Effect of Graphene Layers on Phenomena Occurring at Interface of Sn-Zn-Cu Solder and Cu Substrate

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Cu and graphene-coated Cu substrates spread with Sn-Zn eutectic-based alloy containing 0.5 wt.%, 1 wt.%, or 1.5 wt.% Cu have been studied at 250°C. Soldering experiments were performed for wetting time of 3 min, 8 min, 15 min, 30 min, and 60 min in (1) presence of flux without argon protective atmosphere and (2) fluxless in argon atmosphere. Solidified solder–pad couples were cross-sectioned and examined using scanning electron microscopy with energy-dispersive spectroscopy to study their interfacial microstructure. To assess the effect of graphene coating on solder, Cu pads were covered by graphene using chemical vapor deposition. The results revealed that the liquid solder did not wet the graphene-coated copper in the absence of flux. Wetting took place only with use of flux, because it destroyed the graphene layer and enabled contact of the liquid solder with the copper. Experiments were designed to demonstrate the effect of Cu addition and graphene coating on the kinetics of the formation and growth of Cu5Zn8 and CuZn4 phases identified by x-ray diffraction analysis, Raman spectroscopy, and energy-dispersive spectroscopy. A decrease of about 60% in the thickness of the intermetallic layer was observed when applying the graphene interlayer in presence of flux. Addition of copper to the Sn-Zn alloy improved the wettability as the copper content was increased.

Key words: Pb-free solder, graphene layer, interfacial reaction, intermetallic growth kinetics, spreading test

INTRODUCTION

The search for alloys which can eliminate Sn-Pb solders from conventional use is ongoing. At present, the commonly applied alternatives are based on Sn-Ag and Sn-Ag-Cu (SAC) eutectics. The properties of these alloys have been widely studied, revealing several disadvantages. Solder alloys based on Sn-Zn are competitive because of their lower manufacturing cost, which is estimated to be approximately 50% lower than in the case of Sn-Ag and Sn-Ag-Cu alloys. In addition, these alloys are characterized by lower melting point (about 198°C), improved mechanical properties, and lack of hazardous whiskers in the joint, but they have worse wetting and anticorrosion properties compared with SAC alloys. According to study by Grobelny and Sobczak, addition of a small amount of copper to Sn-Zn alloys can greatly improve their anticorrosive properties. Yu et al. found that increasing the copper content in Sn-Zn-Cu alloy improved its wettability. Also, solders based on Sn-Zn eutectic may be useful for joining aluminum with copper. Soldering processes in electronics are always accompanied by formation of intermetallic phases. These phases are brittle and reduce the mechanical strength of the joint. They also have worse electrical properties. Extensive growth of a layer of intermetallic compounds (IMCs) at the interface between the liquid solder and substrate
usually worsens the properties and reliability of solder joints, making it important to control the growth kinetics of these layers. Therefore, new materials and technologies are being sought to restrain formation of intermetallic layers or inhibit their growth. Tsai et al. proposed addition of TiO₂ particles to solder. Generally, to reduce the thickness of IMC layers, copper is covered with a layer of nickel or gold. These layers prevent oxidation of copper. However, use of nickel or copper results in formation of new, equally harmful phases.

Graphene is a material whose properties have been extensively studied. It is characterized by excellent electrical conductivity and mechanical properties. Graphene coatings have several applications in electronics, e.g., corrosion protection for copper tracks and prevention of electromigration, while in soldering processes they can act as a barrier to growth of harmful intermetallic layers that can form at the interface between Cu and liquid solder. Other prospective applications of graphene are related to its use as a substitute for silicon, or in optoelectronics or photovoltaics, to form transparent electrodes to replace indium-doped tin oxide. Production of graphene is growing, thus its price is falling rapidly. Covering a copper surface with a graphene layer could protect the copper substrate against corrosion, and help to control the growth kinetics of the IMC layer. There are papers describing wetting of carbon-coated metals and ceramics at high temperatures. However, the work presented herein relates to a low-temperature (250°C) soldering process. At this temperature, solder does not wet carbon or carbon coatings. Previous articles about wetting of graphene mainly describe the process of wetting graphene-coated copper with water. Those studies suggested that a monolayer of graphene on a metal substrate is transparent to water and does not affect the wetting. With increasing numbers of graphene layers, the contact angle of water on the copper surface gradually attains the value for water on the surface of graphite. In the most recent published work describing wetting of copper and copper covered by graphene with Sn-Ag-Cu (SAC) solder, the authors describe the role of the graphene coating as a diffusion barrier, suggesting that the graphene layer should reduce copper diffusion from the substrate and thereby inhibit growth of the intermetallic layer. Cu atoms diffuse from the substrate through defects in the graphene coating. However, that work ignored the effect of flux in the process of wetting the substrate coated with graphene. It would be of interest to determine the mechanism of wetting of materials with graphene coatings with liquid metals and its effect on the growth kinetics of IMCs.

Description of the formation of intermetallic phases and the kinetics of their growth, as well as the influence of various alloying additions and technological conditions, are separate issues. The authors of Ref. 26 studied the reactions between Sn-Zn solders and a copper substrate in the range of 230°C to 280°C. They observed formation of three phases at the solder–Cu boundary (γ-Cu₃Zn₄, β-CuZn, and a third, unidentified phase). The total thickness of the intermetallic layers grew with increasing Zn content. Chan et al. investigated the morphology and growth kinetics of the phases at the boundary between eutectic Sn-Zn and Cu (or Ni) substrate at temperature of 250°C, 300°C, 325°C, and 350°C for time intervals of 20 min to 120 min. Those authors noted that the intermetallic reaction front migrated four times faster towards the substrate than towards the liquid alloy. They also found that the total thickness of the intermetallic layers increased both with time and temperature of wetting. The sequence of formation of individual phases at the interface seems interesting as well. The authors reported that, in the first moments of wetting of copper by liquid Sn-Zn + 1% Cu solder, reaction of the solder with the substrate occurs. Then, a high-zinc γ-phase is formed at the interface. After only about 60 s, a γ–phase appears, while the thickness of the intermetallic layer remains practically unchanged. This article describes the wetting of copper and copper coated with graphene by liquid Sn-Zn-Cu alloys. It also considers the role of the graphene coating and the effect of copper addition on the kinetics of the growth of intermetallic phases occurring at the interface. In the soldering process of Cu substrate coated by a graphene layer, wetting is not observed for Sn-Zn-Cu solders without flux, at low temperatures. Therefore, the hypothesis that flux results in destruction of the graphene coating is proposed. This enables the “classic” wetting process of copper by the solder. Moreover, this process slows down the growth of the IMC layer.

**EXPERIMENTAL PROCEDURES**

Cu, Sn, and Zn with purity of 99.999%, produced by Alfa Aesar, were used to prepare the solders. Melting was carried out in a glovebox under high-purity (6 N) argon atmosphere. Copper substrate (99.95%) produced by Alfa Aesar was used for spreading tests. Substrates with dimensions of 30 × 30 × 0.5 mm were degreased with acetone and washed with isopropyl alcohol. Spreading studies were performed using the apparatus described in Ref. 11 on pure Cu substrates and those covered with graphene. Wetting processes were carried out at 250°C with different annealing times (3 min, 8 min, 15 min, 30 min, and 60 min), without a protective atmosphere and with use of Alu-33 flux, produced by Amasan.

A graphene coating was applied to the copper substrate by chemical vapor deposition (CVD). A scheme of the experimental apparatus (designed and built at IMMS-PAS in Krakow) is shown in Fig. 1; the CVD conditions are reported in Ref. 28. To reduce the oxide layer and grain
recrystallization, the copper substrates were subjected to reduction in the same apparatus prior to graphene deposition. The reduction process was carried out at 1000 °C for 15 min by passing an Ar/H₂ (15%) mixture through the reaction chamber. Then, a flow of argon–propane gas mixture at a specific ratio was applied at the same temperature. The process of applying graphene to the copper substrate lasted 20 min, followed by rapid cooling to ambient temperature.

The resulting graphene coatings were tested by micro-Raman spectrometry. Micro-Raman spectra were measured using a Renishaw inVia Raman microscope (100× objective) with a 633-nm HeNe excitation laser, exposure time of 10 s, accumulation of 1, and laser power at 100% (21 mW output power, spatial resolution <1 μm). The Raman spectra are presented in the important Raman shift range for graphene, i.e., from 1000 cm⁻¹ to 3000 cm⁻¹, which includes: (1) the main graphene bands: G and 2D; (2) bands depending on different kinds of defects (vacancy-like defects, boundaries of graphene 2D grains, sp³ defects, out-of-plane carbon bonds inside graphene 2D grains with sp² carbon bonds); D, D', and D + D'; (3) bands of products from damage to the graphene layer (polyene-like 1D fragments, a-C fragments of amorphous carbon below ca. 1 nm). Examination of the quality of the graphene coating by micro-Raman spectroscopy allows determination of the number of graphene layers [on the basis of the intensity ratio of the 2D and G bands, i.e., the I(2D)/I(G) ratio] and also to estimate the defects in the graphene layer from the L_D parameter, i.e., the distance between point defects [on the basis of the intensity ratio of the D and G bands, i.e., the I(D)/I(G) ratio].

Spreading measurements were carried out on the prepared substrates. The first part of the spreading tests on the substrates made from pure copper and with graphene coating was carried out at 250 °C with different annealing times (3 min, 8 min, 15 min, 30 min, and 60 min), without a protective atmosphere, and with use of Alu-33 flux (produced by Amasan). The second part was conducted at 250 °C without flux, but in argon protective atmosphere for annealing times of 3 min and 8 min. In each run, the experiment was repeated three times. The surface propagation of each solder was photographed using a Canon EOS-60D camera. The microstructure of all samples was observed by scanning electron microscopy (SEM) with energy-dispersive spectroscopy (EDS). The thickness of the intermetallic layer was determined using a computer program.

RESULTS AND DISCUSSION

Graphene Layer

Figure 2 shows photos of the copper substrate coated with graphene. Note that the graphene on the copper surface is built in the form of flakes (graphene domains with diameter from several tens up to several hundreds of micrometers) separated by pronounced boundaries. It may be assumed that the bonds of the atoms at the boundaries will be much weaker than those within flakes. The figure also includes the results of micro-Raman spectroscopy analysis to characterize the quality of the initial graphene coating (inside the flakes). This analysis reveals that the copper surface was covered with a single or double layer of graphene [ratio of 2D and G bands I(2D)/I(G) > 4, Table II].

![Fig. 1. Scheme for deposition of graphene by CVD.](image-url)
concentration of defects in the graphene layers was low, with $L_D$ parameter equal to be about 34 nm (intensity ratio of D and G band of 0.3, Table II), indicating good quality. In addition, note that the graphene on the copper surface was built in the form of flakes separated by pronounced boundaries.

Wetting

The Cu and Cu with graphene layer substrates were used to measure the wettability during soldering by Sn-Zn-Cu alloys. To define the wettability, the spreading area was used as a parameter. Figure 3 shows typical images of solidified samples after spreading on copper with (Fig. 3a) and without (Fig. 3b) use of flux for the condition of 0.5 g of wetting solder (Sn-Zn + 0.5 at.% Cu), reflow time of 8 min, and temperature of 250°C. Figure 4 shows photos of the solder deposited on copper substrate coated with graphene with (Fig. 4a) and without (Fig. 4b) use of flux. High-quality argon atmosphere was used only in the case when the soldering process was conducted without flux. The flux induced much faster flow of solder on the copper surface. In the case of the Cu–graphene pads, liquid solder did not wet the surface. Figure 5a shows the surface propagation of 0.5 g of liquid solder (Sn-Zn)_{cut} + Cu on the copper substrate, at 250°C, for different wetting times and various copper contents in the alloy. Figure 5b shows a comparison of the wettability of copper with that of copper–graphene after 3 min. Based on the results of this work, it can be stated that the duration of the test does not affect the wetting properties. Addition of copper to the (Sn-Zn)_{cut} liquid solder increased the surface propagation of the liquid solder, corresponding to improved wettability. As mentioned above, liquid solder wetted the copper substrate much better than the Cu–graphene substrate. The solder joints obtained with use of flux were analyzed by SEM in terms of formation of intermetallic compounds.

Microstructure of Joints and Influence of Graphene on Soldering Process

The liquid solder with flux addition wetted the surface of both the copper and copper–graphene substrates well. In both cases, the substrate was well wetted by the liquid solder and a transition intermetallic layer formed at the solder–substrate boundary (Fig. 3c and Table I). In absence of flux, despite the use of a protective atmosphere, the liquid solders did not wet the copper–graphene surface. This was probably because the Cu-gn (gn—graphene) surface was “seen” by the liquid solder as graphite. What, then, is the effect of the flux? There are four stages of the wetting process (Fig. 6). The first step is melting the solder. The low surface tension of graphene ($\gamma_{gn-air}$) prevents
spreading of the liquid solder. There is a large contact angle (Figs. 4b and 6a). In the second stage, the molten flux increases the surface tension of graphene (\(c_{\text{gn-flux}}\)) and the contact angle is reduced, which enables spreading of the liquid solder. Almost at the same time, the third stage begins, in which the layer of graphene on the copper is built of panels linked by borders (Fig. 2). It is possible that carbon atoms at the border flakes of graphene are saturated by hydrogen atoms. Therefore, the bonding of these flakes is relatively weak. The flux destroys these joints, enabling penetration of liquid metal between the borders of the flakes. Furthermore, it appears that parts of the torn flakes migrate through the liquid solder to the surface, in turn increasing the contact area of the liquid solder from the copper pad. This process is difficult to analyze, since the surface of the solder is highly polluted by aggressive flux and the products of the reaction. This flux is soluble in water, so after washing it disappears from the surface with the remains of the graphene sheet. The next step will be to determine the influence of the flux on the graphene coating, and studies in this respect are nearing completion. The flux probably causes the destruction of the panel bondings, helping liquid metal to penetrate between their borders. This destruction and removal of the graphene coating from the interface takes place in the third stage, as confirmed by Raman spectroscopy analysis (Figs. 7, 8, and Table II).

The points denoted by “+B” and “+C” in Fig. 4 are the locations on the sample after reflow at which Raman spectroscopy analysis was performed: (B) is further away from the solder (only action of vapor flux), while (C) is closer to the solder (direct action of flux). The results of this analysis are presented in Fig. 7 and plotted in Fig. 8. The point denoted by “A” presents the results for the initial graphene layer (before soldering and reflow). When damage occurs to the graphene coating, the distance between point defects \(L_D\) decreases and a higher \(I(D)/I(G)\) ratio is observed. However, reduction of \(L_D\) below 3 nm causes this ratio to decrease again, but with a simultaneous increase in the width of the G Raman band,29 as in the case of point C for the graphene layer close to the solder. The graph in Fig. 8 presents the dependence of the \(I(D)/I(G)\) ratio on the distance between point defects \(L_D\) on the basis of Refs. 29–31. Note that, with great damage to the graphene layer, a mixture of nanocrystalline graphene with amorphous carbon (Fig. 7b) formed. At point A (initial state of the sample before soldering), no flux action takes place, so the graphene coating is of good quality (\(L_D = 34\) nm, Table II). The vapor flux caused the destruction of the layer of graphene at point B (Figs. 4 and 8), and \(L_D\) decreased from 34 nm to 7.5 nm (Table II). The greatest destruction of the graphene coating occurred at point C. At point B, the graphene layer showed serious defects (large D and D' peaks), while at point C it was almost completely destroyed. Some time is needed to reveal the entire surface of the copper.

The process of the destruction of the graphene coating and unveiling of the entire surface of the copper takes time. Eventually, the graphene coating reduces the kinetics of IMC growth, as proved below. Reference 25 describes the wetting of copper and copper covered with graphene by Sn-Ag-Cu (SAC) solder. Those authors suggested that wetting of copper with the graphene coating occurs by diffusion of Cu atoms from the pad into the liquid solder through defects in the graphene coating. They demonstrated that, when using

Fig. 3. Spreading test for 0.5 g of Sn-Zn + 0.5 at.%Cu solder on copper substrate with (a) and without (b) flux, and (c) microstructure after wetting at 250°C.
graphene coatings on copper pads, the growth of IMC layers at the interface is less than 20% of that on pure copper pads. (The thickness increase of the total IMC layers at the interfaces with multiple layers of graphene was only 71% and 78%, compared with the interface without graphene. Thus, the multiple layers of transferred graphene suppressed the growth of IMCs by more than 20%.) However, it seems unlikely that reflow (500 s) diffusion of copper atoms by defects in graphene coating was possible in such a short time.

**Fig. 4.** Spreading test for 0.5 g of Sn-Zn + 0.5 at.% Cu solder on copper–graphene substrate with (a) and without (b) flux after wetting at 250°C.

**Fig. 5.** Spreading tests for 0.5 g of solder at $T = 250°C$ on (a) Cu substrate for different reflow times, and (b) Cu and Cu–graphene substrate for reflow of 3 min at $T = 250°C$.

**Table I.** SEM EDS analysis marked on Fig. 3

| No. of marked point | SnK | CuK | ZnK |
|---------------------|-----|-----|-----|
| 1                   | 0   | 35  | 65  |
| 2                   | 3   | 19  | 78  |
| 3                   | 4   | 20  | 76  |
| 4                   | 1   | 18  | 81  |
| 5                   | 86  | 1   | 13  |
| 6                   | 0   | 100 | 0   |
IMC Layers at Cu Substrate

Figure 9 shows the microstructure of the joints on the copper substrate, and Fig. 10 presents them on the copper–graphene substrate. It was established that Cu–Zn (CuZn4 and Cu5Zn8) intermetallic phases formed at the interface between the solder and substrate more easily than Cu–Sn (Cu6Sn5 and Cu3Sn) phases, due to the high values of the Gibbs free energy for the Cu–Zn system.

The CuZn4 phase formed first, due to the reaction between Cu and the liquid alloy. Next, Cu5Zn8 intermetallic phase appeared as a result of solid-state reaction between Cu and the Cu-Zn eutectic. Growth of the Cu5Zn8 phase thickness was observed with increased wetting time (Fig. 11). For the eutectic Sn-Zn solder containing 0.5 at.% and 1.0 at.% Cu, the α-phase disappeared after 15 min of heating. Greater addition of copper (1.5 at.%) stabilized this phase (Fig. 11). A similar effect was observed during wetting of the Cu–graphene substrate by the Sn-Zn eutectic with Cu addition (Fig. 12). Therefore, it can be concluded that higher concentrations of copper in the liquid solder stabilize the α-phase. In general, Cu5Zn8 phase is brittle and has a negative effect on the quality of joints to copper. Figure 12 presents a comparison of the growth kinetics of the α- and γ-phases on the copper and copper–graphene substrates. The growth rate is described by the equation $D = k \times t^{0.5}$, where $D$ is the thickness of the layer.
$k$ is the growth rate of the phase, and $t$ is time. This figure indicates that the graphene coating significantly reduced the growth rate of both the $\gamma$- and $\varepsilon$-layers. In addition, it was established that the plots of layer thickness versus annealing time could be divided into two parts. The plot of total thickness of intermetallic layer versus time is shown in Fig. 13. Analyzing it, one can see that the growth of the intermetallic phases proceeds by the mechanism of dissolution, crystallization, and volume diffusion. The first of these is dominant during the first 15 min, after which another prevails. Figure 13 confirms the earlier hypothesis of the role played by flux in the process of Cu–graphene pad wetting. The rate of intermetallic phase growth on copper ($k = 5.2$) in the first stage is significantly higher compared with that on copper covered with graphene ($k = 4.0$). This is because cleaning the Cu surface of graphene occurs after destruction of the graphene pad bondings by the flux. This process takes about 15 min. Thereafter, graphene no longer covers the Cu substrate,

![Graphene layer destruction by flux](image)

Fig. 8. Destruction of graphene layer by flux: $I(D)/I(G)$ intensity ratio for initial graphene layer (A) and at different places after reflow: (B) further away from the solder, and (C) closer to the solder (relationship between intensity ratio of Raman D and G bands and average distance between point defects $L_D$ on the basis of Refs. 29–31).

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| Sample                                      | $I(D)/I(G)$ | $I(2D)/I(G)$ | $G$ FWHM a (cm$^{-1}$) | $G$ R.shift (cm$^{-1}$) | $2D$ FWHM a (cm$^{-1}$) | $2D$ R.shift (cm$^{-1}$) | $I(D)/I(D')$ | $L_D$ b (nm) | No. of layers c |
|---------------------------------------------|-------------|--------------|------------------------|------------------------|-------------------------|-------------------------|---------------|---------------|----------------|
| Initial sample (graphene on copper before reflow) | 0.29        | 3.2          | 16                     | 1589                   | 34                      | 2660                    | 21            | 34            | 1              |
| Sample after reflow, location farther from solder | 3.5         | 2.3          | 28                     | 1584                   | 74                      | 2653                    | 11.7          | 7.5           | 1–2            |
| Sample after reflow, location close to solder   | 1.14        | 0.49         | 42                     | 1583                   | 64                      | 2662                    | 1.3           | 1.5           | >8             |

Characterization of graphene: $L_D$—average distance between point defects in graphene, no. of graphene layers. aFull-width at half-maximum. bOn the basis of Ref. 29. cNumber of graphene layers on the basis of Refs. 30 and 31.

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![Interfacial microstructure](image)

Fig. 9. Interfacial microstructure of Sn-Zn-0.5Cu/Cu couples after wetting time of 3 min, 15 min, and 60 min at $T = 250^\circ$C.
so the growth rates of the IMC layers become similar ($k = 2.2$ and $k = 2.4$).

The influence of the graphene layer on the thickness of the IMCs at the interface is shown in Fig. 14. The ordinate axis presents the relative decrease in thickness of the intermetallic phase layer \( \left( \frac{\delta_{Cu} - \delta_{Cu+gn}}{\delta_{Cu}} \right) \times 100\% \), where $\delta_{Cu}$ is the thickness of IMCs on the Cu substrate and $\delta_{Cu+gn}$ is the thickness of IMCs on the Cu substrate coated with the graphene layer. The results show that, at the beginning of the spreading test (3 min), the thickness of IMCs on the Cu substrate coated with the graphene layer is around 55% lower compared with that on the Cu substrate. This difference diminishes with increasing time, reaching 25% after 60 min. This confirms that the destruction of the graphene layer takes place in the initial period of deposition.

Fig. 10. Interfacial microstructure of Sn-Zn-0.5Cu/Cu + graphene couples after wetting time of 3 min, 30 min, and 60 min at temperature of $T = 250^\circ$C.

Fig. 11. Growth kinetics of IMCs.

Fig. 12. Thickness of IMCs versus time for (a) Cu$_5$Zn$_8$ and CuZn$_4$ using Sn-Zn + 0.5Cu alloy, and (b) Cu$_5$Zn$_8$ and CuZn$_4$ using Sn-Zn + 1.5Cu alloy (at.%), on Cu and Cu–graphene substrates at temperature of $T = 250^\circ$C.
CONCLUSIONS

Apparatus for deposition of graphene on copper by CVD was designed and constructed. The resulting graphene layer was monoatomic with few defects, indicating good quality. Spreading tests were carried out on copper and graphene-coated copper substrates. The liquid solders applied under flux properly wetted the surface of both the copper and copper–graphene. Those without flux wetted well only the surface of copper. The lack of wetting of the substrates with graphene coating was due to the fact that the flux separated the boundaries of graphene panels, enabling penetration of liquid metal and contact with copper, followed by removal of graphene from the copper surface. The surface of the copper substrate was free from graphene after 15 min, which was why the rates of IMC layer thickness growth were similar \((k = 2.2)\) and \((k = 2.4)\). The graphene layer significantly reduced the growth of intermetallic phases, by 55% at the beginning of the spreading test to 25%. Further studies of the initial period of wetting of copper coated with a graphene layer by liquid metal are necessary.

With increasing wetting time, the thickness of the \(\varepsilon\)-layer increased. For pure eutectic Sn-Zn alloy and solders containing 0.5% or 1% Cu, the \(\varepsilon\)-phase disappeared after heating time of 15 min, whereas for alloy containing 1.5% Cu, it remained. A similar effect was observed when the copper–graphene substrate was wetted with Sn-Zn eutectic solder with Cu addition. This indicates that higher copper concentrations in the liquid solder stabilized the \(\varepsilon\)-phase. Moreover, the graphene coating significantly reduced the growth rate of intermetallic phases. Addition of 1.5% Cu to Sn-Zn alloy caused CuZn4 to remain, even after a long soaking phase. This may be important when applying this alloy as a protective coating. This phase slows down diffusion in the ageing process, and extends the duration of protection. Addition of copper to Sn-Zn alloys also affects the wettability, which improves as the copper content is increased.

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