Self-organized Formation of Layered Nanostructures Produced by Oscillatory Electrodeposition

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Introduction

Self-organized formation of ordered micro-and nano-structures of metals and semiconductors at solid surfaces has attracted strong attention in view of nanotechnology. The self-organization method has an advantage over photolithography and the surface probe method, in that it meets both conditions of an atomicscale technique and adaptability to mass production. Electrochemical reactions with nonlinear kinetics show self-organized and dynamic spatiotemporal patterns, such as electrochemical oscillations. It is possible to record ever-changing self-organized spatiotemporal patterns formed through an oscillatory electrodeposition as architecture of electrodeposits. Here is our key strategy to construct ordered nanostructures.

In the present paper, we show that the current oscillation during CuSn-alloy electrodeposition gives layered nanostructures with periodical modulation of Cu and Sn contents. The revealed mechanism of the oscillation enables the accurate control of the oscillatory behavior and the resulting nano-structure.

Experiment

Polycrystalline Au disc was used as the working electrode, together with Pt plate as the counter electrode and Ag|AgCl electrode as the reference electrode. The electrolyte was 0.6 M $H_2SO_4 + 0.5$ M citric acid containing certain amounts of CuSO₄, SnSO₄, and surface surfactant (Amiet-320, Kao corp.). Elemental analyses were performed by scanning Auger electron spectroscopy (AES) with a scanning electron microscope operating at 10 kV.

Result and Discussion

Figure 1(a) shows *j*-*U* curves obtained in the electrolytes with and without surfactant. It can be seen that a negative differential resistance (NDR) appears only in the presence of surfactant at around -430 mV where CuSn-alloy phase is electrodeposited. In case the *U* was fixed around the potential region of the NDR, current oscillation appears spontaneously as shown in Fig.1 (b).

Figure 2 shows AES depth profile of the deposits obtained under oscillatory condition, in which Cu and Sn contents show periodical modulations. In order to analyze the cross section of the film in more detail, we obtained a bowl-like hole in the film, which is produced by Aretching in vacuum. Figure 3(a) shows SEM image (topview) of the hole, in which concentric rings with white and black colors can be seen. Figure 3(b) shows a 2dimentional mapping of Sn content. (A part of the rings shown in Fig. 3(a) is enlarged.) It was revealed by comparing Figs. 3(a) and (b) that the white and black parts in the SEM image are Sn-rich and Cu-rich layer, respectively. It should be noted here that the number of the set of the white and black layers is always in accordance with that of the number of the oscillation period, meaning that the layered nanostructure is induced by the current oscillation.

It is well known that an autocatalytic process is necessary for the appearance of chemical oscillation. According to recent theoretical work on electrochemical oscillation, the autocatalytic process becomes to appear by coupling of the NDR in the *j* vs. U curve and the ohmic drop in the electrolyte. Therefore, it is very important to clarify the origin of the NDR for understanding the mechanism of the electrochemical oscillation. As shown in Fig. 1(a), the NDR in the present case appears only when the surfactant is added to the solution. On the basis of the result, the mechanism of the NDR can be explained as follows. The codeposition of Cu and Sn, in which the Cu deposition is dominant, should result in a negatively polarized surface owing to a difference in the electronegativity (or work function) between Cu and Sn as well as the principle of the equal Fermi level of electrons within a conductor. The negatively polarized surface induces the adsorption of the surfactant that is protonated and positively charged in acidic solution, which in turn suppresses the diffusion of metal ions and causes a decrease in j. Such a decrease in j becomes stronger with negative potential shift, thus causing the appearance of the NDR. We are going to report more detailed mechanism of the self-organized formation of the layered nanostructures as well as the other experimental results.



Fig. 1 (a) *j vs. U* curves in the presence (solid curve) and absence (dashed curve) of Amiet-320. (b) A Time course of current oscillation at U = -432 mV. Electrolyte: 0.15 M CuSO₄ + 0.15 M SnSO₄ + 0.6 M H₂SO₄ + 0.5 M citric acid + 0.5 mM Amiet-320.



Fig. 2 Auger depth profiles of composition in growth direction of the film obtained under oscillatory condition.



Fig. 3 (a) SEM top-view image of the CuSn-alloy layered nanostrucutre. The hole is produced by Aretching. (b) 2-dimensional mapping of the Sn content of the enlarged part of Fig. 3(a).