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# Electrochemical Alloying of Copper Substrate with Tin Using Ionic Liquid as an Electrolyte at Medium-Low Temperatures

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Electrochemical alloying of Cu substrates through a reduction-diffusion method was investigated using an ionic liquid, trimethyl*n*-hexylammonium bis[(trifluoromethyl)sulfonyl]amide, as a solvent for an electrolytic bath. The use of the ionic liquid made it possible to raise the processing temperature beyond 100°C and form the Cu–Sn layers faster than with an aqueous media. The layers obtained from a Cu thin layer under a potentiostatic condition were silver-gray speculum metal composed of Cu<sub>6</sub>Sn<sub>5</sub>, Cu<sub>3</sub>Sn, and Cu<sub>10</sub>Sn<sub>3</sub> intermetallic phases, while those prepared under a galvanic contact condition involved a  $\beta$ -Sn phase containing a trace amount of copper. The formation of each Cu–Sn phase is discussed in terms of alloy formation thermodynamics. © 2007 The Electrochemical Society. [DOI: 10.1149/1.2776230] All rights reserved.

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The electrodeposition of alloys and compounds is a key technology for thin-layer processing in the fields of, for example, surface finishing and electronic materials. Cu-Sn alloy coating with composition of 40-60 wt % Sn, called "speculum metal," is silver-gray and has been investigated as promising alternative to an allergenic nickel coating,<sup>1-3</sup> which is used, for example, as an underlayer for chromium or gold electroplating. The layer also has potential as a novel anode material for lithium batteries.<sup>4-6</sup> In both cases, an electroplating technique will provide a useful route to form the Cu-Sn layer. Although electrodeposition technology is generally considered to be a "soft solution process," the waste bath treatment sometimes involves cumbersome and complicated procedures. Especially, the treatment of conventional alloy deposition bath, entropy of which is high, because the bath contains two or more metal components, is energy-consuming in some cases. In 2003, Fujiwara' demonstrated that a Cu-Sn speculum metal layer can be electrochemically formed on a Cu substrate by a reduction-diffusion (RD) method using an electrochemical contact immersion, or galvanic contact, process, where the substrate is immersed into an aqueous citrate bath containing only Sn(II) ions and is short circuited to an auxiliary metallic Sn electrode dipped in the same bath. Here, the Cu substrate and Sn electrode constitute a kind of short-circuited galvanic cell, where the former acts as a cathode and the latter as an anode. By applying this technique, it is thought that a Cu-Sn alloy layer may be obtained on any conductive or nonconductive substrate through electrodeposition or electroless deposition of a Cu layer from appropriate baths containing only Cu(II) ions followed by the RD process to give a Cu-Sn alloy. Figure 1, for example, compares the scheme of conventional decorative chromium electroplating process using nickel underlayer to that using Cu-Sn underlayer prepared through the RD alloying on both conductive and nonconductive substrates. Although this requires two steps to obtain the Cu-Sn alloy layer, the consecutive use of baths, each containing a single-metal component, makes the waste bath treatment simple and easy.

For the continuous growth of Cu–Sn alloy by the RD process, rapid diffusion of deposited Sn atoms into the Cu substrate to form the alloy phase is essential in order to keep the activity of tin,  $a_{\rm Sn}$ , in the alloy less than unity (i.e.,  $a_{\rm Sn} < 1$ ). In other words, the diffusion of Sn atoms is a rate-determining step in this process and, hence, a relatively high process temperature is required.<sup>7</sup> As long as aqueous or volatile organic baths, if any, are employed, however, a process temperature higher than 100°C is technically difficult in the ambient atmosphere without a special vessel, such as an autoclave. In contrast, more recently, we tried using a nonvolatile and nonflammable

hydrophobic ionic liquid, trimethyl-*n*-hexylammonium bis[(trifluoromethyl)sulfonyl]amide (TMHA–Tf<sub>2</sub>N), as the solvent for the galvanic contact formation of the Cu–Sn layer,<sup>8</sup> and it was demonstrated that the use of this ionic liquid rendered it possible to raise the processing temperature up to 150°C, thus forming alloy layers faster than with aqueous media (Fig. 2). The growth rate of the alloy layer increased with increasing bath temperature, and the rate at 140–150°C was more than three times that at 90°C in aqueous or TMHA–Tf<sub>2</sub>N media. The data plotted in Arrhenius fashion (Fig. 2b) gave a single straight line with an apparent activation energy of 58 kJ mol<sup>-1</sup>, indicating that, in both aqueous and TMHA–Tf<sub>2</sub>N media, the rate-determining step of the growth is the solid-phase interdiffusion of Cu and Sn atoms in the growing Cu–Sn layer.

In the previous study,<sup>8</sup> we employed a bulk Cu sheet (thickness, 0.2 mm) as a Cu substrate for alloying. In this case, only the surface of the sheet was converted to Cu–Sn alloy and the interior of the sheet remained unalloyed. To develop the processes in Fig. 1b and c, for example, the complete alloying of a thin copper layer should be developed so as to ensure the long-term thermodynamic stability of the resulting Cu–Sn layer. In the present study, we tried using a thin Cu layer (thickness, 0.5  $\mu$ m), electrodeposited from an aqueous solution, as a substrate for Cu–Sn alloying and discuss the thermodynamics of alloy formation.

## Experimental

The ionic liquid, TMHA–Tf<sub>2</sub>N, was prepared by the metathesis of trimethyl-*n*-hexylammonium bromide (TMHABr; Tokyo Kasei Kogyo Co., Ltd., 98%) with lithium bis[(trifluoromethyl)sulfonyl] amide (LiNTf<sub>2</sub>; Fluka, 99%) as

$$n-C_{6}H_{13}(CH_{3})_{3}NBr + LiN(SO_{2}CF_{3})_{2}$$
  
 $\rightarrow n-C_{6}H_{13}(CH_{3})_{3}N^{+}N^{-}(SO_{2}CF_{3})_{2} + LiBr$  [1]

After drying the resulting TMHA–Tf<sub>2</sub>N in vacuo for more than 2 h at 120°C in a flask connected to a liquid N<sub>2</sub> trap, the residual water contents, checked by coulometric Karl-Fischer method, were <50 ppm. Tin(II) salt, Sn(Tf<sub>2</sub>N)<sub>2</sub>, was prepared under ambient atmospheric conditions using the acid-base reaction of SnO (Nacalai Tesque Inc.) with bis[(trifluoromethyl)sulfonyl]amine (HNTf<sub>2</sub>, Fluka, 99%) as

$$\text{SnO} + 2\text{HNTf}_2 \rightarrow \text{Sn}(\text{Tf}_2\text{N})_2 + \text{H}_2\text{O}$$
 [2]

The detailed procedure was described in our previous paper.<sup>9</sup> Note that the resulting  $Sn(Tf_2N)_2$  salt may contain residual water and/or HNTf<sub>2</sub>. In the present RD process, however, these residues, if any, have an insignificant effect on the reduction of  $Sn^{2+}$  to Sn, since the potential of  $Sn^{2+}/Sn$  redox couple ( $E_{Sn^{2+}/Sn}$ ) is not that negative. It is also expected that most of these volatile residues spontaneously va-

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Figure 1. Chromium electroplating using (a) Ni underlayer (conventional process) and (b, c) Cu–Sn underlayer (alternative process) where copper layers for RD alloying are (b) electrodeposited on a conductive substrate or (c) electroless deposited on a nonconductive, e.g., resin, substrate.

porize away when the bath for alloying is operated at a medium-low temperatures, e.g., 130°C.

In order to prepare the  $Sn(Tf_2N)_2$ -TMHA-Tf\_2N solution, that is, the bath for alloying, the metal salt  $Sn(Tf_2N)_2$  was weighed in a glove box and dissolved into the TMHA-Tf<sub>2</sub>N to yield a metal ion concentration of 0.05 mol dm<sup>-3</sup>. The Cu-Sn alloying was carried out under atmospheric conditions (not in the glove box). To avoid the oxidation of Sn(II) ions to Sn(IV) state, the Sn(Tf<sub>2</sub>N)<sub>2</sub>-TMHA-Tf<sub>2</sub>N bath was deaerated with nitrogen gas. A thin copper layer (thickness, 0.5 µm) electrodeposited galvanostatically at 60 mA cm<sup>-2</sup> from a conventional room-temperature aqueous sulfate plating bath containing 0.8 mol dm<sup>-3</sup> CuSO<sub>4</sub> and 0.5 mol dm<sup>-3</sup> H<sub>2</sub>SO<sub>4</sub> on a glassy carbon sheet (10 mm  $\times$  20 mm; thickness 0.5 mm) was used as the Cu substrate for the RD alloying. In the present study, we employed two types of electrochemical setups for the alloying: one was galvanic contact and the other used a potentiostatic method. In the former case using the galvanic contact, the Cu substrate, which acted as the cathode, was short circuited with a Sn sheet (10 mm  $\times$  100 mm; thickness 1.5 mm), i.e., the anode, using a zero-shunt ammeter (Hokuto Denko, HM-104). Here, a Sn rod (2 mm  $\times$  1.5 mm  $\times$  90 mm) immersed in the same solution was used as a quasi-reference electrode to monitor the cathode potential. For potentiostatic alloying, a conventional potentiostat (Hokuto Denko, HA-151) with a three-electrode configuration was



**Figure 2.** Temperature dependence of the thickness of Cu–Sn layers plotted (a) on a linear scale and (b) in Arrhenius fashion; the layers were formed on a bulk copper sheet by galvanic contact RD alloying for 72 h using 0.05 mol dm<sup>-3</sup> Sn(Tf<sub>2</sub>N)–TMHA–Tf<sub>2</sub>N solution (open circles; Ref. 8). The thickness was determined from scanning electron microscope (SEM) images of the cross section of the layers. The thickness of the layer from aqueous solution (Ref. 7) is also indicated by filled circles; the data of Ref. 7 (temperature 70°C, 80°C, and 90°C; alloying time 16 h) was recalculated for the alloying time of 72 h, assuming the parabolic low, i.e., thickness  $x = kt^{1/2}$ , where *k* is a constant.

used for the same set of Cu substrate (cathode), Sn sheet (anode), and Sn rod (reference). For both electrochemical setups, the bath was thermostated at 130°C (403 K) and agitated at  $\sim$ 500 rpm using a magnetic stirring unit. The reaction time for the alloying was kept at 72 h, if not otherwise specified.

The surface morphology of the resulting Cu–Sn layers was examined by scanning electron microscope (Keyence VE-7800). The average compositions of the Cu–Sn layers were determined by electron probe microanalysis (EPMA) using Hitachi S-3500-H spectrometer. The X-ray diffraction (XRD) measurements of the layer were carried out with a scan mode of  $2\theta$ - $\theta$  using a Rigaku RINT 2200 X-ray diffractometer fitted with a copper X-ray tube.

## **Results and Discussion**

Galvanic contact alloying .- Although the galvanic contact alloying of the bulk Cu sheet yielded a uniform silver-gray Cu-Sn layer with metallic luster,<sup>8</sup> the alloying of a thin Cu layer under the same condition gave a dark gray layer, with spongelike deposits at the edges (Fig. 3). The potential of the substrate during the alloying was spontaneously kept between +2 mV to 0 mV vs  $\text{Sn}^{2+}/\text{Sn}$  (Sn rod), which was almost the same value for the galvanic contact alloying of bulk Cu substrate at 130°C.<sup>8</sup> Figure 4 shows the XRD patterns of the resulting layers obtained by alloying for 72 h and 240 h. Each pattern demonstrated that the layers were crystalline, composed of  $Cu_6Sn_5$ ,  $Cu_3Sn$ , and  $Cu_{10}Sn_3$  intermetallic phases like the case of the bulk Cu sheet<sup>8</sup> (note that three broad peaks, or halos, at 20 of 20–30°, 40–60°, and 75–90° were due to a glassy carbon substrate underneath). There was no diffraction of face-centered cubic (fcc)-Cu phase, i.e., the elemental Cu phase, indicating that all Cu thin layers were converted to Cu-Sn alloys. Also of interest here is that some amounts of the  $\beta$ -Sn phase were recognized at the cathode. The emergence of spongelike morphology may well be attributed to the deposition of the  $\beta$ -Sn phase. This, however, seemed strange because, under the galvanic contact condition using a pure  $\beta$ -Sn anode ( $a_{\text{Sn}} = 1$ ), deposition of the pure  $\beta$ -Sn phase on Cu substrate, i.e., the cathode, is thermodynamically impossible. Here, the potential of the copper substrate is automatically kept more positive than the potential for pure  $\beta$ -Sn deposition, and therefore, the activity of tin  $a_{\rm Sn}$  deposited at the cathode should be less than unity  $(a_{\text{Sn}} < 1)$ .

To ascertain the cause of the deposition of the  $\beta$ -Sn phase, the spongelike portion was carefully collected and detailed analysis of the deposits was further carried out. Although the XRD pattern (Fig. 5) indicated that the spongelike portion was almost pure  $\beta$ -Sn without any additional phase, the inductively coupled plasma atomic emission spectrometry of the diluted H<sub>2</sub>SO<sub>4</sub> aqueous solution, in which a fraction of the spongelike deposit was dissolved, revealed that the  $\beta$ -Sn phase contained a trace amount of copper. In other words, it is expected that the  $a_{\text{Sn}}$  of the  $\beta$ -Sn phase that formed on the cathode was slightly less than unity, making the deposition thermodynamically feasible. The driving force behind the galvanic contact alloying is the difference in  $a_{\text{Sn}}$ , or difference in potential

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**Figure 3.** Appearance of the Cu thin layer (a) before and (b) after Cu–Sn alloying by galvanic contact for 72 h using a 0.05 mol dm<sup>-3</sup> Sn(Tf<sub>2</sub>N)<sub>2</sub>–TMHA–Tf<sub>2</sub>N bath at 130°C. (c, d) Surface SEM images of the spongelike portion of the layer (b). (d) is an enlargement of (c).

 $E_{\text{Sn}^{2+}/\text{Sn}}$ , between the growing Cu–Sn layer and auxiliary Sn anode  $(a_{\text{Sn}} = 1)$ . Under such a condition, the system moves automatically in such a way that the  $a_{\rm Sn}$  of the deposit on cathode is as close to 1 as possible within the range  $a_{\text{Sn}} < 1$ . On shortcircuiting, the Cu layer is alloyed from the surface and, here, it is expected that the Sn atoms are first dissolved into the fcc-Cu phase, where  $a_{Sn}$  lies at the lowest possible level. Then, intermetallic phases, i.e., Cu<sub>10</sub>Sn<sub>3</sub> (36 wt % Sn), Cu<sub>3</sub>Sn (38 wt % Sn), and Cu<sub>6</sub>Sn<sub>5</sub> (61 wt % Sn), with higher  $a_{Sn}$  values start to grow. It is important that, even after the conversion of the whole layer to these intermetallic phases, there remains some potential difference between the cathode and anode, and the next phase with the highest possible  $a_{\rm Sn}$  value, that is the  $\beta$ -Sn phase containing Cu atoms, can be grown on the surface. In the case of galvanic contact alloying of the bulk Cu sheet,<sup>8</sup> we have never experienced formation of the  $\beta$ -Sn phase on the cathode, probably because the thick Cu sheet was not completely alloyed within 72 h.

Potentiostatic alloying.— It turned out that the RD alloying of thin Cu layer is possible using the galvanic contact method, but the resulting layer involved a spongelike  $\beta$ -Sn phase. As described above, the cathode potential of the Cu substrate during the galvanic contact condition lies between +2 mV and 0 mV vs Sn<sup>2+</sup>/Sn, and such a knife-edge potential might be a cause for the  $\beta$ -Sn deposition. To avoid deposition of the  $\beta$ -Sn phase, therefore, we tried alloying using a potentiostatic condition at more positive potentials.



Figure 4. XRD patterns of Cu–Sn layers obtained by galvanic contact RD alloying for (a) 72 h and (b) 240 h using a 0.05 mol dm<sup>-3</sup> Sn(Tf<sub>2</sub>N)<sub>2</sub>–TMHA–Tf<sub>2</sub>N bath at 130°C.

Figure 6 depicts the appearance and surface SEM photos of the resulting Cu–Sn layers. Each of the layers obtained in the potential range +1 mV to +40 mV vs Sn<sup>2+</sup>/Sn grew uniformly and appeared as silver-gray layers without the codeposition of a spongelike phase. A set of XRD patterns showed that the layers were only composed of intermetallic phases, Cu<sub>6</sub>Sn<sub>5</sub>, Cu<sub>3</sub>Sn, and Cu<sub>10</sub>Sn<sub>3</sub>, and the  $\beta$ -Sn phase was not found (Fig. 7). As in the galvanic contact method, the fcc-Cu phase was not detected either, indicating that the Cu layers on the glassy carbon substrate were thoroughly converted to inter-



Figure 5. XRD pattern of spongelike portion formed at the edge of the Cu–Sn layers obtained by galvanic contact for 72 h using a 0.05 mol dm<sup>-3</sup> Sn(Tf<sub>2</sub>N)<sub>2</sub>–TMHA–Tf<sub>2</sub>N bath at 130°C.



Figure 6. Appearance of the thin Cu layer (a) before and (b,c) after Cu–Sn alloying by the potentiostatic method for 72 h using a 0.05 mol dm<sup>-3</sup> Sn(Tf<sub>2</sub>N)<sub>2</sub>–TMHA –Tf<sub>2</sub>N bath at 130°C. Surface SEM images of the layer (d) before and (e–g) after the alloying are also indicated. The potentials for alloying were (b,e) +5 mV, (c,f) +10 mV, and (g) +20 mV vs Sn<sup>2+</sup>/Sn. Lower SEM images are enlargements of the upper ones.

metallic compounds. It should be noted that resulting Cu-Sn intermetallic phases depended on the applied potential for alloying. The abundance of the Sn-rich phase, i.e.,  $Cu_6Sn_5$ , whose tin activity  $a_{Sn}$ is the highest of the three, increased with decreasing potential for alloying. In other words, a higher  $a_{Sn}$  phase(s) was deposited at relatively lower potentials, while a lower  $a_{Sn}$  phase(s) was deposited at higher potentials. When assessed from the XRD patterns, the main phase was Cu<sub>6</sub>Sn<sub>5</sub> at +5 mV, while the layers obtained at +10 mV and +20 mV were composed mainly of the Cu<sub>3</sub>Sn and Cu<sub>10</sub>Sn<sub>3</sub> phases. This behavior is also supported by a set of average composition data obtained by EPMA for each of the layers formed at five different potentials between +1 mV and +40 mV (Fig. 8). The average compositions of the layers obtained at +1 mV and +5 mV were close to the Cu<sub>6</sub>Sn<sub>5</sub> (45.5 atom % Sn) phase, while those at 10-40 mV were close to the Cu<sub>3</sub>Sn (25.0 atom % Sn) or Cu<sub>10</sub>Sn<sub>3</sub> (23.1 atom % Sn) phase.

As evidenced by Fig. 8, it was found that Cu–Sn "speculum metal" layers, i.e., 40–60 wt % Sn, could easily be prepared by controlling the alloying potentials between +1 mV and +5 mV vs Sn<sup>2+</sup>/Sn. Figure 9 compares a set of current density data during the



Figure 7. XRD patterns of Cu–Sn layers obtained by potentiostatic RD alloying for 72 h at +5 mV, +10 mV, and +20 mV vs  $Sn^{2+}/Sn$  using a 0.05 mol dm<sup>-3</sup> Sn(Tf<sub>2</sub>N)<sub>2</sub>–TMHA–Tf<sub>2</sub>N bath at 130°C.

galvanic contact and potentiostatic alloying at 130°C. The main point of interest here is that Cu-Sn alloying under the potentiostatic condition was self-terminated and currents were automatically reduced to zero within 72 h, while that under the galvanic contact method did not stop even after 72 h of reaction. In the case of potentiostatic alloying, as mentioned above, each potential corresponds to the activity  $a_{Sn}$  of the phase to be deposited and, therefore, the current stops on completion of the phase with given  $a_{Sn}$ . In contrast, galvanic contact alloying of both bulk Cu sheet and thin Cu layer did not stop within 72 h. The former was due to the presence of an unalloyed fcc-Cu phase to which Sn atoms can further diffuse. The latter is probably because the formation of  $\beta$ -Sn phase was not completed within this time period. The higher current density obtained during the alloy formation while thin Cu layer was used is also attributed to the formation of spongelike  $\beta$ -Sn phase with a larger surface area.

Thermodynamics of the Cu-Sn alloying.- To gain thermodynamic insight into the alloying behaviors, a sampled-current,



Figure 8. Average composition of Cu–Sn layers obtained by potentiostatic RD alloying for 72 h at five different potentials using a 0.05 mol dm<sup>-3</sup>  $Sn(Tf_2N)_2$ -TMHA–Tf<sub>2</sub>N bath at 130°C.



Figure 9. Change in current density during RD alloying by (a) galvanic contact method and (b) potentiostatic conditions at +5 mV, +10 mV, and +20 mV vs Sn<sup>2+</sup>/Sn using a 0.05 mol dm<sup>-3</sup> Sn(Tf<sub>2</sub>N)<sub>2</sub>–TMHA–Tf<sub>2</sub>N bath at 130°C.



Figure 10. Sampled-current cathodic voltammogram for 0.05 mol dm<sup>-3</sup> Sn(Tf<sub>2</sub>N)<sub>2</sub>-TMHA-Tf<sub>2</sub>N bath at 130°C. The increment potential and step period were 1 mV and 20 s, respectively. Averaged currents during the final 5 s of each potential step were sampled.

i.e., staircase, cathodic voltammogram for the  $0.05 \text{ mol dm}^{-3}$ Sn(Tf<sub>2</sub>N)<sub>2</sub>-TMHA-Tf<sub>2</sub>N bath was measured using a Cu sheet as a working electrode (Fig. 10). In this experiment, current density data were collected by stepping down the potential at 1 mV intervals from +140 mV to 0 mV vs  $Sn^{2+}/Sn$ . During each step, the potential was kept constant for 20 s and averaged current density data during the final 5 s of each step were sampled. The cathodic current started to increase from +123 mV, suggesting that the reduction of  $\mathrm{Sn}^{2+}$ ions to Sn atoms and concomitant dissolution of the atoms into the fcc-Cu phase start from this potential. The cathode current plateaued between +105 mV to +60 mV and further increased stepwise with decreasing potential toward 0 mV due to the formation of intermetallic phases. Considering the results of potentiostatic alloying (Fig. 8), it is likely that the three onsets found at +57 mV, +45 mV, and +15 mV correspond to Cu<sub>10</sub>Sn<sub>3</sub>, Cu<sub>3</sub>Sn, Cu<sub>6</sub>Sn<sub>5</sub> phases in order of activity  $a_{Sn}$ .

Using a set of thermochemical data,<sup>10</sup> average activities of tin  $a_{\rm Sn}$  of the Cu<sub>6</sub>n<sub>5</sub> and Cu<sub>3</sub>Sn phases were calculated to be 0.677 and 0.126, respectively, at 130°C. According to the Nernst equation for the reaction,  $\operatorname{Sn}^{2+} + 2e = \operatorname{Sn}$ , these  $a_{\operatorname{Sn}}$  values correspond to the redox potentials +6.8 mV and +36 mV vs Sn<sup>2+</sup>/Sn. Here, we omitted the  $Cu_{10}Sn_3$  phase, since this phase is metastable at 130°C.<sup>11</sup> In addition,  $a_{Sn}$  of the fcc-Cu phase, where Sn atoms fully dissolved (i.e., 0.7 atom % Sn<sup>11</sup>), was estimated to be  $5.1 \times 10^{-5}$ , corresponding to +172 mV vs Sn<sup>2+</sup>/Sn. It is worth noting that, as listed in Table I, the experimentally observed potentials for the formation of each phase were in rough agreement with the redox potentials calculated from the thermochemical data.

Table I. Potentials for formation of each of Cu-Sn phases stable at 130°C (mV vs Sn<sup>2+</sup>/Sn)

Phase	Experimental	Calculated
Sn in fcc-Cu	+123	+172
Cu <sub>3</sub> Sn	+45	+36
Cu <sub>6</sub> Sn <sub>5</sub>	+15	+6.8

#### Conclusion

In this study, we tried using the ionic liquid TMHA-Tf<sub>2</sub>N as a nonvolatile and nonflammable solvent for the reduction-diffusion (RD) formation of Cu-Sn alloy layers at elevated temperatures beyond 100°C. When a thin Cu layer was alloyed by the galvanic contact method, Cu-Sn layers composed of intermetallic phases,  $Cu_6Sn_5$ ,  $Cu_3Sn$ , and  $Cu_{10}Sn_3$  were formed, but the  $\beta$ -Sn phase with a trace amount of copper was codeposited. In contrast, uniform Cu-Sn layers were prepared through potentiostatic alloying at +1 mV to +40 mV vs Sn<sup>2+</sup>/Sn. The intermetallic phases formed were dependent on the alloying potential applied, which roughly agreed with the value estimated from a set of thermochemical data. This demonstrated that a Cu-Sn alloy layer can easily be prepared through successive electrochemical processes using two baths, each containing different metal ions,  $Cu^{2+}$  and  $Sn^{2+}$ : the electrodeposition of a Cu layer from an aqueous  $Cu^{2+}$  bath followed by potentiostatic alloying using an ionic liquid-based Sn<sup>2+</sup> bath. Recently, we have been investigating the transport properties of several metal ions in TMHA–Tf<sub>2</sub>N and found the diffusion coefficient of Sn<sup>2+</sup> ions to be  $3.5 \times 10^{-7}$  cm<sup>2</sup> s<sup>-1</sup> (50°C),<sup>12</sup> which is two orders of magnitude less than that for aqueous media. Such a slow ionic diffusion in TMHA-Tf<sub>2</sub>N is attributed to the high viscosity of the liquid and can become an obstacle when applying the liquid to electrochemical deposition technology. In fact, however, the transport of Sn<sup>2+</sup> ions in TMHA-Tf<sub>2</sub>N did not control the growth rate of Cu–Sn in the present study.<sup>8</sup> This is because the viscosity of TMHA-Tf<sub>2</sub>N is improved, or lowered, at elevated temperatures. In other words, the present alloying process effectively utilizes the advantages of the ionic liquid, i.e., nonvolatility and nonflammability, without the drawback regarding ion transport, paving the way for a novel type of electrochemical deposition using ionic liquids.

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