Effect of Polyethylene Glycol Additives on Pulse Electroplating of SnAg Solder

HSIAO-YUN CHEN,[1] CHIH CHEN,[1,4] PU-WEI WU,[1,4] JIA-MIN SHIEH,[2] SHING-SONG CHENG,[3] and KARL HENSEN[3]

1.—Department of Materials Science and Engineering, National Chiao Tung University, Hsinchu 30050, Taiwan, ROC. 2.—National Nano Device Laboratories, Hsinchu 30078, Taiwan, ROC. 3.—BASF Electronic Materials Taiwan, Taoyuan 32853, Taiwan, ROC. 4.—e-mail: chih@cc.nctu. edu.tw: ppwu@mail.nctu.edu.tw

Eutectic Sn-3.5wt.%Ag alloy is one of the most promising lead-free solders in low temperature processes for wafer bumping. Near eutectic composition of deposited alloy films could be readily acquired by pulse electroplating with a proper combination of active ingredients including $K_4P_2O_7$, KI, $Sn_2P_2O_7$, and AgI, as well as polyethylene glycol (PEG), with molecular weights of 200, 600, 2,000, and 4,000, as an inhibitive agent. Pulse electroplating was carried out with current in alternating polarity to conduct electroplating and electropolishing sequentially. As a result, alloy films with grains of less than 1 μm and uniform surface morphology can be obtained. The addition of PEG was necessary for the stabilization of the plating baths to promote a wider process window for the desirable eutectic composition. Electrochemical characterization established that PEG with molecular weight of 4,000 exhibited the strongest inhibition behavior. In contrast, PEG with molecular weight of 200 demonstrated the least interference. Energy dispersive X-ray and differential scanning calorimeter data confirmed the formation of eutectic alloy as a function of deposition current density. X-ray diffraction results indicated that a biphasic structures of β-Sn and ε-Ag_3Sn was present in the as-deposited film.

Key words: Pb-free solder, packaging, electroplating solder

INTRODUCTION

The adoption of flip-chip technology has received increasing acceptance for high density and fine pitch interconnection.[1] In the flip-chip bumping process for high volume production, the electroplating method is considered to be the most efficient fabrication approach among possible solutions for delivering fine pitch configurations at reasonable cost.[2–4] Conventional solder material employs lead and tin alloy. Codeposition of Pb and Sn via electroplating is relatively straightforward as both elements exhibit similar standard reduction potential (Sn^{2+}: –0.136 V and Pb^{2+}: –0.125 V). With rising emphasis of "lead-free" materials, Pb-Sn solder

itself has become the primary target for replacement. Hence, electroplating of alternative binary alloys, such as Sn-Ag,[5–11] Sn-Bi,[12,13] Sn-Cu,[14,15] as well as the ternary system of Sn-Ag-Cu,[16–17] has been aggressively pursued.

Unfortunately, due to intricate interactions between thermodynamics and kinetics, today's plating technology is unable to deliver exact ternary compositions for the wafer level requirement. As a result, binary SnAg and SnCu solders are used in applications for flip-chip technology. Between them, Sn-Ag is better suited to replace Pb-Sn because its intrinsic properties, such as melting temperature and surface tension, closely resemble those of Pb-Sn alloys.[18]

However, there are inherent challenges associated with electroplating of Sn-Ag alloy. First, in the Sn-Ag binary phase diagram, a small deviation of Ag amount from the eutectic composition (Sn-3.5wt. %Ag) induces a substantial increase of temperature

along the solidus line. This leads to higher working temperature in subsequent soldering operation. For process reliability and repeatability, therefore, it is preferred to acquire the deposited film at the exact eutectic composition. Second, Ag^+ exhibits a much more positive standard reduction potential (0.799 V) than that of Sn^{2+} (–0.136 V). As a result, Ag^+ would be favored for "plating out" in electrolyte solution and the composition of the derived film differs considerably from that of the electrolyte phase. In contrast, the difference of standard reduction potential between Sn^{2+} and Pb^{2+} is much smaller (ΔE = 0.0113 V),[19] ensuring sufficient composition replication from electrolyte phase to the plated film.

To mitigate the relatively high activity of Ag^+, a complexing agent is used to stabilize Ag^+ for retardation of preferential precipitation. Electrodeposition of binary alloys with large difference in standard reduction potentials has been well-documented with the aid of complexing agents.[20,21] For example, using citrate, glycine, and triethanolamine as complexing additives, Mizushima et al. have achieved optimized Ni-W alloy films with minimized residual stress.[22,23] Understandably, the concentrations of complexing agent and Ag^+ in plating solution require diligent control for targeted film composition. To sum up, in order for the electroplating of Sn-3.5wt.%Ag to proceed as intended, strict controls over plating formulations, additives, and plating methods are critical.

Pulse electrodeposition is known to produce alloy films with varied materials properties. Recently, in a Cu-Ni alloy system, it was reported that composition, lattice constant, and magnetic properties could be controlled by parameters used in pulse plating.[24] In addition, pulse plating using on-off mode has been reported to yield elaborate bumps with smooth and homogeneous surfaces using triethanolamine, Triton X-100, sorbitol, sodium gluconate, and 1,4-hydroxy-benzene as agents.[25] Further, additive such as polyethylene glycol (PEG) has been studied extensively as an inhibitive agent in electroplating of Cu for integrated circuit fabrication.[26–30] However, its applicability to SnAg plating formulation is relatively unknown. In this paper, we explored the pulse plating with alternative polarities on SnAg plating solutions containing PEG with different molecular weights. Electrochemical analysis of the plating formulations and characterization of the resultant deposits were performed to identify proper plating parameters for desirable eutectic Sn-3.5wt.%Ag solder film.

EXPERIMENTAL

The experiment for electrochemical deposition of SnAg film was conducted in a tank of non-conducting polymeric material. To study the physical properties of SnAg alloy, a Ti plate of 10 cm $\times$ 10 cm was used as the counter electrode and a Si wafer of 2 cm $\times$ 3 cm was used as a working electrode. Ta ($\sim$600 Å) was sputtered on a Si wafer as

adhesion layer. Then, an overcoat of Cu ($\sim$1 μm) was sputtered as conductive layer prior to electroplating. The electrodeposition process was carried out in pulse plating mode at 25°C in which the working electrode was imposed with a periodic current swing of 1 s at –1 mA/cm^2 and 5 s of current density controlled between 4.5 mA/cm^2 and 9.0 mA/cm^2. The entire pulse plating process lasted about 900 s with agitation of electrolyte. Variables such as current density, solution formulation, as well as PEG additives were investigated to identify the optimized combination for eutectic Sn-3.5wt.%Ag deposition. Detailed makeup of the aqueous electroplating solutions used in our experiments is listed in Table I. The basic formulation follows what was reported by Arai et al. in 2003[31] where $K_4P_2O_7$ and KI were used as complexing agents, $Sn_2P_2O_7$ and AgI were selected as ion sources, and PEG600 (polyethylene glycol with molecular weight of 600) and formaldehyde were employed as inhibitors. In our formulations, STD1 to STD5 contain identical ratio of ion sources and complexing agents ($K_4P_2O_7$:KI:$Sn_2P_2O_7$:AgI = 0.5:1.0:0.125:0.0025) as Arai's, but the concentrations of those in our plating bath were reduced by half. The purpose is to slow down the electroplating process for better characterization. From Bath7 to Bath10, the concentration of AgI is reduced further to 0.00125 M while 0.001 M of PEG with molecular weight of 200, 600, 2,000, and 4,000 is added individually to study particularly the influence of PEG molecular weight over plating behavior and the resultant solder film.

To study the electrochemical characteristics of electrodeposition, current–potential curves of each plating bath were measured using EG&G potentiostat/galvanostat 273A in which a Pt plate was used as counter electrode, Ag/AgCl was chosen as reference electrode, and Cu plate of 1 cm^2 (99.99% Cu) was employed as the working electrode. Before each experiment the working electrode was first mechanically ground and cleaned with deionized (DI) water. The scanning rate was set at 0.5 mV/s and the conditioning time was 150 s.

The surface morphology of the plated films was examined by scanning electron microscope (JEOL 6500) and the chemical compositions were determined quantitatively by energy dispersive X-ray (EDX). Differential scanning calorimeter (DSC) was utilized to validate the alloy composition by recording endothermic solidus temperature with thermal scan performed from 80°C to 260°C at a 3°C/min heating rate. Four-point-probe and X-ray diffraction (XRD) (Siemens D-5000 with CuKα line at wavelength of 1.54 Å) were used to identify electrical resistivity and phase of the resultant solder films.

RESULTS AND DISCUSSION

Composition Characterization

The formulation of STD1 contains all the necessary ingredients without any PEG additive.

Table I. Composition of SnAg Electroplating Baths (mol dm^{-3}) in Our Study

	STD1	STD2	STD3	STD4	STD5	STD6	Bath7	Bath8	Bath9	Bath10
$K_4P_2O_7$	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5
KI	1.0	1.0	1.0	1.0	1.0	0.5	1.0	1.0	1.0	1.0
$Sn_2P_2O_7$	0.125	0.125	0.125	0.125	0.125	0.125	0.125	0.125	0.125	0.125
AgI	0.0025	0.0025	0.0025	0.0025	0.0025	0.0025	0.00125	0.00125	0.00125	0.00125
PEG200		0.001		0.002			0.001			
PEG600			0.002		0.001			0.001		
PEG2000									0.001	
PEG4000										0.001

Therefore, we started out with STD1 by exploring plating conditions to pinpoint the necessary process parameters for eutectic Sn-3.5wt.%Ag deposit. A typical profile of the pulse plating mode is illustrated in Fig. 1a. The purpose for alternating current polarity during pulse plating is to obtain better control in morphology and film composition as both electropolishing and electroplating operate sequentially. We have reported similar results in Cu damascence process in which much improved surface uniformity of Cu layer is observed by reversing current polarity intermittently.[32]

As shown from Fig. 1a and b, desirable Sn-3.5 wt. %Ag film was confirmed with the pulse plating mode at positive current density of 6.0 mA/cm^2 and negative current density of 1.0 mA/cm^2 for processing time of 15 min. Figure 1b is the SEM picture illustrating the surface morphology of the as-deposited film with grain clearly seen larger than 1 μm. Insert in Fig. 1b is the EDX analysis result suggesting an uniform distribution of Sn and Ag without notable segregation. As described previously, the solidus temperature of the Sn-3.5wt.%Ag solder is extremely sensitive to the concentration of Ag in the binary system. Hence, endothermic event of solidus temperature serves perfectly well as an indicator reflecting the exact amount of Ag in the as-deposited alloy. In the DSC analysis in Fig. 1c, an endothermic peak was recorded at 221.79°C which is consistent with what we expect from the eutectic temperature of Sn-3.5wt.%Ag. In addition, the resistivity of the resultant film was measured at 15.64 $\mu\Omega$ cm. The growth rate of the deposited film was determined to be 0.231 μm/min using SEM to measure the thickness of the film.

Figure 2 illustrates the relationship for the current density at positive polarity and the resultant Ag concentration in the SnAg film for several plating formulations. The amount of Ag was determined by EDX. The observed high amount of Ag in the low current density region is attributed to the relatively positive reduction potential of Ag$^+$ as compared to that of Sn^{2+}. As expected, the Ag concentration decreases sharply with increase in the current density for every plating bath. This behavior is in agreement with a previous report on electrodeposition of SnAg via galvanostatic and potentiostatic

approaches.[31] It is because as the overpotential becomes considerable at higher imposed current, less favored reactions, such as reduction of Sn^{2+}, are able to participate, and low concentrations of Ag$^+$, in the electrolyte becomes diffusion limited.

After examining pulse electroplating with positive current density ranging between 4.5 mA/cm^2 and 9.0 mA/cm^2, we collected the as-deposited films and analyzed with a four-point probe for resistivity. Their results are listed in Table II. The current range for desirable eutectic Sn-3.5wt.%Ag, defined as the process window, is also provided. Typically, a wider range of process window is favored for better plating tolerance. Relatively wide process window of 4.5–9.0 mA/cm^2 was observed for formulation STD2, Bath7, and Bath8. In contrast, Bath9 and Bath10 exhibited somewhat narrower process window of 6.0–7.5 mA/cm^2, while STD1 delivered the eutectic composition approximately at 6.0 mA/cm^2. Unfortunately, the eutectic composition of SnAg was not available from STD3, STD4, STD5, and STD6. It seems that reduction of Ag$^+$ concentration in plating formulation is beneficial to establishment of process window as evidenced by Bath7–10. This accords nicely with the understanding that large difference in reduction potential between Ag$^+$ and Sn^{2+} causes composition instability in the as-deposited film. Consequently, inhibition of Ag$^+$ activity is necessary for a repeatable plating process. The values for resistivity of the as-deposited films fall within a reasonable range as expected for Sn-Ag alloy. In short, Table II indicates the importance of strict control over formulations and plating parameters for composition management in binary alloy plating.

The influence of PEG with different molecular weights is of great interest in Cu plating studies. Previously, Kelly et al.[33] and Healy et al.[27] suggested that PEG in the presence of Cl$^-$ would adsorb on the substrate and inhibit subsequent reduction of Cu^{2+}. However, adding PEG alone exhibits a relatively small effect. In our study of Sn-Ag plating formulation, PEG shows a rather pronounced effect. Bath7–10 include identical composition in $K_4P_2O_7$, KI, $Sn_2P_2O_7$, and AgI, while PEG200, PEG600, PEG2000, and PEG4000 are added individually. PEG of higher molecular weight is likely to provide
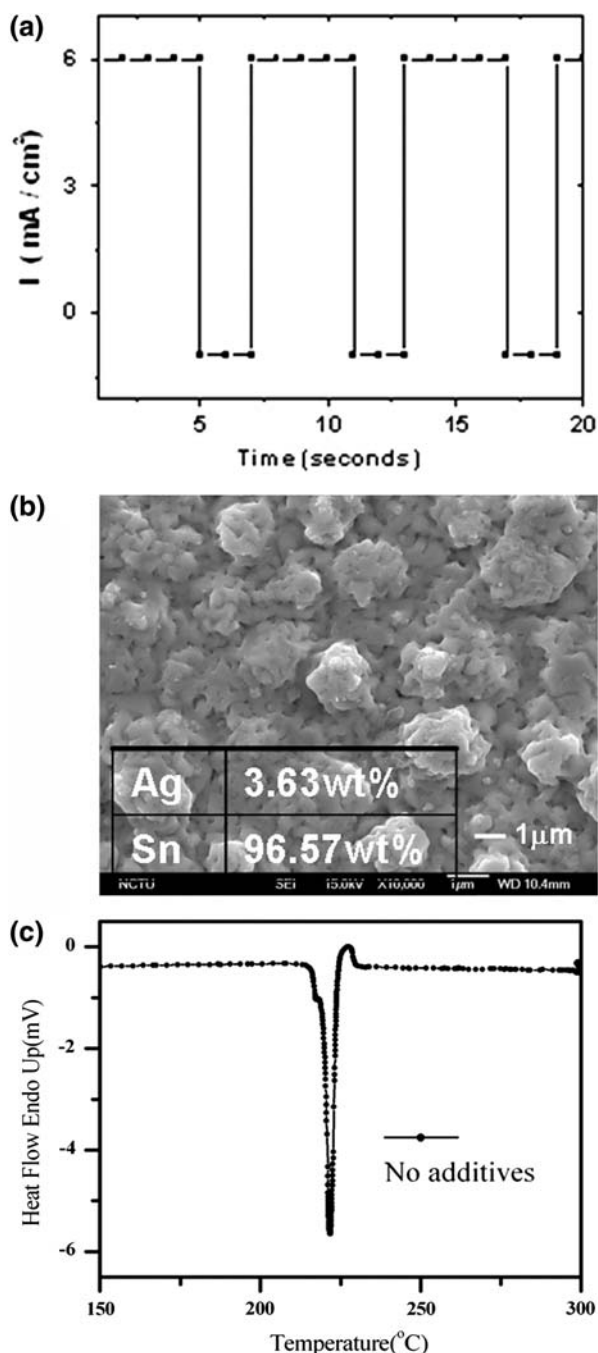
Fig. 1. Characterizations of the as-deposited SnAg film from pulse electroplating of STD1 formulation; (a) current profile for the electrodeposition process, (b) SEM micrograph of typical surface morphology, and the EDX analysis of film composition: Sn: 96.57 wt.%; Ag: 3.63 wt.%, and (c) DSC curve with endothermic peak recorded at 221.8°C.

Fig. 2. Relationship between current density at positive polarity and the resulting Ag concentration in the alloy film for various baths.

Table II. Composition Analysis of the SnAg film from Various Plating Baths with the Process Window Listed for Eutectic Sn-3.5wt.%Ag. Also Listed is the Resistivity of the As-deposited Film

	Process Window for Eutectic Sn-3.5wt.%Ag	Resistivity ($\mu\Omega$ cm)
STD1	~6.0 mA/cm^2	15.86
STD2	4.5–9.0 mA/cm^2	18.5
STD3	N/A	19.10
STD4	N/A	18.37
STD5	N/A	17.02
STD6	N/A	15.39
Bath7	4.5–9.0 mA/cm^2	16.85
Bath8	4.5–9.0 mA/cm^2	17.21
Bath9	6.0–7.5 mA/cm^2	18.46
Bath10	6.0–7.5 mA/cm^2	18.79

solution to mitigate favored "plating-out" of Ag$^+$. Indeed, Bath9 and Bath10 exhibit a narrower range of process window (6.0–7.5 mA/cm^2 versus 4.5–9.0 mA/cm^2 of Bath7–8).

Electrochemical Analysis

Current–potential curves for selective plating baths with PEG as additive as well as STD1 formulation are provided in Fig. 3. Electrochemical reduction of Ag$^+$ took place initially at approximate −0.5 V to −0.55 V and the reducing current rose sharply when the potential became more negative as Sn^{2+} participated in the reduction process. As expected, the I–V curve of STD1 exhibited the highest current since PEG is well-established as inhibition additive. Bath7–10 contain PEG with molecular weight of 200, 600, 2,000, and 4,000, respectively. Among them, formulation with PEG4000 demonstrated the lowest current with the onset voltage of −0.55 V. In contrast, the curve from formulation with PEG200 showed negligible

more coverage of active sites as well as stronger complexing reaction as compared to PEG of lower molecular weight. Therefore, PEG with higher molecular weight exerts a stronger influence over the plating process and thus the parameters for desirable composition are relatively confined. Nevertheless, PEG is needed to stabilize the plating
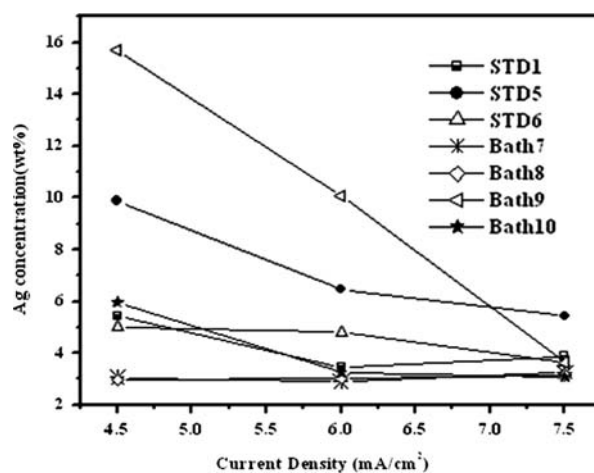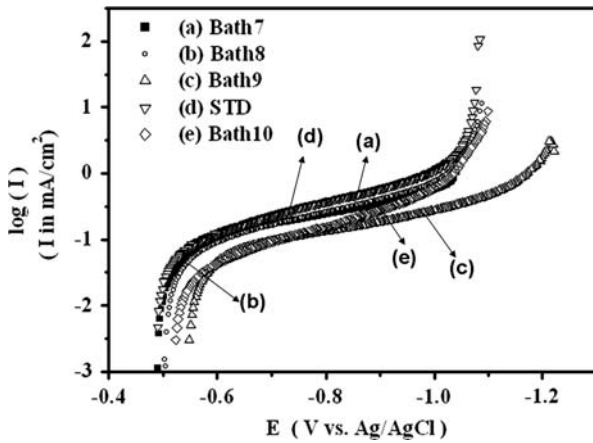
Fig. 3. Current–potential curves for several baths with PEG as additive. STD1 is included for comparison.

lowest one. As expected, PEG200 was shown to have a better process window than PEG4000.

It is to be noted that the current density used in our pulse deposition is between 4.5 mA/cm^2 and 9.0 mA/cm^2, which is in the upper range of the reducing current recorded here in I–V curve. Thus, it is suggested that substantial polarization occurred in pulse plating that promotes the reduction of Sn^{2+} and as a result, near eutectic Sn-3.5wt.%Ag film was obtained at regime of relatively high current density.

Deposit Microstructure and Phase Identification

Figure 4 shows SEM micrographs of the surface morphology of the as-deposited SnAg films from several plating formulations. The films were obtained with current density of 6.0 mA/cm^2 and the deposition process lasted 15 min. Figure 4a exhibits the as-deposited film from STD1 where grains larger than 1 μm and uneven surface were clearly observed. In contrast, as evidenced from

difference as compared to that of STD1. Thus, we conclude that PEG4000 delivered the highest inhibition performance, while PEG200 carried the
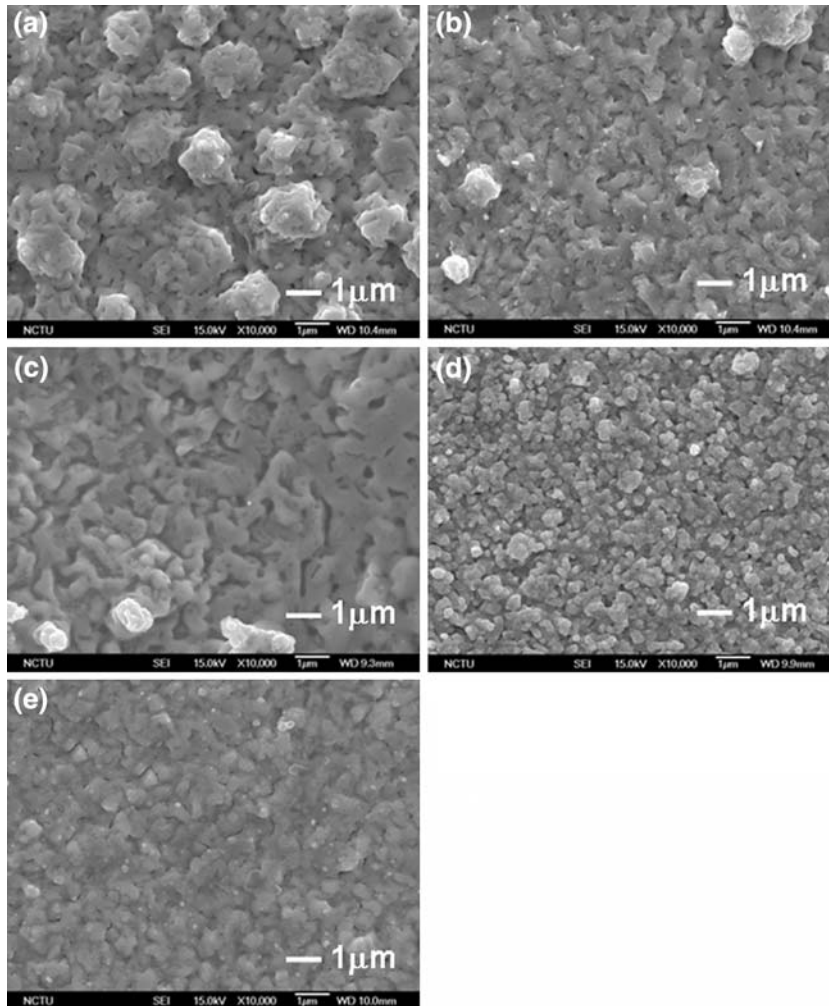

Fig. 4. SEM images of surface morphology of the as-deposited SnAg alloy films for (a) STD1, (b) STD5, (C) STD2, (d) Bath9, and (e) Bath10. EDX data confirmed their near-eutectic composition.
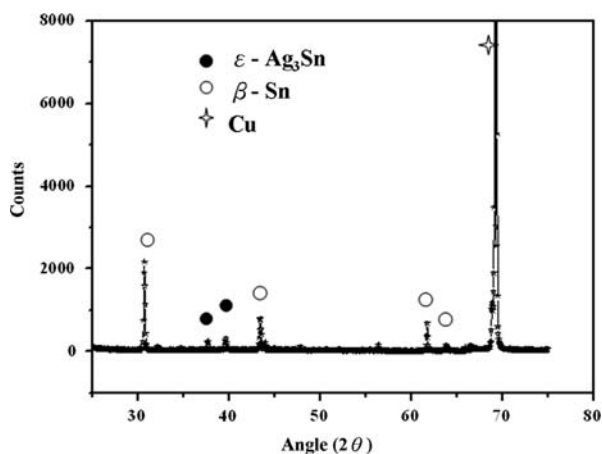
Fig. 5. XRD data for eutectic Sn-3.5wt.%Ag film showing coexistence of β-Sn and ε-Ag$_3$Sn.
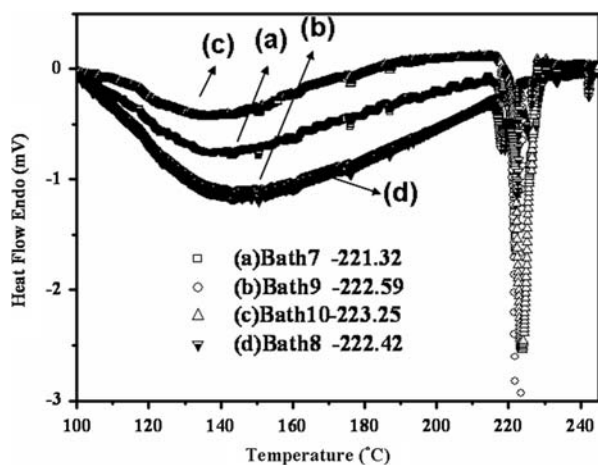

Fig. 6. DSC curve of heat flow for occurrence of solidus temperature of as-deposited SnAg film from different plating baths.

Fig. 4b–d, the addition of PEG4000, PEG2000, PEG600, and PEG200 results in significant improvement in surface morphology and much finer grains. This trend suggested the positive influence of PEG as an plating additive.

Figure 5 shows the XRD pattern of the as-deposited film from Bath7 with the positive current density of 6.0 mA/cm^2 for deposition time of 15 min. The diffraction peaks confirmed the existence of β-Sn and ε-Ag$_3$Sn phases suggesting that biphasic structures of eutectic Sn-3.5wt.%Ag could be readily acquired from our pulse electrodeposition approach.

Figure 6 exhibits DSC curves of the as-deposited film from formulation Bath7, Bath8, Bath9, and Bath10. As mentioned previously, the solidus temperature is sensitive to the exact composition of the SnAg alloy. In DSC, the negative heat flow represents endothermic reaction that corresponds to onset of melting for the alloy film. The temperatures of the endothermic peaks fall between 221°C and 222°C, which coincide nicely to the theoretical

eutectic point of Sn-3.5wt.%Ag at 221°C. Hence, we are confident that eutectic SnAg solder film can be readily deposited in the pulse plating method.

CONCLUSIONS

The eutectic Sn-3.5wt.%Ag alloy films with homogenous composition and smooth surface morphology were readily obtained from pulse electrodeposition for plating formulations containing AgI and Sn$_2$P$_2$O$_7$ as ionic salts, K$_4$P$_2$O$_7$ and KI as complexing agents, and polyethylene glycol with molecular weights of 200, 600, 2,000, and 4,000 as an additive. Composition analysis of the as-deposited film indicated that Ag concentration decreases with increasing deposition current. From data of DSC, EDX, and X-ray, we concluded that the processing window for desirable eutectic Sn-3.5wt.%Ag composition can be extended once PEG additive is included. We attribute the widening of process window to the inhibitive characteristics of PEG molecules that retard preferential deposition of Ag$^+$ ions. In addition, SEM micrographs showed that the as-deposited films with PEG as an additive exhibit grains smaller than 1 μm and much improved surface morphology. From the current–voltage curve, we identified that PEG with molecular weight of 4,000 demonstrates the highest inhibition capability while PEG with molecular weight of 200 exhibits the least. In addition, we established that the process window can be expanded by simply reducing the concentration of active Ag$^+$ concentration.

REFERENCES

1. International Technology Roadmap for Semiconductors, *Assembly and Packaging Section* (San Jose, CA: Semiconductor Industry Association, 2003), p. 4.
2. D. Suraski and K. Seeling, *IEEE Trans. Electron. Packag. Manufact.* 24, 244 (2001).
3. K. Nimmo, *Proc. Electron. Goes Green 2000+* (Berlin, Germany, Sep., 2000), p. 43.
4. K. J. Puttlitz, *Proc. Short Course, 50th Electron. Comp. Technol. Conf.* (Las Vegas, NV, 2000).
5. H. Nawafune, K. Ikeda, H. Kitamura, S. Mizaunoto, T. Takeuchi, and K. Aoki, *J. Surf. Fin. Soc. Jpn.* 49, 759 (1998).
6. S. Arai and T. Watanabe, *J. Surf. Fin. Soc. Jpn.* 49, 73 (1998).
7. T. Kondo, K. Obata, T. Takeuchi, and S. Masaki, *Plat. Surf. Finish.* February, 51 (1998).
8. S. Arai and T. Watanabe, *Mater. Trans. JIM* 39, 439 (1998).
9. Y. Fujiwara, T. Narahara, H. Enomoto, K. Funada, and T. Omi, *J. Surf. Fin. Soc. Jpn.* 49, 1316 (1998).
10. H. Nawafune, K. Shiba, S. Mizumoto, T. Takeuchi, and K. Aoki, *J. Surf. Fin. Soc. Jpn.* 51, 1234 (2000).
11. S. Arai, N. Kaneko, and N. Shinohara, *Electrochemistry* 69, 254 (2001).
12. M. Jordan, *Trans. IMF.* 75, 149 (1997).
13. H. Tanaka, M. Tanimoto, A. Matsuda, T. Uno, M. Kurihara, and S. Shiga, *J. Electron. Mater.* 28, 1216 (1999).
14. H. Nawafune, K. Ikeda, K. Shiba, S. Mizumoto, T. Takeuchi, and K. Aoki, *J. Surf. Fin. Soc. Jpn.* 50, 923 (1999).
15. M. Fukuda, K. Hirakawa, and Y. Matsumoto, *J. Surf. Fin. Soc. Jpn.* 50, 1125 (1999).
16. S. Arai and N. Kaneko, *Denki Kagaku oyobi Kogyo Butsuri* 65, 1102 (1997).

17. S. Arai, N. Kaneko, and N. Shinohara, *J. Surf. Sci. Soc. Jpn.* 22, 463 (2001).
18. F. Guo, S. Choi, J.O. Lucas, and K.N. Subramanian, *J. Electron. Mater.* 29, 10 (2000).
19. M. Jordan, *Galvanotechnik* 92, 1225 (2001).
20. M. Paunovic and M. Schlesinger, *Fundamentals of Electrochemical Deposition* (New York: John Wiley & Sons, 1998).
21. M. Schlesinger and M. Paunovic, *Modern Electroplating*, 4th ed. (New York: John Wiley & Sons, 2000).
22. I. Mizushima, P.T. Tang, H.N. Hansen, and M.A.J. Somers, *Electrochim. Acta* 51, 888 (2005).
23. I. Mizushima, P.T. Tang, H.N. Hansen, and M.A.J. Somers, *Electrochim. Acta* 51, 6182 (2006).
24. I. Baskaran, T.S.N. Sankara Narayanan, and A. Stephen, *Mater. Lett.* 60, 1990 (2006).
25. B. Neveu, F. Lallemand, G. Poupon, and Z. Mekhalif, *Appl. Surf. Sci.* 252, 3561 (2006).
26. S.C. Chang, J.M. Shieh, K.C. Lin, and B.T. Dai, *J. Vac. Sci. Technol. B* 20(4), 1311 (2002).
27. J.P. Healy and D. Pletcher, *J. Electroanal. Chem.* 338, 155 (1992).
28. T.O. Drews, J.C. Ganley, and R.C. Alkire, *J. Electrochem. Soc.* 150, C325 (2003).
29. E.E. Fardon, F.C. Walsh, and S.A. Campbell, *J. Appl. Electrochem.* 25, 574 (1995).
30. T.P. Moffat, B. Baker, D. Wheeler, and D. Jossell, *Electrochem. Solid State Lett.* 6, C59 (2003).
31. S. Arai, H. Akatsuka, and N. Kaneko, *J. Electrochem. Soc.* 150(10), C730 (2003).
32. S.C. Chang, J.M. Shieh, K.C. Lin, and B.T. Dai, *J. Vac. Sci. Technol. B* 20(6), 2233 (2002).
33. J.J. Kelly and A.C. West, *J. Electrochem. Soc.* 145, 3472 (1998).