

Metal Latticeworks formed by oscillation-coupled electrodeposition

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Introduction

Self-organized formation of ordered micro- and nano-structures of metals and semiconductors at solid surfaces has been attracting keen attention in view of nanotechnology. Recent studies on non-equilibrium, non-linear chemical dynamics have proved a large possibility of self-organized formation of a variety of ordered structures such as stripes, dot arrays, and target patterns, but all the patterns ever reported are 2-dimensional (2-D) and horizontal, lying in parallel to substrate surfaces. The formation of organized “vertical” structures and further organized 3-D structures will need novel strategy that has never been adopted. Electrochemical systems have an advantage in that they can provide spatially non-local and global coupling. Here we report that strikingly well-ordered metal latticeworks, standing perpendicular to the substrate, are formed spontaneously in oscillatory electrodeposition, through ingenious cooperation of various processes with long-range spatiotemporal synchronization. The principle is unique, never realized by other methods, and opens a new promising field for nanostructuring.

Experiment

Polycrystalline Pt (99.97 % in purity, 0.28 cm² in area) was used as the working electrode. A Pt plate and a Ag|AgCl electrodes were used as the counter and the reference electrodes, respectively. The solutions were prepared using special grade chemicals and pure water obtained by purification of deionised water with a Milli-Q water purification system. The inspection of electrode surface with electrodeposits was performed by a high-resolution scanning electron microscope (SEM, Hitachi S-5000). The in-situ observation of the surface during electrodeposition was done by a digital microscope (VH-5000, Keyence) with high magnification lens (VH-Z50, Keyence)

Results

Figure 1 shows (A) an optically microscopic (OM) image of the latticeworks of deposited tin (Sn), together with (B) a schematic illustration of the deposit structure. Brightened images at the upper right edges of the latticeworks in (A) are due to reflection of microscopic light irradiated from the upper right side. The deposition experiments were carried out in 0.2 M Sn(II) + 4.0 M NaOH, with a polycrystalline Sn disc being used as the working electrode. When the electrode potential (E) was scanned from positive to negative, a Sn-depositing cathodic current started to flow at about -1.1 V vs. Ag/AgCl (sat. KCl) and reached the diffusion-limited current at about -1.2 V. A potential oscillation appeared when the current density (j_{ex}), regulated externally with a potentiogalvanostat, exceeded the diffusion-limited current density (j_{diff}), where the current density was calculated for the apparent flat-surface area of the electrode. The Sn networks of Fig. 1 were obtained under oscillating electrodeposition at constant $j_{ex} = -36$ mAcm⁻².

The Sn latticeworks were very fragile, only stable when they were kept in an aqueous electrolyte as they were produced, and therefore it was impossible to transfer them to a sample compartment of a scanning electron microscope (SEM) with no breakage.

We inspected growth processes for the Sn latticework during the potential oscillation under an in-situ condition, using an optical digital microscope and a video camera. In addition, we also inspected pieces of the Sn latticeworks with an SEM by pulling out the electrode from the electrolyte at various stages of the potential oscillation. Pictures in Fig. 2, marked by OM and SEM, show results of such experiments. The numbers with parentheses, (1), (2), (3), and (4), added on the pictures mean that they were taken at a stage of the potential oscillation, marked by the same number in Fig. 2(A). The bottom row just below the OM pictures shows schematic illustrations of the OM images of the Sn deposits. The results shown in Fig. 2 clearly show that the latticework formation is synchronizing with the potential oscillation.

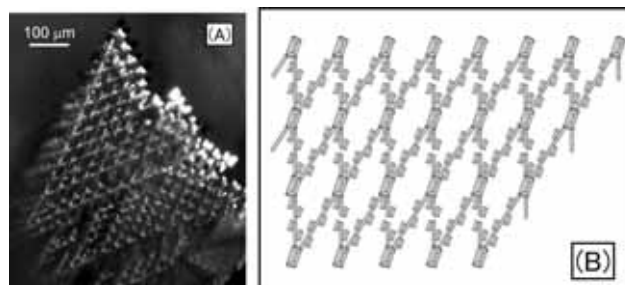


Figure 1 (A) An optically microscopic (OM) image of highly ordered 2-D latticeworks of tin (Sn), produced by oscillation-induced electrodeposition, and (B) a schematic illustration of the latticework structure.

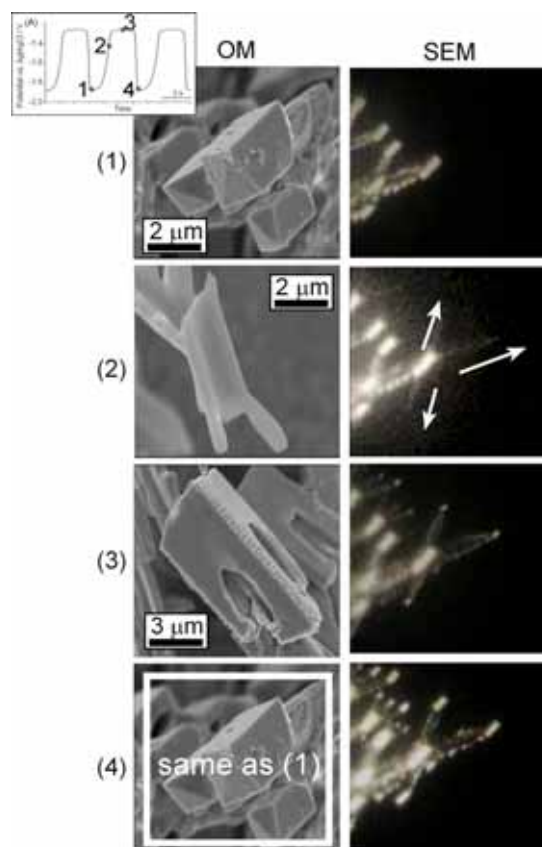


Figure 2 (A) A potential oscillation observed for Sn electrodeposition at a constant externally applied current density $j_{ex} = -36$ mA cm⁻². Pictures marked by OM and SEM show optical microscopic (OM) and scanning electron microscopic (SEM) images of Sn deposits, respectively. The numbers, (1), (2), (3), and (4), added on the pictures mean that they were taken at a stage of the potential oscillation marked by the same number in (A).