Sono-electroplating of Tin Film From Ti(IV)-EDTA Bath∗

A. Chiba† and T. Kojima

Department of Materials Chemistry, Faculty of Engineering,
Yokohama National University, 7-5 Tokiwadai, Hodogaya-Ku, Yokohama 240-8501, Japan
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SnCl4 and EDTA-4Na were dissolved in a 2 mol/dm3 CH3COOH - 2 mol/dm3 CH3COONa buffer solution, and was adjusted to pH4.1 by adding 2 mol/dm3 CH3COOH or 2 mol/dm3 CH3COONa solutions. 100 cm3 of the electrolyte was used. In the stationary state, Sn film was not deposited below 100 mA/cm2, and Sn film deposited in the range of 200 to 1000 mA/cm2. However, thickness was not obtained 1 µm. In the sonication, electrodeposited film obtained 5 ~ 20 µm in the range of 200 to 1000 mA/cm2. Electrodeposition was carried out smoothly, because the mass transfer accelerated with ultrasonic agitation and Sn ion was supplied to electrode surface. Best conditions of sono-electroplating were 0.10 mol/dm3 SnY, pH 4.0, 298 K and 300 mA/cm2. The mass transfer and crystallization processes were most affected with micro-jet and shock wave pressure in the range of 200 ~ 400 m/s/cm2. Exchange current density and reaction rate constant in the sonication increased compared with that in the stationary and vibration states. As for this, an electron reaction becomes fast by the micro-jet or shock wave pressure. Reduction became difficult to break out as sonication was with powerful agitation. The deposited film was smooth and dense surface in the sonication compared with that in the stationary states by the shock wave pressure. [DOI: 10.1380/ejssnt.2006.574]

Keywords: Electrochemical method; Surface morphology; Tin; Metallic film

I. INTRODUCTION

Tin and tin alloys films could be electroplated directly on copper, copper alloys, nickel and undercoats of copper and nickel on ferrous and zinc die cast substrate. Tin and tin alloys have been studied as protective coatings for steel, due to their outstanding no toxicity, corrosion resistance, low friction coefficient and solder ability. Various complexation agents in plating bath used EDTA (ethylenediamine tetraacetic acid, H2Y), citrate, gluconate or tartaric additives for stabilization of tin ion [1–7].

Recently, the solders including lead were problem in an environment. The conditions of lead free plating were similar to those, which are actually used for the deposition of tin-lead alloys. Availability and casts for the lead-free alternative must not be prohibitive to general application of new system. Electroplated deposits were possible alternatives to presently the Sn-M alloys (M1, M2: Bi, Ag, Zn, Cu, etc.), and platings were carried out for lead free solder in the electronic parts.

The effects of sonication during the electrolysis estimated the cavitation phenomena. Those effects were different by the kinds of the electrodeposited metals. The collapse of cavitation bubbles in liquid generated about 1 GPa of sock wave pressure, 120 m/s of micro-jet and 0.2 GPa of water hammer pressure during micro jet [8–14]. Upper operation current density limit rose with sonication [15–17].

In this study, the development of the lead free Sn based alloy solder plating bath was made to be a purpose. As the stability constant of Sn-Y complex was largest and deposited Sn film was soft and malleability, Sn electrodeposition from the Sn (IV) - EDTA bath, crystalline orientation and smooth of film were examined by micro-jet and shock wave pressure.

II. EXPERIMENTAL

The substrate was Cu sheet (99.9% and 0.3 mm thick), with an active area of 1 cm×1 cm. The counter electrode was Pt plate, with an active area of 2.5 cm×4 cm, placed 3 cm from the working electrode. The electrodes were polished with No. 2000 emery paper and immersed in 6 mol/dm3 HNO3 solution for several seconds, then rinsed with distilled water and air-dried before the experiments.

SnCl4 and EDTA- 4Na were dissolved in a 2 mol/dm3 CH3COOH - 2 mol/dm3 CH3COONa buffer solution, and was adjusted to pH4.1 by adding 2 mol/dm3 CH3COOH or 2 mol/dm3 CH3COONa solutions. 100 cm3 of the electrolyte was used. In the stationary state, Sn film was not deposited below 100 mA/cm2, and Sn film deposited in the range of 200 to 1000 mA/cm2. However, thickness was not obtained 1 µm. In the sonication, electrodeposited film obtained 5 ~ 20 µm in the range of 200 to 1000 mA/cm2. Electrodeposition was carried out smoothly, because the mass transfer accelerated with ultrasonic agitation and Sn ion was supplied to electrode surface. Best conditions of sono-electroplating were 0.10 mol/dm3 SnY, pH 4.0, 298 K and 300 mA/cm2. The mass transfer and crystallization processes were most affected with micro-jet and shock wave pressure in the range of 200 ~ 400 m/s/cm2. Exchange current density and reaction rate constant in the sonication increased compared with that in the stationary and vibration states. As for this, an electron reaction becomes fast by the micro-jet or shock wave pressure. Reduction became difficult to break out as sonication was with powerful agitation. The deposited film was smooth and dense surface in the sonication compared with that in the stationary states by the shock wave pressure. [DOI: 10.1380/ejssnt.2006.574]

III. RESULTS AND DISCUSSION

Sn(IV) - EDTA complex was stable in solution as stability constant was 34.5. Main reaction was Eq. (1). The solubility of SnY was limited to 0.15 mol/dm3.

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\text{Sn}^{4+} + \text{H}_2\text{Y}^{2-} \rightarrow \text{SnY} + 2\text{H}^+. \quad (1)
\]

A. Cathodic polarization curve

Figure 1 shows the cathodic polarization curves. Polarization was reduced in order sonication→low fre-
FIG. 1: Effect of sonication and vibration on the V-I curves.

FIG. 2: Effect of current density and SnY concentration on the current efficiency with sonication.

FIG. 3: Effect of pH on the current efficiency of electrodeposited film.

B. Current efficiency

Figure 2 shows the effect of current density and concentration on the current efficiency with sonication. In the stationary state, Sn film was not deposited below 100 mA/cm², and electrodeposited film obtained in the range of 200 to 1000 mA/cm². However, thickness was not obtained 1 μm. In the sonication, the current efficiency increased to about 60% until 200 mA/cm², and maximized at 200 mA/cm². Thereafter current efficiency decreased with increasing of current density. The decreased proportion of the current efficiency in the high current density side was little with increasing of SnY concentration. The solubility of SnY was limited at 0.15 mol/dm³ at 298 K. In the sonication of 28 kHz, the operation current density extended to 100 ∼ 1000 mA/cm².

C. pH and Temperature

Figure 3 shows the effect of pH on the current efficiency. The current efficiency increased until pH 4.1, thereafter current efficiency decreased slowly with increasing of pH in 0.05 mol /dm³ SnY solution. The current efficiency increased comparing with that in 0.10 mol /dm³ solution below pH 4.1 and same above pH 4.1. It was concluded that current efficiency reduced as H₂ gas generated. The current efficiency decreased linearly from 65% at 298 K to 5% at 358 K in 0.05 and 0.10 mol /dm³ solutions.

D. Texture coefficient

Figure 4 shows the effect of current density on the texture coefficient of electrodeposited film. Deposited films were β-Sn (body-centered tetragonal). The space group is I₄₁. The chemistry number unit in unit lattice, Z, is 4. a = 5.8312 Å and c = 3.1819 Å (298 K) is taken. A Young

quency vibration>stationary state. Exchange current density was in order of stationary state (1.0 × 10⁻⁷ mA/cm²)<vibration (1.9 × 10⁻⁴ mA/cm²)<sonication (3.2 × 10⁻³ mA/cm²). Reaction rate was in order of stationary state (2.6 × 10⁻¹⁰ cm/s)<vibration (4.9 × 10⁻⁷ cm/s)<sonication (8.3 × 10⁻⁶ cm/s). Transfer coefficient was in order of stationary state (0.25)<vibration (0.14)<sonication (0.10). Exchange current density and reaction rate increased compared with other state. It was concluded that thickness of electric double layer reduced with shockwave pressure and micro-jet. Transfer coefficient reduced. These results may be related to increasing of agitation.
FIG. 4: Effect of the current density on the texture coefficient of electrodeposited film.

The texture coefficient of (200) plane increased rapidly, and that of (220) plane decreased. It was concluded that Sn ion on electrode was supplied from offshore, and (220) plane which parallel with (100) plane which had lowest surface energy was preferred orientation in the low overvoltage. Conversely, when overvoltage was larger, (200) plane parallel with electrode plane and had high surface energy when overvoltage was small. (200) plane was preferred orientation as Sn ion in electrode-solution interface reduced when overvoltage was large. However (101) and (112) planes of slip plane were rapidly increased in 200 ~ 400 mA/cm². It was concluded that crystal planed generated slip with shock wave pressure.

All texture coefficients were almost same in 0.1 and 0.15 mol/dm³ solution with SnY concentration. At 300 mA/cm², the each crystal planes were almost same texture coefficient in range of pH 4.0 to 4.5. The texture coefficient of (101), (112) and (211) planes decreased, and (220) plane increased in range of pH 4.5 to 5.5 in 0.1 mol/dm³ SnY solution at 298 K.

E. Surface morphology

Figure 5 shows the surface morphology of deposited film in current densities of 300 and 750mA/cm² as the texture coefficient was differed. Surface was rough in stationary state. Some large block observed in vibration state. Surface was smooth and dense in sonication state. Many nucleuses generated comparing with that at 300 mA/cm² of current density. It was concluded as followings. The particles moved to kink by the liquid-jet and growed at kink, as new deposited particle could not be observed on terrace. In the sonication, shock wave pressure added to liquid jet effect. The particle shaved destruction or part off by the shock wave pressure, and the size decreased. Thereafter, the particle moved to kink by the micro-jet. The particles could be plug up in more small clearance (pinhole and defect, etc.). Therefore, the corrugation of surface decreased. The surface was smooth, dense and homogeneity. When the shock wave pressure was applied on the particle that deposited on surface, the particle was crushed and was compressed with adjoining particle. Fi-
Grain size was in order of stationary state (57.1 nm) > vibration (52.7 nm) > sonication (45.8 nm) at 300 mA/cm\(^2\) and in order of stationary state (58.4 nm) > vibration (57.2 nm) > sonication (50.88 nm) at 750 mA/cm\(^2\). It was concluded that particle was small as particle was destroyed with micro-jet and shock wave pressure and the particle and particle collided with strongly agitation on the terrace. The grain (particle) size was smaller at 300 mA/cm\(^2\) than that at 750 mA/cm\(^2\). It was concluded that the grain size that obtained 300 mA/cm\(^2\) was affected with micro-jet.

Figure 6 shows the growth process of deposited film. In electrically charge of 4 Coul./cm\(^2\), kink and step formed in many places. In electrically charge of 9 Coul./cm\(^2\), kink and step reduced and small crystal particles of a diameter are observed at hollow parts of film and formed in many places. In electrically charge of 18 Coul./cm\(^2\), irregularities in the surface reduced and surface was smooth. It was estimated the next stages. (1) Particles deposited on overall substrate with surface diffusion in early stage of electrodeposited. And kink and step formed at many position with micro-jet. (2) A part of particles on sight or transferred to hollow portions of kink and step. (3) Film was in a thick layer at the bottom.

Figure 7 shows the dent when a particle collides head-on with film. Generally, when particle moved to reassure, a particle is crushed, and smooth elaborate film formed. Furthermore, a film became thick with hollow parts in accordance with an increase of a deposited amount, and a good film of few gloss of unevenness is formed.

IV. CONCLUSION

1) Best conditions of sonoelectroplating were 0.10 mol/dm\(^3\) SnY, pH 4.0, 298 K and 300 mA/cm\(^2\).

2) In the stationary state, electrodeposited Sn film was not deposited under 100 mA/cm\(^2\), and electrodeposited film obtained in the range of 200 to 1000 mA/cm\(^2\). However, thickness was not obtained over 1 \(\mu\)m. In the sonication, electrodeposited film obtained 5 ∼ 20 \(\mu\)m in the range of 200 to 1000 mA/cm\(^2\). Electrodeposition is carried out smoothly, because the mass transfer accelerate with ultrasonic agitation and Sn ion was supply to electrode surface.

3) The mass transfer and crystallization processes were most affected with micro-jet and shock wave pressure in the range of 200 ∼ 400 mA/cm\(^2\).

4) Polarization, exchange current density and transfer coefficient were reduced in order sonication > low frequency vibration > stationary state.

5) The surface was smooth and dense in sonication compared with that in other states. It was concluded that a surface was smooth was a shock wave pressure.

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