Nonlinear Electrochemical Oscillations during Tin Electrodeposition in the Presence of Surface Surfactant

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Electrochemical reactions with nonlinear kinetics show a variety of interesting dynamic behavior such as periodic and chaotic oscillations [1,2]. Recently, growing attention has been paid to the observation and understanding of spatiotemporal patterns arising from nonlinear kinetics, such as traveling chemical waves [3,4] and Turing patterns [5]. However, the number of reports about the oscillatory electrochemical deposition of metals is far less than the other electrochemical oscillators, such as oscillations during anodic metal dissolution and electrocatalytic reactions. Very recently, nonlinear reactions in electrochemical deposition are gradually regarded as useful phenomena for applying to noble methods for constructing self-organized structures on solid surfaces. In the present paper, we report that the formation of a flat surface of tin by the use of nonlinear electrochemical oscillation.

Figure 1(a) shows a current density (*j*) vs. potential (*U*) curve in a 0.3 M $SnSO_4$ + 0.6 M H_2SO_4 solution when the potential was scanned toward the negative at a rate of 10 mV/s under a potential-controlled condition. A small cathodic current due to the Sn reduction starts at ca. –0.20 V vs. Ag/AgCl and it increases suddenly at –0.45 V. A current due to hydrogen evolution is overlapped from –0.7 V. In the presence of 0.5 mM surface surfactant (POOA-10), a current decrease, i.e., negative differential resistance (NDR), is observed in a potential region from –0.55 V to –0.65 V as shown in Fig. 1(b). When an external resistance (40 Ω) is inserted between WE and RE, a current oscillation appears on the NDR (Fig. 1(c)). The oscillation continues for 20 min at a constant potential (-0.86 V).

The appearance of NDR (Fig. 1(b)) is explained by considering that the adsorbed POOA-10 inhibits the Sn reduction. Since the POOA-10 is a quaternary ammonium cation in acidic solutions by absorbing proton, its coverage increases with the negative shift of electrode potential. So the Sn reduction current is suppressed as the negative potential shift, i.e., NDR appears. In the potential region of the NDR, the electrochemical system becomes unstable and current oscillation appears. A mathematical simulation also confirms this model.

Figure 2 shows SEM images of electrode surfaces. Figure 2(a) is for a deposition with a current oscillation. On the other hand, Fig. 2(b) is for a deposition under a constant applied potential and a current. In case the Sn is electrodeposited under a condition where the reduction current oscillates, the electrode surface is more smooth than that obtained under a constant current. In a current oscillation, the Sn reduction occurs in the entire electrode surface synchronously. This is why the smooth surface is obtained under a current oscillation. The details will be mentioned in the presentation.

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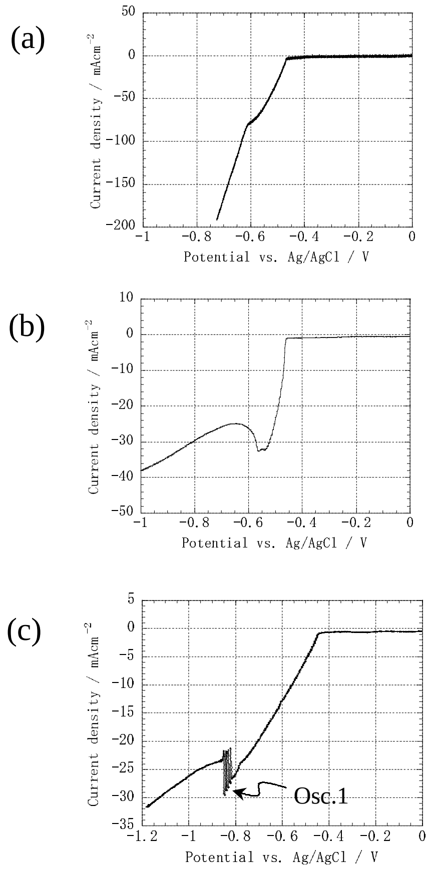

Fig. 1 (a) 0.6M H_2SO_4 + 0.3M $SnSO_4$, (b) 0.6M H_2SO_4 + 0.3M $SnSO_4$ + 0.5mM POOA-10, and (c) 0.6M H_2SO_4 + 0.3M $SnSO_4$ + 0.5mM POOA-10 + 40 Ω external resistance.

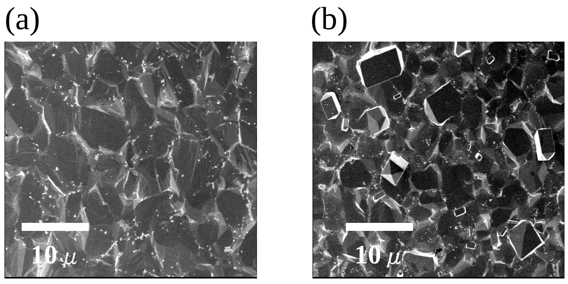

Fig. 2 SEM images of the electrode surfaces obtained under a current oscillation for (a) and under a constant current for (b)