AuSn20 Eutectic Electrodeposition through Alternative Complexing of Pyrophosphoric Acid: Insights from Electrochemical and DFT Methods

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ABSTRACT: Eutectic AuSn20 solder is an important material for electronic packaging technology due to its superior mechanical and thermal conductive properties. In this work, AuSn20 alloy films are prepared via the electrodeposition method for the first time. The electrodeposition is cost-effective with improved control over the alloy content when compared to traditional powdered metallurgy methods. Pyrophosphoric acid was found to be an effective complexing agent to minimize the difference of the deposition potentials between Au and Sn, making the codeposition of AuSn alloys possible. Importantly, electrochemical characterization was combined with density functional theory (DFT) calculations to provide insight into the mechanism of the alloy codeposition when pyrophosphoric acid was used as the complexing agent. In particular, natural bond orbital (NBO) charge distribution and the lowest unoccupied molecular orbital (LUMO) characteristics of [P2O7]4−Sn(II) and [P2O7]4−Au(I) complexes are calculated, suggesting that [P2O7]4− is able to coordinate more strongly with Sn(II) than Au(I). As a result, it can thus shift the deposition potentials of Au(I) and Sn(II) much closer. As the DFT predicted, the role of pyrophosphoric acid as a complexing agent has been experimentally verified, making codeposition of Au and Sn realistic. The structures of the obtained AuSn20 films are determined using scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX) and found to be consistent with AuSn/Au5Sn eutectic as predicted by the Au−Sn phase diagram. Additionally, the measured melting point is in good agreement with the theoretically determined one. Relevant tests demonstrated in this work indicate that the newly developed electrodeposited AuSn20 alloy coatings are suitable for microelectronic soldering applications.

INTRODUCTION

AuSn20 eutectic solder is extensively employed in the electronic packaging of optoelectronic and high-powered electronic components1−3 due to its superior mechanical and thermal conduction properties.4 In addition, it plays a key role in some special technologies, including gas leak sealing treatments, high-powered laser diode packaging,5 and non-soldering flux packaging.6

The AuSn20 eutectic consists of AuSn and Au5Sn phases7 with a Sn content of 20 wt %8. AuSn20 solder is commonly prepared by powder compacting9 or sputtering10 methods due to the incompatibility of Au and Sn. However, the AuSn20 solder fabricated using these techniques cannot meet the demand for microscaled soldering applications due to limitations of thickness and pattern formation. Thus, selective electroplating of AuSn20 solder would be an attractive way overcoming such limitations. Such an electrodeposition technique, however, has yet to be fully developed for AuSn2011,12 due to the large difference in electrodeposition potentials between Au and Sn. In principle, codeposition of metals with different deposition potentials requires the use of complexing agents. Thus, proper choice of the effective complex agent becomes a key to realizing the Au and Sn codeposition via an electrochemical method. In this work, we found that the Sn deposition potential is drastically reduced after adding pyrophosphoric acid into Sn(II) solution. On the other hand, pyrophosphoric acid has a less significant effect on the deposition potential of Au(I). This suggests that pyrophosphoric acid should enable codepositing these two metal ions simultaneously. As a result, AuSn20 eutectic films can be successfully electrodeposited from an aqueous solution in the presence of the pyrophosphoric acid, and the eutectic characteristics of the electrodeposited AuSn20 films are confirmed by scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX), and melting point measurements. Importantly, the complexing behavior of pyrophosphoric acid with Sn(II)/Au(I) is analyzed using electrochemical characterization and density functional theory (DFT). This theoretical study clearly elucidates the mechanism.

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that the deposition potential of Sn(II) is more strongly affected by pyrophosphoric acid than Au(I), thereby resulting in a codeposition of Sn(II) and Au(I).

**EXPERIMENTAL SECTION**

Preparation of AuSn20 Films by Electrodeposition. Al₂O₃ ceramic is used as a substrate for the electrodeposition process. These substrates are metalized with a tungsten and titanium alloy using magnetron sputtering. An Au film is then electroplated on the surface followed by ethanol and acetone cleaning. Finally, the AuSn20 alloy is electrodeposited on the pretreated substrates using an electrolyte containing 5 g/L [KAu(CN)₂], 7 g/L SnSO₄, and 60 g/L potassium pyrophosphate (K₄P₂O₇). All chemical agents used are analytically pure. All solutions are prepared with deionized water with an electric conductivity over 18.0 MΩ. The temperature of the electrolyte is controlled at 50 ± 1 °C. All electrolytes are purged with nitrogen before using. The pH value of electrolyte is adjusted to 6.0 using diluted H₂SO₄ solution. The current density used for the AuSn20 electrodeposition is 0.6 A/dm².

Electrochemical Measurements. Cathodic polarization measurements are performed on an electrochemical workstation (model ref. 600, Gamry Inc., Warminster, PA) in a conventional three-compartment Pyrex cell. A defined sample area of 1.0 cm² is exposed to the electrolyte. A Luggin capillary is placed near the working electrode to minimize the ohmic drop. A saturated mercurous sulfate electrode (MSE) and a platinum sheet are used as the reference and the counter electrodes, respectively. All electrode potentials are with respect to the MSE in this work unless stated otherwise. In order to study the complexing characteristics of pyrophosphoric acid, solutions containing 5 g/L [KAu(CN)₂] and 7 g/L SnSO₄ with or without adding 60 g/L K₄P₂O₇ are prepared for a comparison to study the role of the complexing agent.

Characterization of AuSn20 Alloy Films. Field-emission scanning electron microscope (FE-SEM) images are obtained using a JSM-6330F scanning electron microscope (JEOL Ltd., Tokyo, Japan). The elemental composition of different areas in the eutectic is determined by an energy-dispersive X-ray spectrometer (EDX) on a Link-ISIS-300 (Oxford Corp., Beverly, MA). The melting point of AuSn20 eutectic samples is measured by differential scanning calorimetry (DSC) on a Netzsch STA 449C instrument under flowing N₂. The rate of increasing temperature is 10 °C/min.

**RESULTS AND DISCUSSION**

According to the Au–Sn thermodynamic phase diagram, the AuSn20 eutectic occurs at 20.0 wt % or 29.0 at. % Sn and consists of ζ phase (Au₅Sn) and δ phase (AuSn). The lattice structures of ζ phase (Au₅Sn) and δ phase (AuSn) are HCP and NiAs structure, respectively, as shown in Figure 1. Although the melting points of Au₅Sn and AuSn are 190.0 and 419.3 °C, respectively, the melting point of AuSn20 is 278.0 °C, as indicated by the blue area in Figure 1.

The standard deposition potentials of Au(I) to Au(0) and Sn(II) to Sn(0) are 1.692 V and −0.136 V vs normal hydrogen electrode (NHE), respectively, as shown in eqs 1 and 2. E° is the standard potential.

\[
\text{Au}^+ + e^{-} \rightarrow \text{Au} \quad (E^\circ = 1.692 \text{ V}) \\
\text{Sn}^{2+} + 2e^{-} \rightarrow \text{Sn} \quad (E^\circ = -0.136 \text{ V})
\]

To realize electrochemical codeposition of Au and Sn, the deposition potentials of both metals should be relatively close, which is not the case for Au and Sn at their standard conditions. Considering a Au(I) precursor of [KAu(CN)₂] in solution at a concentration of 5 g/L, the real deposition potential can be

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**Figure 1.** Au and Sn alloy phase diagram and lattice structure of Au₅Sn and AuSn. Au and Sn atoms are represented by yellow and gray spheres, respectively.
calculated based on the Nernst equation (eq 3) using a stability constant of complex \([\text{Au(CN)}_2]^-\) of \(2 \times 10^{38.27,28}\):

\[
E = E^0 + \frac{RT}{nF} \ln C = -0.764V
\]  

Likewise, the reduction potential of Sn is calculated to be \(-0.184\ V\) vs NHE for a SnSO\(_4\) solution at a concentration of 7 \(g/L\):

\[
E = E^0 + \frac{RT}{nF} \ln C = -0.184V
\]

The potential differences of MSE and NHE are 0.616 \(V\). According to Nernst calculation results in eqs 3 and 4, the deposition potentials of Au and Sn are \(-1.380\) and \(-0.800\ V\) vs MSE, respectively. During the metal electrodeposition process, a higher cathodic overpotential is beneficial for forming fine grain particles. Therefore, if these solutions and concentrations are to be used for electrochemical codeposition, it is necessary to shift the deposition potential of Sn to a negative direction and lower than that of Au by using a proper complexing agent.
In fact, the shifting potential of Sn is more desirable, compared to shifting the potential of Au to a positive direction, because the former can result in a larger overpotential and lead to fine-grained particles.

In the absence of a complexing agent, as shown in Figure 2a, the measured reduction potential of Sn is $-0.645$ V independent of the concentration of Sn(II) ranging from 1 to 5 g/L, while the corresponding reduction peak of current density increases from $-2.620$ to $-6.270$ mA/dm$^2$. It is worth noting that the measured reduction potential of Sn is slightly higher than the value predicted by the Nernst equation, probably due to the nonideal behavior in the real electrolyte. In the case of Au(I), the measured reduction potential of Au is about $-1.121$ V (Figure 2b), which is also slightly higher than the theoretical value ($-1.380$ V). Compared to Au(I), the reduction potential of Sn(II) is found to be $0.647$ V higher in the solutions before adding complex agent.

In Figure 3, the reduction potential of Sn shifts negatively from $-0.645$ V (Figure 2) to $-0.850$ V when the addition of pyrophosphate acid is up to 60 g/L. No significant shift of potential can be observed when further increasing the concentrations of pyrophosphate. This is probably due to that the Sn(II) ions are fully complexed by $[P_2O_7]^{4-}$ at this concentration. Thus, it was found that pyrophosphate can drastically decrease the deposition potential of Sn(II) and make it possible to electrochemical codeposition of Sn(II) and Au(I) simultaneously.

The polarization curves shown in Figure 4 demonstrate that the as-prepared solution electrodeposition potentials of Sn(II) and Au(I) with 60 g/L $K_2P_2O_7$ are $-0.896$ and $-1.066$ V, respectively. After they were mixed together, the codeposition potential moves to $-1.045$ V. This indicates that $K_2P_2O_7$ is more easily to complex with Sn(II), compared to Au(I), because the potential shifts more negatively for Sn(II). Therefore, the addition of pyrophosphate is critical to realize the negative shifts of Sn(II) reduction potentials.

In order to explain the difference in shifts of deposition potential between Sn(II) and Au(I) resulting from pyrophosphate, DFT calculation was used to provide more insight into
the codeposition mechanism. Figure 5a shows the natural charge distribution and the structure for \([P_2O_7]^{4−}\) coordinated with Sn(II). This Sn\(_2\)P\(_2\)O\(_7\) structure has been previously reported by Buchner.\(^{29}\) According to our interpretation of NBO charge distribution calculations, end position O atoms are more negatively charged with charge values ranging from \(-1.212\) to \(-1.244\). The charge of Sn(II) atoms are \(1.529\). The charge differences between O and Sn(II) are \(2.741\) and \(2.773\), which are significantly less than those calculated from the O/Sn(II) complexed system. Apparently, the electrostatic interaction between oxygen atoms and Sn(II) is much stronger, compared to that between oxygen atoms and Au(I) in the complexing environment.

Figure 6 shows the calculated lowest unoccupied molecular orbital (LUMO) structure for the \([P_2O_7]^{4−}\)/Sn(II) complex (Figure 6b). As a result, the DFT computation indicates that interaction between \([P_2O_7]^{4−}\) and Sn(II) is much stronger than that between \([P_2O_7]^{4−}\) and Au(I). These findings are consistent with the experimentally observed shifts in deposition potential.

In order to study the morphology of the prepared AuSn20 films, the electrodeposited Au–Sn alloys are analyzed by SEM as displayed in Figure 7a and b. Reflective gray and dark gray areas are observed on the alloy surface, indicative of two phases being present in the sample. To identify the composition, both phases are analyzed using EDX (Figure 7c). According to the elemental analysis, the dark gray and reflective gray areas are δ phase (AuSn) and ζ phase (Au\(_5\)Sn), respectively.

Finally, AuSn20 solder bump arrays were deposited on Al\(_2\)O\(_3\) ceramic via the developed electrodeposition methods, as illustrated in Figure 8a. Importantly, the edges of the solder bumps are very even, suggesting a superior platform for fabricating standard solder bumps, as evidenced by Figure 8b and c. In addition, differential scanning calorimetry (DSC) measurements show that there is a single absorption peak at 280.9 °C (Figure 8d). This indicates a melting point of Au–Sn alloy solder bumps prepared through electrodeposition at 280.9 °C, in good agreement with that of the AuSn20 eutectic.

**CONCLUSION**

Eutectic AuSn20 films were electrochemically deposited on Al\(_2\)O\(_3\) ceramic surfaces by using a pyrophosphoric acid
complexing agent. The electrodeposition potential of Sn(II) shifts negatively and approaches that of Au(I) in the presence of pyrophosphoric acid. To provide some insights into the mechanisms, the coordination behavior between \( [\text{P}_2\text{O}_7]^{4-} \) and cations Sn(II) or Au(I) is investigated by NBO charge distribution and LUMO characteristics. These results indicate that \( [\text{P}_2\text{O}_7]^{4-} \) strongly complexes with Sn(II), relative to Au(I), thereby altering the deposition potential. Using this technique, AuSn20 eutectic solder bump arrays were, for the first time, successfully fabricated via an electrochemical codeposition method.

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**Notes**

The authors declare no competing financial interest.

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