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Electrochimica Acta 50 (2005) 5050-5055

electrochimica Actu

www.elsevier.com/locate/electacta

Tuning of the spacing and thickness of metal latticeworks by modulation of self-organized potential oscillations in tin (Sn) electrodeposition

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Received 11 November 2004; received in revised form 20 January 2005; accepted 20 January 2005 Available online 11 July 2005

Abstract

The spacing and thickness of tin (Sn) latticeworks, formed in oscillatory electrodeposition, were tuned through modulation of the oscillation by changing the applied current density (j_{ap}) and the concentration of Sn(II) ions (C_{Sn}) in the electrolyte. When the j_{ap} was made higher or the C_{Sn} was made lower, the time of transition from the negative-side to positive-side potential (t_1) of the oscillation became longer and the lattice spacing (d) of the latticework was enlarged. The modulation by the j_{ap} change was especially interesting because it was simple and produced, e.g., a latticework with different spacings. The tuning of the latticework by the oscillation modulation was understood within the framework of our previously proposed model for the formation of latticeworks by oscillatory electrodeposition. © 2005 Elsevier Ltd. All rights reserved.

Keywords: Oscillation; Electrodeposition; Self-organization

1. Introduction

Oscillatory electrodeposition is an interesting target from the point of view of production of micro- and nano-structured materials because it has a possibility to produce ordered electrodeposits by recording ever-changing self-organized spatiotemporal patterns during the oscillation. To date, some examples have been reported on formation of regulated structures by oscillatory electrodeposition. One example is layered structures, which were formed in a number of systems, such as Cu/Sn [1,2], Cu/Cu₂O [3], Ni/NiP [4,5] and Ag/Sb [6] deposition. It is expected that this type of deposits is formed by layer-by-layer electrodeposition synchronizing with spontaneous electrochemical oscillations.

Another example is dendritic crystal growth accompanied by potential or current oscillations [7-12]. These type

of deposits are very attractive from the point of view of two- or three-dimentional structurization because the electrodeposits grow vertically from substrates in this case. Very recently, we found [11] that metal latticeworks lying vertical to the electrode surface were spontaneously produced in synchronization with a potential oscillation in tin (Sn) electrodeposition. It was shown that periodic occurrence of three successive processes (autocatalytic growth of needlelike tin under the diffusion-limited condition, steady growth of cuboid-shaped tin under the reaction-limited condition and autocatalytic surface oxidation of the needles and cuboids) led to the oscillation and the formation of latticeworks. For normal dendrite formation, only the autocatalytic growth of needle-like metals continues to occur with occasional branching. The mechanism of the above oscillatory electrodeposition is quite unique, operating under particular conditions, and the formation of metal latticeworks has never been realized by other methods. It should be noted that the proposed mechanism has a certain generality because we found [12]

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^{0013-4686/\$ –} see front matter @ 2005 Elsevier Ltd. All rights reserved. doi:10.1016/j.electacta.2005.01.055

that zinc (Zn) electrodeposition leading to periodic growth of stacked hexagonal wafers also proceeded by a similar mechanism.

In the present paper, we report that the spacing and thickness of the latticeworks for Sn are tunable by the modulation of the oscillation, induced by changing the applied current density (j_{ap}) and the concentration of Sn(II) ions (C_{Sn}).

2. Experimental

The experimental setup for electrochemical measurements and in situ observation of deposits is schematically shown in Fig. 1. A polycrystalline Sn disc was used as the working electrode. It was etched with 1 mM HCl just before experiment. A Pt plate (1 cm²) and an Ag|AgCl|saturated KCl electrode were used as the counter and reference electrodes, respectively. The applied current density (j_{ap}) versus potential (U), and U versus time (t) curves were measured with a potentiogalvanostat (Nikko-Keisoku, NPGS-301) and recorded with a data-storing system (Keyence, NR-2000) at a sampling frequency of 100 Hz. The deposits formed on the surface of the working electrode was observed with an optical microscope with a digital CCD camera (OM, VH-5000, Keyence), placed on a side of the electrode (see Fig. 1). Detailed inspection of electrodeposits was carried out with a high-resolution scanning electron microscope (SEM, Hitachi S-5000).

The Sn(II) solution for Sn deposition was prepared by addition of SnO powder into 4.0 M NaOH. Special grade chemicals were used together with pure water, which was obtained by purification of deionised water with a Milli-Q water purification system. The solution was kept stagnant in all experiments in order to avoid disruption of fragile metal latticeworks as the deposits. The ohmic drop in the solution



Fig. 1. Schematic illustration of an experimental setup used in this work.

between the working electrode and the reference electrode was not corrected in the present work.

3. Results

Fig. 2 shows a j_{ap} versus U curve (for Sn deposition) in 4.0 M NaOH containing 0.4 M Sn(II), obtained in the first negative scan of j_{ap} under a j_{ap} -controlled condition. With the increasing j_{ap} in the absolute value, the U shifts gradually from -1.15 V toward the negative. When the j_{ap} reaches and exceeds the diffusion-limited $j(j_{dl})$ for the Sn deposition, the U jumps to a large negative value and a potential oscillation starts to occur, as reported previously [11].

Fig. 3 shows wave forms of the potential oscillation at fixed j_{ap} values in 4.0 M NaOH with (a) 0.2 M and (b) 0.4 M Sn(II).



Fig. 2. Current-controlled j_{ap} vs. U curve in 4.0 M NaOH containing 0.4 M Sn(II), obtained in the first negative j_{ap} scan. The scan rate is 0.71 mA cm⁻²s⁻¹.



Fig. 3. Potential oscillations observed at a constant j_{ap} of: (a) -36 mA cm^{-2} in 0.2 M Sn(II) + 4.0 M NaOH and (b) -71 mA cm^{-2} in 0.4 M Sn(II) + 4.0 M NaOH.

The fixed j_{ap} was chosen to be around two times of the j_{dl} for better comparison with each other, by taking into account that the j_{dl} depends on the concentration of Sn(II) ions (C_{Sn}). Hereafter, we focus on two features of the wave form of the oscillation: (1) the transition time, t_1 , from the negative-side to the positive-side potential of the potential oscillation and (2) the amplitude, A, of the oscillation. Comparison of Fig. 3(a and b) shows that the t_1 is shorter in the higher C_{Sn} solution, whereas the A is almost independent of C_{Sn} . It should be noted that stable oscillation continued only for about first 120 and 60 s in the solutions of 0.2 and 0.4 M Sn(II), respectively. The wave form then gradually changed with time and, finally, the oscillation stopped with U at the positive-side potential. The wave form and the latticeworks described below were investigated during the stable oscillation.

Fig. 4 indicates how the latticework as the electrodeposit is formed in synchronization with the potential oscillation. A similar result was reported in our previous letter [11]. Pictures in Fig. 4(b) were taken under in situ conditions with an optical microscope (OM) during the latticework formation. The numbers added to the pictures mean that they were taken at stages of the potential oscillation marked by the same numbers in Fig. 4(a). Fig. 4(c) is a schematic illustration of the latticework for easy understanding. These results show that sharp needles grow during the period of the transition from the negative-side to the positive-side potential of the oscillation (stages (1)–(3)), whereas the needles stops to grow when the potential reaches the positive-side potential. It should be mentioned that long-range synchronization of the periodic needle growth processes all over the needles leads to a highly ordered latticework. Fig. 4(d) shows an SEM image of the latticework, taken at the positive-side potential, in which cuboid crystals are formed at the tips of the needles, indicating the cuboid crystals are formed during the positive-side potential. The cuboid crystal is made of tetragonal Sn (β -Sn) and surrounded with the closest packed, thermodynamically stable (110) and (011) faces. Since the following growth of needles starts at the tips of the cuboid crystals in three crystallographically equivalent directions as seen in Fig. 4(b and c), the cuboid crystals are located at lattice-points of the latticework.

Fig. 5 compares the SEM and OM images of the latticeworks obtained in the solutions of different C_{Sn} , which are the same solutions as in Fig. 3. The latticeworks obtained in the low C_{Sn} solution (Fig. 5(a and b)) have the larger lattice spacing (*d*, see Fig. 4(c)) and smaller sized cuboid crystals than those obtained in the high C_{Sn} solution (Fig. 5(c and d)). An experimental error for the *d* was of the order of several micrometers.

The potential oscillation can also be modulated by controlling the j_{ap} value. The t_1 at a high j_{ap} (Fig. 6(a)) is longer than that at a low j_{ap} (Fig. 6(c)). Fig. 6(b and d) are the OM images of the latticeworks obtained by oscillations of Fig. 6(a and c), respectively. The results show that the higher the j_{ap} , the larger the *d* is. Thus, the *d* and t_1 change simultaneously through the modulation of the j_{ap} .



Fig. 4. (a) A potential oscillation at $j_{ap} = -36 \,\mathrm{mA} \,\mathrm{cm}^{-2}$ in 0.2 M Sn(II) + 4.0 M NaOH. (b) Optical microscopic (OM) images of Sn deposits taken at various stages of the potential oscillation. The number, (1)–(4), added on the OM images mean that they were obtained at stages of the potential oscillation marked by the same numbers in (a). (c) A schematic illustration of the latticework in (b). (d) A scanning electron microscopic (SEM) image of cuboid crystals formed at the stage of the positive-side potential of the oscillation.



Fig. 5. (a and c): OM images of latticeworks. (b and d): SEM images of cuboid crystals formed at the positive-side potential. The electrolyte is 0.2 M Sn(II) + 4.0 M NaOH for (a and b) and 0.4 M Sn(II) + 4.0 M NaOH for (c and d).

Fig. 7 shows results obtained when the j_{ap} is jumped instantaneously from a low to a high value in the course of the oscillation. At the position of the arrow in Fig. 7(a), the j_{ap} was jumped from -43 to -71 mA cm⁻². The wave form of the oscillation changed simultaneously with the j_{ap} jump. Fig. 7(b) shows the OM image of the resultant deposit, in which the arrow indicates the position where the j_{ap} was jumped. We can see clearly that the *d* becomes larger after the j_{ap} is increased in the absolute value, in good harmony with the increase in the opening by the $|j_{ap}|$ increase in Fig. 6.



Fig. 6. (a and c): Potential oscillations in 0.2 M Sn(II) + 4.0 M NaOH at (a) $j_{ap} = -107 \text{ mA cm}^{-2}$ and (c) $j_{ap} = -43 \text{ mA cm}^{-2}$. (b and d): OM images of latticeworks formed by the oscillations of (a and c), respectively.



Fig. 7. (a) Potential oscillation in 0.2 M Sn(II) + 4.0 M NaOH and (b) an OM image of a latticework formed by this oscillation, in which the j_{ap} was changed from -43 to -76 mA cm⁻² at the position of the arrow.

4. Discussion

First, let us explain the mechanism of the latticework formation in synchronization with the self-organized potential oscillation, reported in a previous letter, for later discussion. We have to note that the experiment is done under a galvanostatic condition with $|j_{ap}| > |j_{dl}|$. In the foregoing stage of stage (1) of Fig. 4, the cuboids of β -Sn, surrounded with the thermodynamically stable (110) and (011) faces, were prepared and lastly covered with thin layers of Sn oxide or hydroxide and passivated, as will be explained later. This implies that the effective area (S_{eff}) of the active electrode surface for Sn deposition became small, which led to the negative shift in U until hydrogen evolution occurred in order to maintain the constant j_{ap} . Thus, the U reaches the negative-side potential of the oscillation, namely, stage (1) is attained. At such a large negative potential, the potential-regulated rate of electrodeposition of Sn is very high and the Sn deposition soon becomes diffusion-limited.

Under the diffusion-limited condition, autocatalytic crystal growth starts (Fig. 8). Namely, under the diffusioncontrolled condition, a spherical diffusion layer is formed at a peaked part of the deposit surface. This leads to a high current density at the peaked part compared with other flat parts, causing a high growth rate for Sn at the peaked part. Thus, peaked parts grow rapidly, resulting in formation of sharp needles, as really observed at stage (2) of Fig. 4. The formation of a large number of needles at stage (2), on the other hand, leads to a large increase in the S_{eff} and hence a large decrease in



Fig. 8. Schematic drawings of Sn deposits in the course of the transition from the negative-side to positive-side potential of the oscillation.

the effective current density (j_{eff}) under the constant j_{ap} . The decrease in j_{eff} in turn leads to a positive shift in U, which continues until the autocatalytic crystal growth stops, namely, the diffusion-controlled condition disappears. Accordingly, the U reaches the positive-side potential of the oscillation (stage (3)). At stage (3), a normal potential-regulated electrodeposition reaction proceeds under the reaction-limited condition, leading to production of cuboid crystals surrounded with the thermodynamically stable (1 1 0) and (0 1 1) faces.

At stage (3), another autocatalytic process, autocatalytic oxidative passivation, may proceed on the thermodynamically stable faces. Namely, the U at this stage is more positive than the redox potential for Sn oxidation and the Sn sur-

face is gradually oxidized with time. The partial formation of Sn oxide at this stage produces electrically polar bonds, $\operatorname{Sn}^{\delta+}-\operatorname{O}^{\delta-}$, here and there at the surface and the resultant $\operatorname{Sn}^{\delta+}$ atoms induce positive polarization of adjacent surface Sn atoms, which in turn causes an easier attack of negatively charged species OH^- on them. This autocatalytic mechanism works most effectively at thermodynamically stable closepacked faces [13]. Thus, the (110) and (011) faces of the cuboids are rapidly covered with Sn oxide as soon as they are formed. The rapid oxidation leads to a rapid decrease in S_{eff} and a rapid increase in j_{eff} under the constant j_{ap} , which causes a rapid negative shift in U. Thus, the negative potential state [stage (4) which is equivalent to stage (1)] is reached again. Repeated occurrence of such processes gives rise to a potential oscillation together with the latticework formation.

The experimental results shown in the preceding section can be explained within the framework of the above mechanism. First, let us consider the C_{Sn} dependence of the oscillation (Fig. 3) and the latticework (Fig. 5). The crystal growth in the higher C_{Sn} solution is expected to be faster than that in the lower C_{Sn} solution. This means that the period of time of the transition from the negative-side to positive-side potential (t_1) becomes shorter with the increasing C_{Sn} , explaining the C_{Sn} dependence of the wave form in Fig. 3. On the other hand, the reason for the C_{Sn} dependence of the *d* in Fig. 5 is not clear yet. A possible explanation is that thick needles are formed in a high C_{Sn} solution (Figs. 5 and 9) and for such thick needles, the effective surface area (S_{eff}) rapidly increases compared with thin needles because the $S_{\rm eff}$ is in proportion to the square of the radius of the needles, in contrast to the length of the needle. Namely, the Seff in higher C_{Sn} solution can reach the value giving the reaction-limited j at a stage of short needles, as schematically shown in Fig. 9.

Second, let us consider the j_{ap} dependence of the *d* of the latticework. All the experiments in this work were performed



Fig. 9. Schematic illustrations of growth of needles in solutions of high and low C_{Sn} for explanation of the C_{Sn} dependence of *d*.



Fig. 10. Schematic drawing of the j_{ap} vs. *U* curve to explain the increase of the amplitude *A* of the potential oscillation with the increasing $|j_{ap}|$. ΔA is a difference in *A* between oscillations at low and high j_{ap} .

under the constant j_{ap} ($|j_{ap}| > |j_{dl}|$). Therefore, a hydrogen evolution current should contribute to the total current at the negative-side potential of the oscillation where the S_{eff} is small. When the j_{ap} was made higher, the *U* on the negativeside of the oscillation shifts to the more negative to keep the constant j_{ap} or to get a more contribution of hydrogen evolution current, as schematically shown in Fig. 10. This can explain the expansion of the amplitude *A* in the negativepotential direction, as seen in Fig. 6(a and c). The negative shift of the negative-side potential requires the growth of longer needles for the potential to reach the reactionlimited condition at the positive-side potential, resulting in the increase in *d* (Figs. 6 and 7). If the rate of Sn electrodeposition is nearly constant, this implies that the t_1 becomes longer.

In conclusion, the present work has revealed that the spacing and thickness of Sn latticeworks formed in synchronization with self-organized potential oscillations are tunable by the modulation of the oscillation through changes in the j_{ap} and C_{Sn} . The tuning by the j_{ap} change is very attractive for constructing modulated latticework structures because the *j* can be controlled simply in a reversible manner. Actually, the latticeworks with two spacings were obtained by controlling

the j_{ap} as shown in Fig. 7, in which the history of a dynamic potential oscillation was recorded directly in the resulting latticework.

Acknowledgements

The authors thank the Core Research for Evolutional Science ence and Technology (CREST) program of the Japan Science and Technology Agency (JST) for financial support. This work was partly supported also by a Grand in Aid of the Ministry of Education, Culture, Sport, Science and Technology (MEXT) for scientific research and by the Kao Foundation for Arts and Science. One of the authors, K.F., wishes to thank for financial support by the 21st Century Center of Excellent (COE) program, "Creation of Integrated EcoChemistry", of Osaka University.

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