PHYSICAL REVIEW E VOLUME 58, NUMBER 5 NOVEMBER 1998

Reactive flow of molten Pb(Sn) alloys in Si grooves coated with Cu film

C. Y. Liu and K. N. Tu
Department of Materials Science and Engineering, University of California at Los Angeles, Los Angeles, California 90095-1595

(Received 27 January 1998)

We present an experimental study of the wetting behavior of Pb on flat and grooved Cu surfaces. The alloying of even 1–2 wt. % Sn into Pb can lead to dramatic changes in wetting angle and length flow into the grooves. The observed flow behavior disagrees with models based on the classical Washburn flow [E. W. Washburn, Phys. Rev. **17**, 273 (1921)]. We conclude that the driving force of reactive wetting must take into account, besides the capillary force, the free energy change due to intermetallic compound formation. [S1063-651X(98)14311-8]

PACS number(s): 68.45.Gd, 47.60.+i, 47.70.Fw, 68.10.Cr

The spontaneous wetting of a liquid drop on a solid surface is an irreversible process. The wetting lowers the liquid-solid interfacial energy. It leads to the equilibrium state depicted by Young's equation [1] of forming a spherical liquid cap on the solid. The wetting reaction involves bonding across the liquid-solid interface but ignores any extended reaction between them [2,3]. The extended reaction may be dissolution of the solid or intermetallic compound formation. An example of the latter is a molten eutectic SnPb solder on Cu forming Cu-Sn compound [4–6] and the former a drop of Bi on Au dissolving the Au [7]. These extended reactions occur if the molten solders stay on the metals. We recall that Young's equation was obtained by minimizing only the surface and interface energies. The justification of ignoring the extended reactions seems to be that the spreading of a liquid cap on a solid surface is too fast to allow them to happen. Indeed, Yost and co-workers have performed the wetting of molten eutectic SnPb solder on mechanically grooved Cu surfaces [8–10] and showed that the wetting rate in those grooves obeys Washburn's equation [11], so it is plausible that the driving force of the wetting requires only capillary force and no free energy of Cu-Sn compound formation.

Owing to the new electronic packaging technology of direct attachment of a flip chip to a card or board, solder wetting on thin metal films has currently attracted much attention. Also area array of solder joints is being recognized to be the only reliable way to offer a very large number of chip-to-substrate interconnects for the future devices. In one of our studies of wetting of molten eutectic SnPb on metal surfaces, we found no stable wetting (contact) angle exists on Pd [12]; the angles decreases with wetting time and the diameter of the solder cap keeps increasing. Instability of the wetting angle on Pd suggests that we may not ignore the effect of compound formation [13]. Indeed, we have observed an extremely fast $PdSn_4$ formation at the interface [14]. To reexamine the wetting process, we report in this paper a systematic study of molten pure Pb and dilute Pb(Sn) alloys on flat and grooved Cu surfaces. We have chosen them because pure Pb does not form a compound with Cu, nevertheless it wets a flat Cu surface with a wetting angle of 95°. Pure Sn reacts with Cu to form Cu_3Sn and Cn_6Sn_5 compounds [4–6]. When we add 1 wt. % Sn, 2 wt. % Sn, and so on into Pb, the wetting angle drops dramatically. Furthermore, we prepared very regular V-shaped grooves on (001) Si wafer surfaces using lithography and etching, then we coated the grooves with a Cu film. Again, while pure Pb does not run into the grooves, the dilute Pb(Sn) alloys wet the grooves with a rate strongly dependent on Sn concentration. In addition the wetting configuration of the grooves does not obey Young's equation. Based on these measurements and the observed morphology [15], we assert that the effect of compound formation on wetting exists.

To begin the experiments, we prepared solder beads of diameter of about 1 mm by melting tiny pieces of solder of about 2 mg each in hot flux kept at 350 °C. After cooling, we collected them. Besides pure Pb, beads of five dilute Pb(Sn) alloys of 1, 1.5, 2, 5, and 10 wt. % Sn were also prepared. To perform sessile drop tests, we reflowed these beads on the flat and the grooved Si surfaces immersed in flux kept at 350 °C on a hot plate. The solder caps are stable on the flat surface of Si coated with Cu film and the wetting angles not change much with time. After 1 min of reflow, we cooled and rinsed them for scanning electron microscopic study. Figure 1 shows the sideview of the six samples and their wetting angles. Figure 2 is a plot of the measured angles versus Sn concentration. The inset in Fig. 2 is a plot of the surface energy of pure Pb and dilute Pb(Sn) alloys measured in flux ambient reported in the literature [16]. We note that these surface energies (or the flux-solder interfacial energies) are practically constant, independent of Sn concentration up to 20 wt. % Sn. Surface spectroscopy analysis showed that Pb segregates to the alloy surface [17], hence for the dilute Pb(Sn) alloys, their surface energies obey Henry's law. We note that these surface analyses were carried out using flat surfaces, not the curves surfaces between the flux and solder cap as shown in Fig. 1. However, the cap curvature is large enough that the Gibbs-Thomson effect can be ignored. In Young's equation,

$$\cos\theta = \frac{\gamma_{fs} - \gamma_{sl}}{\gamma_{lf}}, \tag{1}$$

where γ is the interfacial energy and the subscript *f*, *l*, and *s* indicate the flux, molten, solder, and substrate, respectively. Among them, the interfacial energy between the flux and Cu, γ_{fs}, is the same for all the samples. Since we have shown in the inset in Fig. 2 that the interfacial energies between the flux and the solders, γ_{lf}, are practically constant, it implies

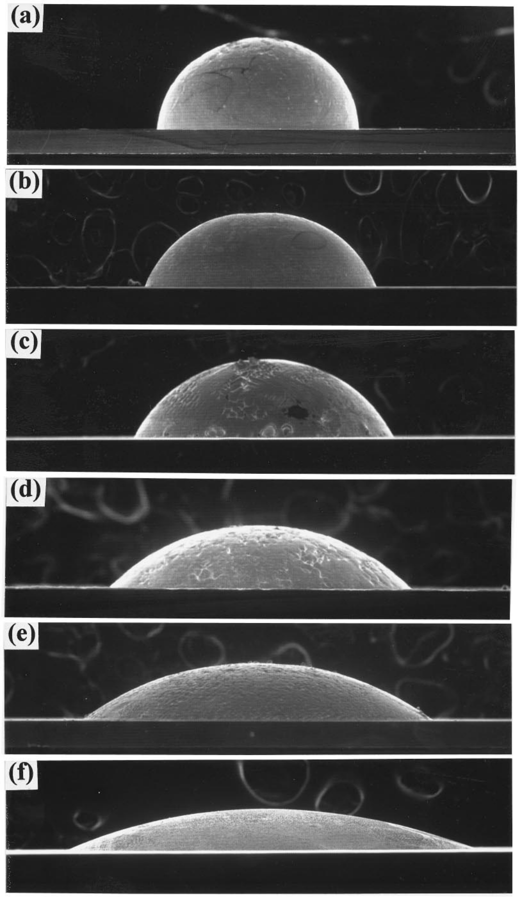

FIG. 1. SEM images of side view of the six samples reflowed at 350 °C for 1 min on the flat Cu surface: (a) pure Pb, (b) Sn_1Pb_{99}, (c) $Sn_{1.5}Pb_{98.5}$, (d) Sn_2Pb_{98}, (e) Sn_5Pb_{95}, (f) $Sn_{10}Pb_{90}$.

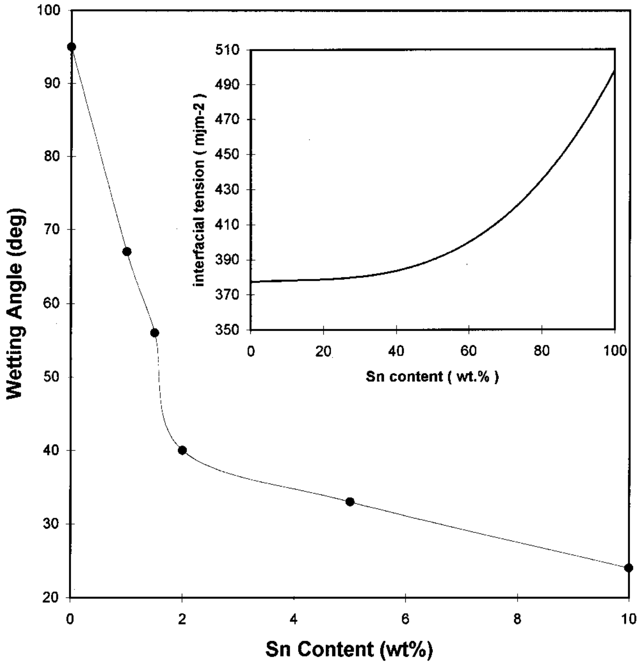

FIG. 2. Wetting angles vs Sn content at 350 °C after 1 min reflowing. (inset: the interfacial tension of SnPb solder/flux as a function of Sn content, replotted from Howie and Hondro [16]).

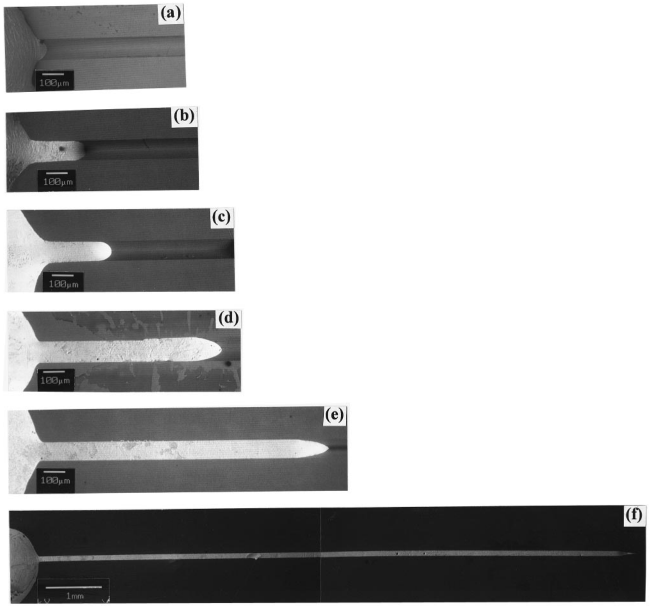

FIG. 3. SEM images of Pb and dilute Pb(Sn) alloys flow in V-shaped grooves: (a) pure Pb, (b) Sn_1Pb_{99}, (c) $Sn_{1.5}Pb_{98.5}$, (d) Sn_2Pb_{98}, (e) Sn_5Pb_{95}, (f) $Sn_{10}Pb_{90}$.

that the wetting angle θ depends only on the interfacial energy between the solder and Cu, γ_{sl}. Hence the observed very large drop in θ by adding 1 wt. % Sn or 2 wt. % Sn to Pb indicates that the small amount of Sn has affected significantly the interface between the solder and Cu. If the effect were caused by changing only a few percent of the interfacial bonds of Cu-Pb to Cu-Sn, it would not have led to such large changes in wetting angles. We cannot help but conclude that during the wetting spread a very large number of Cu-Sn bonds must have been formed across the interface and the number increases with Sn concentration, or even a certain amount of Cu-Sn compound may have formed. Yet, the question is how much since the wetting spread may last only a fraction of a second. To answer that we need to determine the wetting rate, which can be measured from the rate of solder wetting the grooves.

To prepare the grooves, the standard lithographic technique in Si technology was used to pattern line openings along the (110) direction on (001) Si wafers coated with photoresists. V-shaped grooves of width of 80 and 20 μm were developed by an anisotropic etching; the sides of the grooves are (111) planes of Si. The length of the grooves can be as long as 6 cm. Thermal oxidation was used to grow an SiO_2 layer of about 50 nm over the grooved Si surface and followed by consecutive *e*-beam depositions of 50 nm Cr and 750 nm of Cu. Since Cu reacts extremely fast with Si, we need the SiO_2 as diffusion barrier and in turn the Cr as adhesive layer. To carry out the sessile drop experiment, we repeated the procedure used in wetting the flat surface. A piece of the Si was kept in hot flux at 350 °C and a solder bead was dropped onto the grooved surface. Instead of letting the reflow laser for 1 min, we removed the Si piece from the hotplate as soon as the bead melts. Figure 3 shows six images of the wetted grooves. The composition of these solders is the same as those shown in Fig. 1. Figure 3(a) shows no run of pure Pb into the groove as expected. For the dilute Pb(Sn) alloys, the length of solder in the groove increases

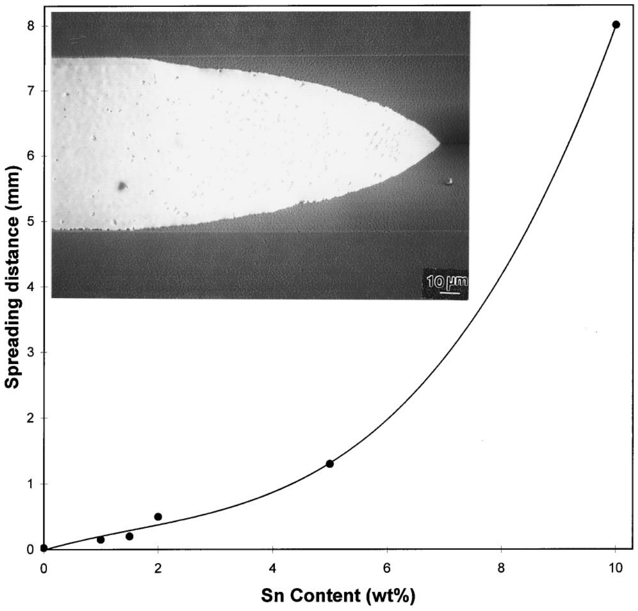

FIG. 4. Spreading distance of solders in grooves vs Sn content (inset: the spreading tip of Sn_5Pb_{95}).

dramatically with increasing Sn concentrations. For the 10 wt. % Sn alloy, it is almost 1 cm. Figure 4 is a plot of the solder length versus Sn concentration. The inset in Fig. 4 is a close-up SEM image of the wetting tip of the 5 wt. % Sn in a groove. Due to limited space here, we shall report the morphology of the wetting tip elsewhere.

The flow kinetics of a liquid in surface grooves has been analyzed by Yost and coworkers [6,7]. It obeys the Washburn flow and follows the general form,

$$z^2 = \frac{K(\alpha,\theta)\gamma h t}{\mu}, \tag{2}$$

where z is the length of the liquid in the groove after a wetting time of t, h is the height of the groove, γ and μ are surface energy and viscosity respectively of the liquid, and K is a geometrical parameter and is a function of the wetting angle θ and the angle α between the wall of the groove and the sample surface; see Fig. 5(a).

$$K(\alpha,\theta) = \frac{(\cos\,\theta - \cos\,\alpha)}{2\pi\,\sin\,\alpha}. \tag{3}$$

In the present case, $\alpha = 54.7°$, which is the angle between the (001) and (111) planes in Si. Based on the theoretical analysis [6], the condition of the liquid flow into grooves is $\alpha > \theta$, and there is no flow if $\theta > \alpha$. On the basis of the θ values shown in Fig. 1, pure Pb and Pb-1 wt. % Sn alloy should not flow into the grooves. However, Fig. 3(a) shows that the condition of no flow is not true for the 1 wt. % Sn alloy; it has run into groove [9,10]. The effect of 1 wt. % Sn has changed the wetting behavior dramatically.

Furthermore, Figs. 5(b)–5(f) show the cross-sectional views of five grooves wetted with the five Pb(Sn) solders, except the pure Pb. These cross sections were taken from the middle of each one of them as shown in Fig. 3. The most surprising finding in Fig. 5 is that the solder surfaces are all rather flat. In other words, the solder flow in the grooves does not obey Young's equation; the θ as defined in Fig. 5(a) is nearly the same for the five solders, so it is independent of the solder composition. This is different from those wetting angles shown in Fig. 1, where they change dramatically with solder composition. However, we note that if the solder surface is flat, there should be no flow according to the published analysis [8,9]; see Eq. (3).

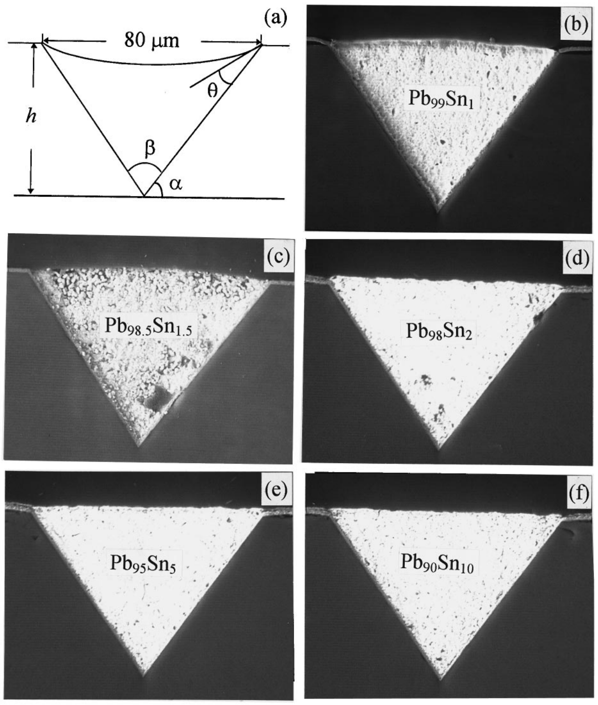

FIG. 5. Cross-sectional SEM pictures of (b) pure Pb, (c) Sn_1Pb_{99}, (d) $Sn_{1.5}Pb_{98.5}$, (e) Sn_2Pb_{98}, (f) Sn_5Pb_{95}, (g) $Sn_{10}Pb_{90}$ flow in V grooves, and (a) a sketch of the configuration of the experimental V groove.

Our preliminary measure of the fastest wetting speed in the grooves of the Pb−10 wt. % Sn alloy is less than 1 cm/sec, which is slower than but of the same order of magnitude as that reported for eutectic SnPb in mechanically made grooves. If we take half of the solder cap size (shown in Fig. 1) to be 1 mm then the time of spreading of a solder cap is about 0.1 sec. If we assume a solid state diffusivity from 10^{-9} to 10^{-15} cm^2/sec for compound formation at 350 °C, we could have a Cu-Sn compound layer of 100–0.1 nm in thickness. The assumed diffusivity range is reasonable since the melting points of Cu_3Sn and Cu_6Sn_5 compounds are 680 °C and 415 °C, respectively. Thus, the free energy of compound formation could have augmented the capillary force to pull the solder into the grooves. It could affect the rate as well as the θ-dependent configuration. Clearly, we must reanalyze the kinetic process of groove wetting by taking into account the free energy of compound formation.

Owing to the extensive use of Pb-Sn solders, Sn is obviously the first element to be added to Pb for wetting study. To check whether the effect of compound formation is overwhelming, we must also investigate other solutes in Pb, such as Ni, which forms solid solution with Cu but no compounds, and Bi, which forms neither solid solutions nor compounds with Cu. They are under further study and the results will be reported.

In summary, we reported the use of Cu coated grooves on Si to study the wetting behavior of pure Pb and dilute Pb(Sn) alloys. We showed that the addition of a small amount of Sn has significantly affected the wetting angle as well as the rate of groove wetting of Pb. These results indicate that the effect of intermetallic compound formation must be taken into account in reactive wetting. Since the etching of Si grooves is highly reproducible and the grooves can be coated with various kinds of materials, they are unique substrates for studying the flow properties of liquids.

The research has been supported by NSF Contract No. DMR-9705195, and SRC Contract No. PJ-356. The authors would like to thank Chih Chen (UCLA) for assistance in lithography.

---

[1] T. Young, Philos. Trans. R. Soc. London **95**, 65 (1805).
[2] P. G. de Gennes, Rev. Mod. Phys. **57**, 827 (1985).
[3] W. J. Boettinger, C. A. Handwerker, and U. R. Kattner, *The Mechanics of Solder Alloy Wetting and Spreading*, edited by F. G. Yost, F. M. Hosking, and D. R. Frear (Van Nostraud, New York, 1993), Chap. 4, p. 132.
[4] P. J. Kay and C. A. Makay, Trans. Inst. Metal Finishing **54**, 68 (1976).
[5] D. Frear, D. Gravas, and J. W. Morris, Jr., J. Electron. Mater. **16**, 181 (1986).
[6] H. K. Kim and K. N. Tu, Phys. Rev. B **53**, 16 027 (1996).
[7] M. Hausen and K. Anderko, *Constitution of Binary Alloys*, 2nd ed. (Genium, New York, 1985).
[8] J. A. Mann, Jr., L. Romero, R. R. Rye, and F. G. Yost, Phys. Rev. E **52**, 3967 (1995).
[9] R. R. Rye, J. A. Mann, Jr., and F. G. Yost, Langmuir **12**, 555 (1996).
[10] R. R. Rye, F. G. Yost, and J. A. Mann, Jr., Langmuir **12**, 4625 (1996).
[11] E. W. Washburn, Phys. Rev. **17**, 273 (1921).
[12] Y. Wang, H. K. Kim, H. K. Liou, and K. N. Tu, Scr. Metall. Mater. **32**, 2087 (1995).
[13] Y. Adda, M. H. Ambroise, and F. Barbier, Mater. Sci. Forum **155-156**, 511 (1994).
[14] Y. Wang and K. N. Tu, Appl. Phys. Lett. **67**, 1069 (1995).
[15] D. Gravas, D. Frear, L. Guan, and J. W. Morris, Jr., J. Electron. Mater. **15**, 355 (1986).
[16] F. H. Howie and E. D. Hondros, J. Mater. Sci. **17**, 1434 (1982).
[17] X. Graham, C. Smith, and Colin Lea, Surface Spreading Liq. Met. **19**, 145 (1986).