The complexity behavior and co-electrodeposition mechanism of Au-Sn alloy in a highly stable non-cyanide bath were studied by electrochemical analysis and quantum chemical calculation based on density functional theory (DFT). The interactions between metal ions and multiple complexing agents were revealed, and the mechanism on the high stability of the Au-Sn bath was clarified. The complexing agents potassium pyrophosphate (K₂P₂O₇) and ethylene diamine tetraacetic acid (EDTA) have a synergetic complexation to Sn ions, which exist in one valence state of Sn⁵⁺ to form three complex ions, i.e., [Sn(P₂O₇)₃]²⁻, [Sn(P₂O₇)₂]⁴⁻ and Sn-EDTA; while the complexing agents of 5,5-dimethylhydantoin (DMH) and sodium sulfite (Na₂SO₃) have a complexation to Au ions, which exist in two different valence states (i.e., Au³⁺ and Au⁴⁺) to form two complex ions of [Au(DMH)₄]²⁻ and [Au(SO₃)₂]⁴⁻. Moreover, the existence of [Au(DMH)₄]²⁻ inhibits the decomposition of [Au(SO₃)₂]⁴⁻. Meanwhile, EDTA participates in some form of coordination with Au⁴⁺, inhibits the decomposition of [Au(SO₃)₂]⁴⁻ and facilitates the reduction of [Au(SO₃)₂]¹⁻. The co-electrodeposition of Au-Sn alloy is a diffusion-controlled process, and the nucleation of Au-Sn alloy is a progressive nucleation process. The antioxidant catechol significantly increases the overpotential of Au-Sn co-electrodeposition and improves the brightness of electrodeposited films of Au-Sn alloys.

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Manuscript submitted November 29, 2017; revised manuscript received February 12, 2018. Published February 27, 2018.

The increasing demand for miniaturization of electronic devices has prompted the generation and development of new packaging technologies. For instance, flip chip (FC) technology has been extensively employed in advanced electronic packaging, due to the benefits of good electrical performance, small packaging size, excellent heat dissipation and improved signal integrity for high-frequency designs. The solder bumps, functioning as electrical connection, mechanical support and heat dissipation, are downsizing to 50 μm in flip chip packaging. With the continuous downsizing of solder bumps, solder bumping by electroplating will be widely used to replace the prefabricated solder balls. As for 3D packaging, the higher density of patterns and the more complex circuit lead to the inevitable requirement of electrodeposition for solder bump fabrication. Compared to the other solder bump preparation methods including solder preform and sputtering, electroplating has outstanding advantages such as high deposition rate, controllable micro-pattern formation, cost-effective and time-consuming. As a result, electroplating is recommended as a practical and promising technology for solder bump manufacturing.

Recently, lead-free solders are compulsively used to replace Sn-Pb solder alloys due to the environmental concerns. Among various Pb-free solder alloys, Au80Sn20 eutectic, which is regarded as a hard solder (melting point 278°C) has been extensively used in microelectronic and optoelectronic packagings due to its superior mechanical and thermal properties, such as high strength and thermal conductivity, excellent creep and fatigue resistance, and flux-less bonding. These outstanding advantages make it suitable to be applied in some special packaging technologies, including high-powered LED packaging, gas leak sealing treatments, laser diodes and non-flux soldering packaging.

In the past decades, the Au electrodeposition is traditionally realized from cyanide containing bath because of the high complexing constant of Au ion with CN⁻, and the electrodeposition of Au-Sn eutectic solder was achieved using alternating deposition of multiple Au/Sn/Au films from two separate plating bath followed by thermal interdiffusion. Compared with sequence deposition method, co-electrodeposition of Au-Sn solders as an alternative was preferred due to the innate advantages of low cost, low probability of Sn oxidation and void formation. However, with the increasing healthy and environmental concerns, CN⁻, as one of the most toxic chemicals was gradually banned in the electroplating industry. Moreover, CN⁻ can bring damage to photoresist in solder bumps preparation process. Chen et al. developed a green gold electrodeposition bath using hypoxanthine as complexing agent and bright gold deposits were successfully obtained. To the best of our knowledge, only a few reports investigated co-electrodeposition of Au-Sn alloys in non-cyanide plating baths and most publications were from patent literature. The primary challenge for the development of non-cyanide Au-Sn electroplating bath lies in its poor stability. Therefore, screening appropriate complexing agents is critical to realize the high stability of Au-Sn bath. D.G. Ivey developed a non-cyanide bath consisting of HAuCl₄, SnCl₂, Na₃AsO₃, ammonium citrate and ascorbic acid and prepared Au-Sn eutectic by alternate deposition of AuSn and Au-Sn. However, the non-cyanide bath had a short shelf-life of only three days, which cannot meet the demand of long-term use of Au-Sn co-electrodeposition. Moreover, the present researches mainly focused on the effects of constituent variations and processing parameters on the electrodeposited morphology, electrodeposition composition, electrodeposition rate and current efficiency, however, deep insights into the coordination behavior between complexing agents, metal ions, electroplating mechanism and nucleation of Au-Sn alloys are of great interest. Bozzini et al. investigated the nucleation process using chronoamperometry in acidic KAu(CN)₄ and SnCl₂ · H₂O solutions with 4-cyanopyridine as an additive and found that the nucleation mechanism of Au-Sn alloy was an instantaneous nucleation process. Nevertheless, there is inadequate understanding of the fundamental electrochemical mechanism in the non-cyanide Au-Sn baths.

In the present work, a highly stable non-cyanide Au-Sn bath, for co-electrodeposition of Au-Sn alloys was proposed. Cyclic voltammetry (CV) and density functional theory (DFT) calculation were carried out to investigate the coordination effect between metal ions and selected multiple complexing agents, and the reason for the high stability of Au-Sn bath was clearly clarified. In our previous study, the Au-Sn bath without the DMH addition would decompose with the formation of black powered gold after sealed storage for 20 days. The investigation in the present work is the effect of DMH addition. The electrodeposition behavior, the rate controlling step, and the nucleation mechanism were investigated using cyclic voltammetry and chronoaaperometry techniques. The influence of antioxidant catechol on the morphology of Au-Sn electrodeposits and cathodic polarization was also discussed.
Experimental

Au-Sn alloy electrodeposition.—The Au-Sn electroplating bath consisted of 0.01 mol/L HAuCl₄, 0.12 mol/L 5,5-dimethylhydantoin (DMH), 0.12 mol/L Na₂SO₄, 0.01 mol/L Sn₂P₂O₇, 0.11 mol/L K₃P₂O₇, 0.01 mol/L EDTA, and 0.03 mol/L catechol. Among these chemicals, HAuCl₄ and Sn₂P₂O₇ were used as a source of Au³⁺ and Sn²⁺ ions, respectively. DMH, Na₂SO₄, K₃P₂O₇, and EDTA were used as the complexing agents. Catechol was used as an antioxidant to prevent the oxidation of Sn²⁺ to Sn⁴⁺. The pH of the baths was adjusted by adding 1.0 mol/L KH₂PO₄ and K₂HPO₄ solution. All the chemicals used in the present work were analytical grade. The bath components were modified according to the different experimental conditions, and the pH was kept at a constant of 7.50.

The electrodeposition of Au-Sn alloy was carried out on Si chips sputtered with TiW (0.2 μm)/Au (0.2 μm) blanket metallization (4 × 9 mm² in size). The TiW acted as an adhesion layer and the Au acted as a seed layer. The Si chips were cleaned thoroughly in acetone and deionized water before electroplating. A platinized titanium mesh was used as the anode.

Electrochemical evaluation.—The electrochemical analyses were performed on an electrochemical workstation, VERSASTAT4-400 (AMTEK Inc. USA). All the electrochemical measurements were conducted in a three-electrode system. A saturated calomel electrode (SCE) was used as the reference electrode, and a Pt electrode was used as the counter electrode. A Luggin capillary tip was set 2 mm from the surface of the working electrode. A glassy carbon electrode (GCE) with a working area of 0.07 cm² (Ø = 3 mm) was used as the working electrode. The temperature of electroplating baths was maintained at 40 ± 1°C with a thermostat.

Quantum chemical calculation.—The structure optimizations of the Au complexes were analyzed by DFT methods using the hybrid density functional B3LYP in Gaussian 09 program suite. For elements N, S, O and H, 6–31+G(d) basis sets were used. The LANL2DZ basis sets were adopted for modeling of Au atom. Solvent effects of water were taken into account using the IEFPCM model. All the local minima were confirmed by no imaginary mode from vibrational analyses. Based on the optimized structures, the bond length and bond energy of the Au complexes were calculated. The bonding energy between Au³⁺ and complexing agents was calculated by the Eq. 1:

\[
E_{\text{bonding}} = E_{\text{part1}} + E_{\text{part2}} - E_{\text{total}} \tag{1}
\]

\(E_{\text{total}}\) is the total energy of the complexes containing Au³⁺ and complexing agents, and \(E_{\text{part1}}, E_{\text{part2}}\) are the energy of the separated two segments, which is formed due to the bond cleavage between Au atom and the coordination atom, respectively.

Characterization of the Au-Sn electrodeposit.—The morphology of the Au-Sn electrodeposits was characterized using a scanning electron microscope (FE-SEM, Zeiss Supra 55) at 15 kV working voltage. The compositional constituents of the Au-Sn electrodeposits were measured by energy dispersive X-ray spectrometer (EDX) equipped in the SEM. The Empyrean XRD-6000 X-ray diffractometer (XRD) was used to identify the phases of Au-Sn eutectic electrodeposits.

Results and Discussion

Analysis of complexation and stability mechanism of Au-Sn electroplating bath.—In order to study the complexation behavior of metal ions and clarify the high stability mechanism of Au-Sn electroplating bath, the cyclic voltammetry was used to study the electrochemical behavior of single metal ions of Sn and Au in the electrolyte. Fig. 1a shows the CV curve of Sn on the GCE. During the forward scan toward negative potentials, the onset potential of Sn deposition was at about −1.05 V. Three cathodic reduction waves were observed at the potentials of −1.16 V, −1.31 V and −1.47 V, which is attributed to the reduction of Sn in three different coordination forms. When the potential was swept negatively to −1.56 V, the hydrogen evolution occurred. When the direction of the sweep was reversed, a “hysteresis loop” was observed in the potential range from −1.09 V to −0.94 V, which is a characteristic of a nucleation and growth process.

An anodic peak S appears at the potential of −0.74 V. The peak corresponds to the dissolution of Sn deposits, which is confirmed when the reverse scan potential was −0.90 V, peak S disappeared during the anodic scan, as shown in the inset of Fig. 1a. It is noted that the coulomb integration below the cathodic curve (potential from initial deposition of Sn to the onset reduction of proton) is almost equal to the anodic one, and thus it is concluded that the exchange electron number in the reverse anodic period is equal to 2, which means the peak S corresponds to the reaction of Sn→Sn²⁺ + 2e⁻. Fig. 1b shows the CV curve of Sn bath without EDTA. Two cathodic peaks were observed at the potential of −1.09 V and −1.46 V, respectively. An anodic peak at the potential of −0.73 V was also observed with the similar potential shown in Fig. 1a. In the absence of EDTA, [Sn(P₂O₇)₂]²⁻ and [Sn(P₂O₇)₃]⁶⁻ were considered as the main complexing forms for Sn²⁺ and Sn³⁺ in a Sn₂P₂O₇-K₃P₂O₇ solution when the pH of the bath was 7.50. According to the stability constant of [Sn(P₂O₇)₂]²⁻ and [Sn(P₂O₇)₃]⁶⁻, the concentrations of Sn²⁺-pyrophosphate complexes and free pyrophosphates in the solution can be calculated with the given Sn²⁺ and P₂O₇⁻ concentrations as well as pH considering the equilibrium constants. It was calculated that about 95 mol% Sn²⁺ existed in the form of [Sn(P₂O₇)₂]²⁻ and the residual 5 mol% was in the form of [Sn(P₂O₇)₃]⁶⁻. With the addition of EDTA, the Sn²⁺-pyrophosphate complex was partially substituted by EDTA. As a result, Sn-EDTA complex formed. Hu studied the electroplating of Sn-Bi alloys and found that there was a coordination effect between Sn²⁺ and EDTA, and the concentration...
of EDTA has a significant effect on the cathodic polarization and composition of Sn-Bi electrodeposits.

Fig. 2a shows the CV curve of Au in the bath without the addition of Na2SO3. A large reduction current peak with a current value of 0.3 mA at the potential of −0.79 V was observed. This peak is attributed to the reduction of complex [Au(DMH)4]−. Similarly, Yang et al.26 investigated the electrodeposition behavior of Au on gold electrode and electrolytes in the bath. During the forward scan toward the negative potential, a very small cathodic current density peak occurred, which is ascribed to the simultaneous reduction of Au and proton. On the reverse scan, no anodic current was observed, indicating Au electrodeposition cannot be dissolved in the bath. Compared the CV curves in Figs. 2a and 2b, in the presence of Na2SO3, the reduction potential of Au was significantly shifted toward a more negative value, and the reduction peak current located at −0.79 V in Fig. 2a decreased obviously. Fig. 3 shows the cathodic polarization curves of Au reduction in the electrolytes containing DMH and both DMH and Na2SO3, respectively. With the addition of Na2SO3, the onset potential of Au deposition shifted to a negative value at curve b compared with that at curve a. This phenomenon may be attributed to the two reasons. One is that due to the strong coordination effect of SO32− with Au3+, DMH was partially substituted by SO32−, resulting in the formation of high stable hybrid complexes of Au3+. DFT calculations were performed to study the stability of the Au complexes. Fig. 4 shows the optimized structures of [Au(DMH)3]−, [Au(DMH)3(SO3)2]− and [Au(DMH)2(SO3)2]3− complexes. As shown in Fig. 4a, the structure of [Au(DMH)3]− is square planar in geometry with a C4v symmetry, which is consistent with the crystal structure characterized by X-ray crystallography. Moreover, the calculated structure parameter values were similar to those measured by X-ray crystallography.27 As shown in Fig. 4b, the complex [Au(DMH)2(SO3)2]3− shows no geometry symmetry. As shown in Fig. 4c, [Au(DMH)2(SO3)2]3− is also square planar in geometry with a C2v symmetry. The key parameters of bond lengths and bond energies of these three optimized complexes were summarized in Table I. The bond length between S and Au atoms is larger than that between N and Au atoms due to the large radius of S atom. The bond energy value is a symbol of the interaction effect between the metal ion and coordination atoms. As shown in Table I, the bond energy value between the Au and N atoms in the optimized complex of [Au(DMH)3]− is 314.67 kJ/mol, which is larger than that in the complexes of [Au(DMH)(SO3)2]− (−27.57 kJ/mol and −166.77 kJ/mol) and [Au(DMH)(SO3)2]3− (−271.52 kJ/mol). The bond energy values between the Au and N atoms are negative in the complexes of [Au(DMH)(SO3)2]− and [Au(DMH)(SO3)2]3−, indicating that the complexes of [Au(DMH)(SO3)2]− and [Au(DMH)(SO3)2]3− are difficult to exist in the plating bath. Therefore, the existence of [Au(DMH)3]− (Fig. 4a) is reasonable. The other reason is that due to the reduction property of SO32−, the Au3+ was partially reduced to Au2+ and then coordinated with SO32−. Fig. 5a shows the CV curve of Au deposition with the 0.12 mol/L DMH and 0.12 mol/L Na2SO3, and a peak at −0.74 V was observed, while with more Na2SO3 addition (Fig. 5b), a peak at −1.26 V was obviously observed. Fig. 5c shows the CV curve of Au deposition containing only 0.12 mol/L Na2SO3, one cathodic peak at −1.24 V corresponding to the reduction of [Au(SO3)2]3− was observed, which is similar with that in Fig. 5b. Therefore, it is concluded that with complexing agents of both Na2SO3 and DMH, Au existed in two valence states in the Au plating bath, i.e., [Au(DMH)3]− and [Au(DMH)3(SO3)2]3−. It was found that if DMH was not added to the Au-Sn bath, the solution precipitated after 20 days, indicating that the existence of Au3+ complex could inhibit the decomposition of [Au(SO3)2]3−. Moreover, Fig. 5d shows the CV of Au deposition in the bath containing 0.12 mol/L Na2SO3, 0.12 mol/L DMH, and 0.02 mol/L EDTA. Compared with the CV curve in Fig. 5a, it is noted that the peak current at −1.24 V corresponding to the reduction of [Au(SO3)2]3− became obvious, indicating that EDTA could facilitate the reduction of [Au(SO3)2]3−. Moreover, it was found that the Au electroplating bath was not stable without the addition of EDTA.30 Therefore, it is concluded that EDTA could coordinate with Au3+ in some form and stabilize [Au(SO3)2]3−.
In general, the poor stability of non-cyanide Au-Sn co-electrodeposition bath is attributed to two aspects. One is due to the spontaneous redox reactions between $\text{Au}^{3+}$, $\text{Au}^+$ and $\text{Sn}^{2+}$ ions, since $\text{Au}^{3+}$ (1.50 V) and $\text{Au}^+$ (1.692 V) ions exhibits a much more positive standard electrode potential than that of $\text{Sn}^{2+}$ (−0.136 V). The other one is due to the low stability of monovalent Au complex. Thus, the high stability of the present Au-Sn bath is attributed to the two aspects. One is that the electrode reduction potentials of Au and Sn ions deviate from the standard electrode potential due to the coordination effect of multiple complexing agents with $\text{Au}^{3+}$, $\text{Au}^+$ and $\text{Sn}^{2+}$ ions, which prevented the occurrence of the spontaneous redox reaction to form suspension or precipitation of Au. The other is that the existence of $[\text{Au(DMH)}_4]^{-}$ could suppress the disproportionated reaction of $[\text{Au(SO}_3)_2]^{3-}$, and EDTA could also coordinate with $\text{Au}^+$ in some form and stabilize $[\text{Au(SO}_3)_2]^{3-}$.

In order to further identify the bath stability, cathodic polarization curves were used to study the electrochemical behavior of the new and aged bath containing 0.01 mol/L HAuCl$_4$, 0.12 mol/L 5,5-dimethylhydantoin (DMH), 0.12 mol/L Na$_2$SO$_3$, 0.01 mol/L Sn$_2$P$_2$O$_7$, 0.11 mol/L K$_4$P$_2$O$_7$, 0.01 mol/L EDTA, and 0.03 mol/L catechol on GCE. As shown in Fig. 6, the onset deposition potential and the limited current of Au-Sn co-electrodeposition in the bath after the storage for seven days is almost the same as those in the new bath. After the storage for 15 days, the onset deposition potential was slightly changed toward to a positive one, while the limited current did not change. Moreover, there was no suspension or precipitation occurred in the electrolyte when the bath was sealed for three months at room temperature or heated for 3 h at 70°C, indicating that the stability of the bath was significantly improved compared with that in our previous work, which would decompose to form black powered gold after sealed storage for 20 days or heating up to 60°C for 1 h. The appearance of Au-Sn electrodeposits is bright and compact after continuing electroplating for 5 h at a current density of 25 mA/cm$^2$, indicating that the electrolyte is suitable for a long-time electrodeposition.

### Table I. Bond lengths and bond energy data calculated with B3LYP for the Au complexes.

| Complex | Bond Length / Å | Bond Energy / KJ/mol |
|---------|-----------------|----------------------|
| $[\text{Au(DMH)}_4]^{-}$ | 2.051 | 314.67 |
| $[\text{Au(DMH)}_3(\text{SO}_3)]^{2-}$ | 2.049 | 314.67 |
| $[\text{Au(DMH)}_2(\text{SO}_3)_2]^{3-}$ | 2.051 | 314.67 |

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In order to further identify the bath stability, cathodic polarization curves were used to study the electrochemical behavior of the new and aged bath containing 0.01 mol/L HAuCl$_4$, 0.12 mol/L 5,5-dimethylhydantoin (DMH), 0.12 mol/L Na$_2$SO$_3$, 0.01 mol/L Sn$_2$P$_2$O$_7$, 0.11 mol/L K$_4$P$_2$O$_7$, 0.01 mol/L EDTA, and 0.03 mol/L catechol on GCE. As shown in Fig. 6, the onset deposition potential and the limited current of Au-Sn co-electrodeposition in the bath after the storage for seven days is almost the same as those in the new bath. After the storage for 15 days, the onset deposition potential was slightly changed toward to a positive one, while the limited current did not change. Moreover, there was no suspension or precipitation occurred in the electrolyte when the bath was sealed for three months at room temperature or heated for 3 h at 70°C, indicating that the stability of the bath was significantly improved compared with that in our previous work, which would decompose to form black powered gold after sealed storage for 20 days or heating up to 60°C for 1 h. The appearance of Au-Sn electrodeposits is bright and compact after continuing electroplating for 5 h at a current density of 25 mA/cm$^2$, indicating that the electrolyte is suitable for a long-time electrodeposition.
Figure 6. Cathodic polarization of Au-Sn electrodeposition in pH 7.50 baths with different stored period at a scan rate of 1 mV/s.

Rate controlling step and nucleation mechanism of co-electrodeposition of Au-Sn alloy.—As shown in Fig. 7a, two cathodic peaks with the potential of $-1.00$ V and $-1.17$ V were observed during the scan toward negative potential. During the scan toward positive potential, an anodic peak “Q” appeared at $-0.51$ V. It is noted that the presence of crossovers of the cathodic and anodic branch, typically of the formation of a new phase, involved a nucleation followed by diffusion-limited growth process. When the reverse potential was set at $-1.10$ V (Fig. 7b), the anodic peak current was unobvious due to a limited deposit quantity. The composition of the Au-Sn alloys electrodeposited at these two peak potentials on GCE was identified. The Au-Sn alloy electrodeposited potentiostatically at $-1.00$ V is Au-38.81at.% Sn (Fig. 8a). The Au-Sn alloy electrodeposited potentiostatically at $-1.17$ V is Au-45.63at.% Sn (Fig. 8b). With the further decreasing deposition potential, the Sn content in the Au-Sn deposits increased. Due to the large overpotential, the grain size of Au-Sn deposit in Fig. 8b is smaller than that of Au-Sn deposit in Fig. 8a. It is suggested that the peaks “A” and “B” are both the co-electrodeposition peaks of Au-Sn alloy and the peak “Q” is the dissolution of the intermetallic compound of Au and Sn.

As shown in Fig. 9, CV curves at different scan rates were measured on GCE to investigate the rate controlling step of electrodeposition of Au-Sn alloy. With increasing scan rate, the reduction peak potential $E_p$ of both the two peaks “A” and “B” shifted negatively, indicating that the electrodeposition of Au-Sn in the prepared bath is irreversible. The reduction peak current $i_{pA}$ at more positive potential decreased with increasing scan rate from 50 to 400 mV/s. This is probably due to a slow kinetic reaction of Au-Sn electrodeposition at this potential. The reduction peak current $i_{pB}$ at more negative potential gradually increased with increasing scan rate. When the electrode reaction is controlled by the diffusion process, the relationship between the peak current $i_p$ and the potential scan rate $v$ of CV curves can be expressed as follows:

$$i_p = 0.4958(nF)^{1/2}(ADv^{1/2})^{1/2}(RT)^{-1/2}Ac^*$$

where $A$ is the surface area of the electrode, $D$ is the diffusion coefficient, $c^*$ is the bulk concentration of reducible ions, $n$ is the number of electrons, $R$ is the gas constant, $T$ is the temperature, $F$ is the gas constant, and $v$ is the potential scan rate.
Faraday constant and $\alpha$ is the charge transfer coefficient. As shown in Fig. 10, there is a linear relationship between $i_p$ and $v^{1/2}$, indicating that the electrodeposition of Au-Sn alloy is an irreversible diffusion-controlled process.

As an electrochemical method, chronoamperometry (CA) can analyze current transient and is commonly used to study the kinetics of electrocrystallization. During CA experiments, current-time transients were recorded as the test potential was stepped from the open-circuit potential (OCP) to the potential at which the deposition occurred. It is clear that the form of the current transient is a typical characteristic of an electrochemical nucleation and growth process. As shown in Fig. 11, all transients exhibited a similar behavior; these are illustrated by a rapid decrease of current at a very short time due to the charging of double layer. Then the current increased rapidly due to the isolated growth of all individual AuSn nuclei and the increasing number of the nuclei present on the electrode surface, and consequently the current reached the maximum value followed by a decaying current caused by the diminishing of the concentration of the electroactive species in the depletion zone. Eventually, the current reached a constant value. These feathers are consistent with the theoretical curves for progressive nucleation. In the present work, there is a good linear relationship of $I_t$ vs. $v^{1/2}$ for instantaneous nucleation and $I_t$ vs. $v$ for progressive nucleation. In the present work, there is a good linear relationship of $I_t$ vs. $v^{1/2}$ for instantaneous nucleation and $I_t$ vs. $v$ for progressive nucleation. In the present work, there is a good linear relationship of $I_t$ vs. $v^{1/2}$ for instantaneous nucleation and $I_t$ vs. $v$ for progressive nucleation. In the present work, there is a good linear relationship of $I_t$ vs. $v^{1/2}$ for instantaneous nucleation and $I_t$ vs. $v$ for progressive nucleation. In the present work, there is a good linear relationship of $I_t$ vs. $v^{1/2}$ for instantaneous nucleation and $I_t$ vs. $v$ for progressive nucleation.
Effect of catechol on properties of Au-Sn alloy.—The purpose to use of catechol, a known antioxidant, was to prevent the oxidation of Sn\(^{2+}\) to Sn\(^{4+}\) species due to dissolved oxygen in the plating bath. Meanwhile, it was found that the presence of catechol dramatically improved the morphology of the Au-Sn alloy electrodeposits. The Au-Sn deposit prepared in the bath without catechol was pale gray, while the Au-Sn deposit changed into bright silver with metal luster with the addition of catechol. Fig. 14 shows the SEM images of Au-Sn electrodeposits on the Si chip. As shown in Fig. 14a, in the absence of catechol, the morphology of Au-Sn electrodeposits was coarse with nodules, and the dendritic crystal grain size was large and not uniform. With the addition of 0.01 mol/L catechol to the bath, the morphology of Au-Sn electrodeposits became even, and the grain size became uniform (Fig. 14b). As shown in Fig. 14c, an even smoother surface with fine grains of less than 0.5 \(\mu\)m in size was observed in the presence of 0.03 mol/L catechol. The micro-leveling effect is generally related to the absorption of an additive on the surface of electrode.\(^{37}\) To investigate the influence of catechol on the deposition behavior of Au-Sn electrodeposition in the bath, the cathodic polarization was performed with and without the catechol in the bath. Fig. 15 shows the compared polarization curve of bath with and without catechol. The onset potential of Au-Sn co-electrodeposition changed negatively, and a higher cathode overpotential was required to realize the Au-Sn deposition due to the adsorption of the additive catechol on the gold film. Hubbard\(^{38}\) also reported the adsorption of hydroquinone on the Au surface, which is similar to catechol in structure. The strong adsorption of catechol on the Au surface increased the cathodic overpotential, which accelerated the nucleation rate. As a result, a smooth surface with fine grains was obtained. Fig. 16 shows the XRD pattern of the Au-Sn eutectic electrodeposits with a composition of Au-30.14at.%. XRD analysis identified that the Au-Sn eutectic electrodeposits consisted of \(\delta\) (AuSn) and \(\zeta\) (Au\(_5\)Sn) phases. The grain of the Au-Sn electrodeposits can be calculated according to Scherrer equation (Eq. 5).

\[
D = \frac{k\lambda}{\beta\cos\theta}
\]

where \(D\) is the average grain size of the electrodeposits (nm), \(k\) is a constant (0.89), \(\beta\) is the full width at the half maximum (FWHM) and \(\theta\) is the diffraction angle. It was calculated that the average grain size of Au-Sn electrodeposits is 15 nm. Thus, the electrodeposited Au-Sn eutectic alloy in the developed non-cyanide bath is nano-deposit. Moreover, a high current efficiency of 74% was achieved for the Au-Sn eutectic co-electrodeposition, which shows that the developed bath is suitable for Au-Sn eutectic preparation in advanced electronic packaging.

Conclusions

A highly stable green non-cyanide Au-Sn co-electrodeposition bath containing metal ions of H\(\text{AuCl}_4\) and Sn\(_2\text{P}_2\text{O}_7\), multiple complexing agents of DMH, Na\(_2\)SO\(_3\), EDTA and K\(_4\)P\(_2\)O\(_7\), and antioxidant catechol is developed, which can be sealed stored for at least three months without the black powered gold precipitation at room temperature. EDTA has a synergetic effect with P\(_2\)O\(_7^{4-}\) on Sn\(^{2+}\) coordination, and Sn\(^{2+}\) ions exist in three forms of complex ions, i.e., \([\text{Sn}({\text{P}}_2{\text{O}}_7)^{\text{4-}}]^{\text{2-}}\), \([\text{Sn}({\text{P}}_2{\text{O}}_7)_3]^{\text{3-}}\) and Sn-EDTA, while Au ions exist in two valence states, i.e., Au\(^{3+}\) and Au\(^+\) in the forms of
[Au(DMH)4]− and [Au(SO3)2]3−. DFT calculations show that single ligand complex [Au(DMH)4]− has a higher stability than mixed ligand complexes of [Au(DMH)(SO3)]2− and [Au(DMH)2(SO3)2]3−. Combined with cyclic voltammetry measurements, it is determined that Au3+ is partly reduced to Au+ and complexed with SO32− in the form of Au[(SO3)2]3−. The existence of [Au(DMH)4]− inhibits the decomposition of Au[(SO3)2]3−. Moreover, EDTA participates in some form of coordinated with Au+, inhibits the decomposition of [Au(SO3)2]3− and facilitates the reduction of [Au(SO3)2]3−. Based on the cyclic voltammetry measurements with different scan rates, the co-electrodeposition of Au-Sn alloy is an irreversible and diffusion-controlled process. The chronocoulometry experiments show that the nucleation of Au-Sn co-electrodeposition is a three-dimension progressive nucleation process. The surface morphology is significantly improved with the addition of catechol due to the strong adsorption of catechol on the Au surface, which increases the cathodic overpotential, accelerates the nucleation rate and consequently results in a smooth surface with fine grains.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (grant Nos. 51711036, 51475072, 51511140289 and 51671046) and the Fundamental Research Funds for the Central Universities (grant No. DUT17ZD202).

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