60° .

Figure 3 displays SEM images of the external appearance and cross sections of electrodeposits formed using various amounts of charge transferred. Each patterned electrodeposit grew while maintaining openings not only on the top surface but also on the side surface (Figs. 3a–3c). The deposited copper sheets tended to pile up when the amount of charge transferred increased (Fig. 3c). The cross-sectional SEM images (Figs. 3a'–3c') show that these electrodeposits had pockets of open space even deep within them. Furthermore, the growth of the copper sheets terminated at the sides of the deposits. This means that the copper sheets stop growing when they meet the inner surface of the patterned photoresist. The thickness of the patterned electrodeposits was measured from the cross-sectional SEM images, taking the observation angle into account. Furthermore, the porosity of the deposits was estimated from the measured thickness of the deposits and the calculated thickness of a dense copper deposit using Faraday's law of electrolysis.

Figure 4 shows the relationship between the amount of charge transferred, the thickness of the deposits, and the porosity of the deposits. The thickness of the deposits increased monotonically with increasing amount of charge transferred, but not in a linear fashion. Although the porosity was approximately 70% regardless of the amount of charge transferred, it tended to decrease with increasing energizing quantity. As shown in Figs. 3c and 3c', the copper sheets tended to pile up as the amount of charge transferred was increased. This would be expected to decrease the porosity of thicker patterned deposits. The suppression of such pile-up should be an effective means of maintaining high porosity even for thicker deposits, and this will be addressed in future work.

Summary

Patterned 3DC1 was fabricated using an electrodeposition technique assisted by photolithography. Cylindrical copper electrodeposits

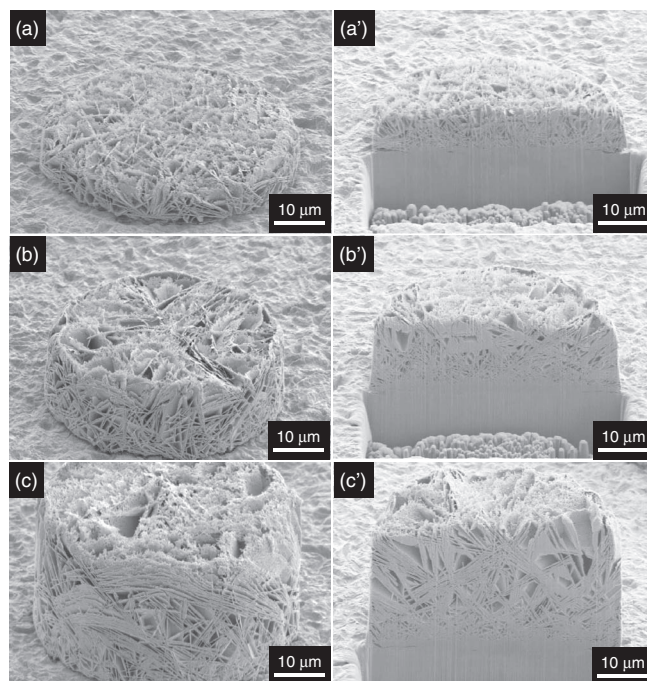


Figure 3. SEM images of patterned deposits formed under various amounts of charge transferred: (a) exterior and (a') cross section at 15 C, (b) exterior and (b') cross section at 30 C, and (c) exterior and (c') cross section at 60 C. The observation angle is 60° .

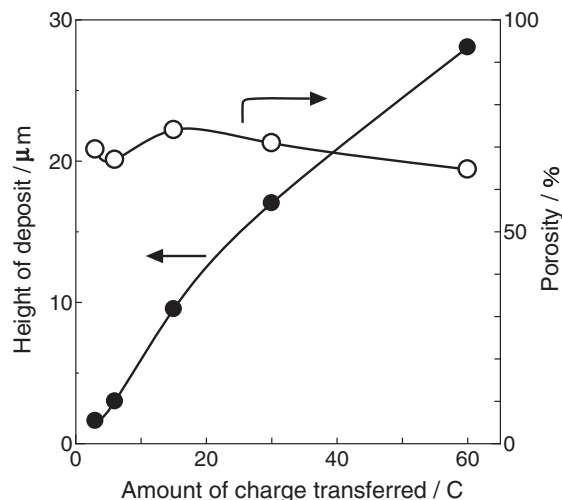


Figure 4. Relationship between amount of charge transferred, thickness of deposit, and porosity.

composed of thin copper sheets with porous interiors were formed. The deposits contained openings not only at the top but also on the sides. Patterned 3DC1 can be applied to high-performance functional electrodes.

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