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Wetting, adhesion and diffusion in Cu–Al/SiO_2 system at 1473 K

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Abstract

Sessile-drop wetting experiments and interfacial microstructure examinations show that at high temperature, Cu alloyed with Al mildly promotes the wettability, yet fails to enhance the adhesion and impede the thermal diffusion between Cu and SiO_2, in contrast to the behavior observed in low-temperature annealing studies.
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Keywords: Wetting; Diffusion; Interface; Copper-aluminium alloys; Microstructure

1. Introduction

Recently, copper has attracted particular interest regarding Cu-based metallization for ultra-large scale integrated devices due to its lower electrical resistivity and longer electromigration lifetime compared with aluminum [1]. However, copper integration as an interconnection metal provides the following problems: (i) poor adhesion of copper to dielectric substrates, including SiO_2; (ii) rapid diffusion of Cu through SiO_2; and (iii) easy oxidation of the exposed Cu surface [1,2]. A method of circumventing these problems is to alloy Cu with additive metals such as Al [2–4], Mg [2,4], Cr [5] and Ti [5]. For instance, Murarka et al. [1–4] reported that alloying Cu with small amounts of Al (0.5–5 at.%) offers a material with good electrical properties, less or no diffusion of Cu into SiO_2, better adhesion and enhanced oxidation resistance. It was suggested that the formation of a thin and dense aluminum oxide layer at the Cu surface and the Cu(–Al)/SiO_2 interface during low temperature (473–673 K) annealing of the Cu(–Al) films in vacuum or argon is the key mechanism for the self-passivation of the Cu surface against oxidation, enhancement in the Cu–SiO_2 adhesion, and effective inhibition of Cu transport into the SiO_2 substrate [3,6]. These findings are obviously interesting and promising. However, the adhesion was evaluated by either a crude qualitative Scotch tape test [3] or a simple semi-quantitative scratch, peel or pull test [5], the results of which could be affected by stress and defects in the films such that the true adhesive energy is difficult to evaluate. On the other hand, the mechanism for the adhesion enhancement by the introduction of Al into Cu is not very clear. In this study, we investigated this effect at a high temperature (1473 K) by measurement of the contact angles and examination of the Cu(–Al)/SiO_2 interfacial microstructures.

2. Experimental

The substrates used were high-purity (99.99 mass%) amorphous SiO_2 tablets (Kojundo Chemical Co., Ltd, Japan) in dimensions of ϕ 20 mm × 5 mm with an average surface roughness (R_a) of less than 5 nm (measured by DEKTAK 3, Veeco Instruments Inc., NY, USA). The metals were high purity Cu (99.99 mass%) and Al (99.99 mass%) in the form of small wire segments (ϕ = 3 mm). The Cu–Al alloys with the desired compositions

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were produced in situ during the experiments as described in the following section.

An improved sessile drop method, described in detail elsewhere [7,8], was employed for the wetting experiments. For comparison purposes, a limited number of tests were done on polycrystalline and $(01\bar{1}2)$-oriented single crystalline α-Al_2O_3 substrates. Before experiment, the Cu and Al samples were first chemically cleaned (in 20 vol.% Nital and 20 mass% NaOH distilled-water solutions, respectively, to remove their surface oxide films) and then proportioned to the desired compositions. The weight was in the range of 0.35–0.60 g, depending on the alloy composition. The metals and the SiO_2 tablet were then ultrasonically cleaned in acetone. After cleaning, the SiO_2 substrate was placed in a stainless chamber in a horizontal position. The chamber was heated in vacuum ($\sim 3 \times 10^{-4}$ Pa) up to the testing temperature (1473 K), at which a purified Ar–3%H_2 gas with an oxygen partial pressure of the order of 10^{-18} Pa (measured by an oxygen sensor of ZrO_2–11mol.%CaO solid electrolyte at 1073 K) was introduced. The atmospheric pressure inside the chamber was controlled at 0.11–0.12 MPa. After the temperature and the atmosphere had stabilized, the Cu and Al samples, which were initially located outside the chamber (refer to Fig. 1 in Ref. [7]), were immediately inserted into the bottom of the alumina dropping tube (99.6 mass% purity) and held for 60 s in order for them to melt and alloy. The molten Cu–Al alloy was then forced out through a small hole ($\phi = 1$ mm) at the bottom of the alumina tube by decreasing the pressure inside the chamber and dropped onto the SiO_2 substrate after about 20 s. At the same time, the oxide film, if still remaining at the liquid surface, was mechanically removed.

After the wetting experiments, the interfacial microstructures in the solidified samples were examined using a laser microscope (Keyence, VK-8550, Japan) and an environmental scanning electron microscope (ESEM-2700, Nikon Co., Japan) equipped with an energy dispersive X-ray analyzer.

3. Results

3.1. Contact angle phenomena

Fig. 1 shows the variation in the contact angles of pure Cu and Cu–Al alloys on the SiO_2 substrates during 30 min isothermal dwells. As can be seen, the initial contact angles of pure Cu on the SiO_2 substrate are slightly larger than those of the Cu–Al alloys, while the dynamic contact angles show a slight decrease in the former but no appreciable decrease in the latter, except for the Cu–50at.%Al alloy. The remarkable decrease in the contact angles of Cu–50at.%Al is produced by the significant decrease in the drop height as a result of the liquid penetration into the SiO_2 substrate rather than by the spreading of the liquid front, as indicated in Fig. 2, which is similar to that found in the Al–SiO_2 system [9].

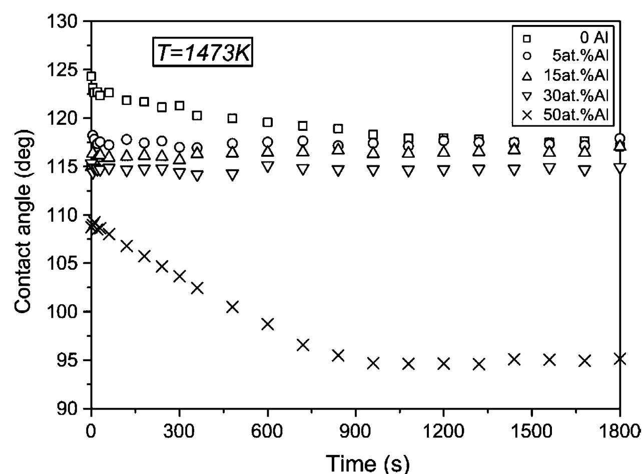


Fig. 1. Variation in the contact angles for pure Cu and Cu–Al alloys on the SiO_2 substrates with time at 1473 K.

Fig. 3 shows the possible true contact angles as a function of Al atomic concentration. These angles were characterized by the average values between 5 s and 60 s, which are less affected by the Cu(–Al)/SiO_2 interdiffusion and/or reaction. The error bars represent the scatters obtained in several runs of the experiments. At high Al concentrations, due to the strong and immediate reaction between Al and SiO_2, the surface/interface in region of triple junction became uneven (see an example of Fig. 4(a)), which could impede the liquid spreading and reaching capillary equilibrium. As a consequence, the scatter in some cases was enlarged.

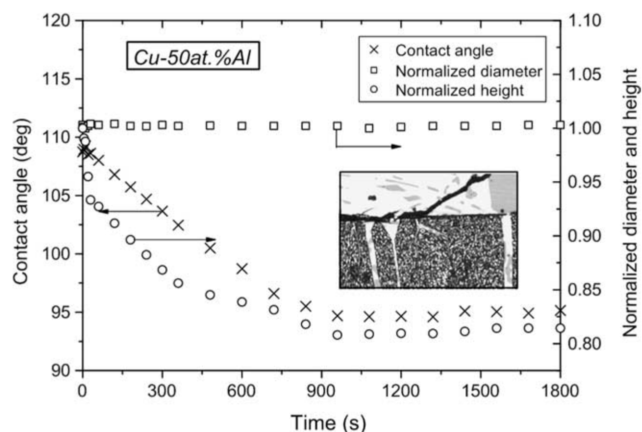


Fig. 2. Variations in the contact angle and normalized drop base diameter and height for the Cu–50at.%Al alloy on SiO_2 with time at 1473 K.

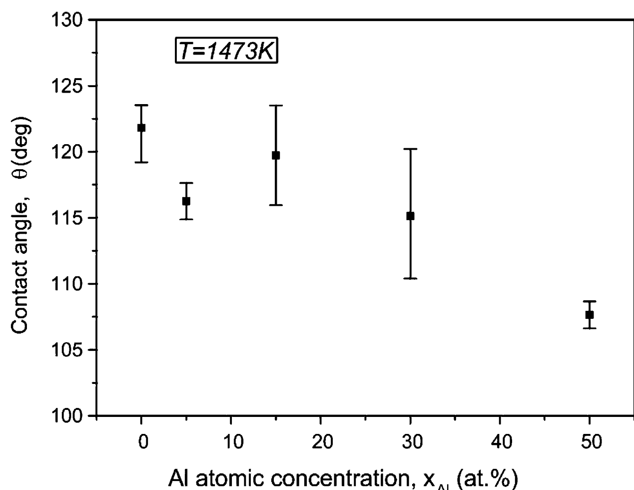


Fig. 3. The possible true contact angle as a function of Al atomic concentration.

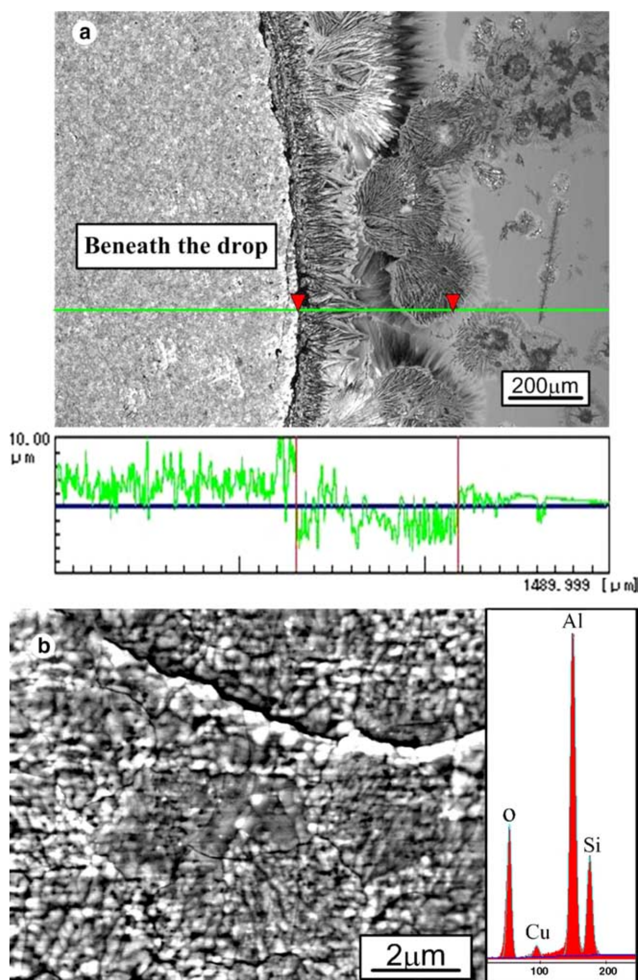


Fig. 4. (a) Top view of the Cu–30at.%Al/SiO_2 interface in region around triple junction (the drop was spontaneously removed from the SiO_2 surface during cooling) and (b) reaction products beneath the Cu–30at.%Al drop. X-ray energy dispersive spectrum indicates that they are aluminum–oxygen (Al_xO)-rich phases with a certain amount of Si as a result of the sacrificial reaction.

3.2. Work of adhesion

The work of adhesion, W_{ad}, can be calculated from the Young–Dupré equation

$$W_{ad} = \sigma_{sv} + \sigma_{lv} - \sigma_{sl} = \sigma_{lv}(1 + \cos\theta) \quad (1)$$

where σ_{sv}, σ_{sl} and σ_{lv} are the interfacial free energies of the solid–vapor, solid–liquid and liquid–vapor interfaces, respectively, and θ is the contact angle. The value of σ_{lv} could be simultaneously determined in our experiments using an axisymmetric-drop-shape analysis program. Fig. 5 shows the σ_{lv} values of the Cu–Al alloys obtained from both the reactive Cu–Al/SiO_2 system and non-reactive Cu–Al/Al_2O_3 system at times between 5 s and 60 s at 1473 K together with the reference values at 1373 K [10]. The measurement error of σ_{lv} in this study was estimated to be within ±2%. The calculated W_{ad} is presented in Fig. 6. As indicated, the addition of Al to Cu does not significantly enhance the adhesion. The decrease in the surface tension with the increase in Al partially offsets the function of the decrease in θ, as it appears in Eq. (1).

On the other hand, it was found that all the drops containing 15 and 30 at.%Al separated from the reacted SiO_2 surfaces after they were cooled to room temperature at a rate of 15 °C/min, whereas, those containing low Al contents (0 and 5 at.%) were not, and fractures, if they were compulsively separated, were found at the interior of the SiO_2 substrates rather than at the Cu–(Al)/SiO_2 interfaces. We conjecture that the local stress developed at the interfaces during cooling is larger for the high Al content alloys than that for the low Al or Al-free alloys, which could influence the interfacial adhesion.

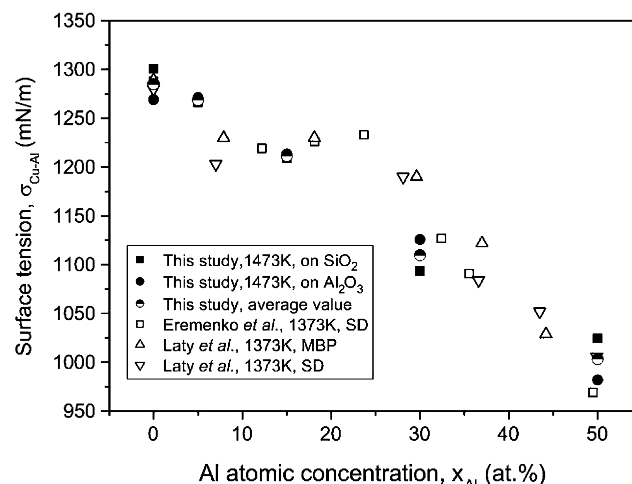


Fig. 5. Variation in the surface tension of the Cu–Al alloys with Al atomic concentration. The values at 1373 K are from Ref. [10]. The legends SD and MBP represent the sessile drop method and maximum bubble pressure method, respectively.

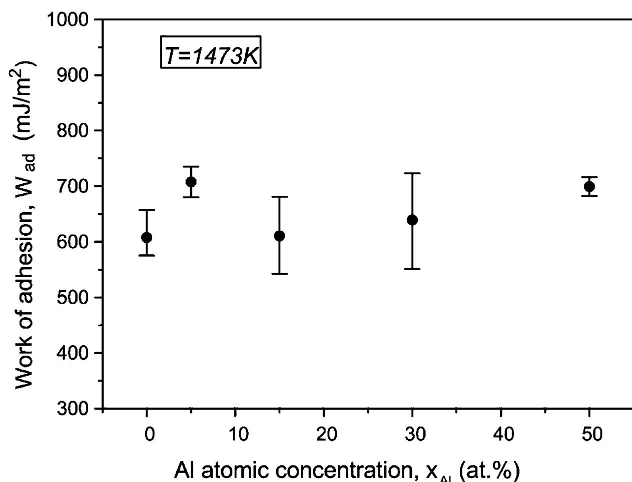


Fig. 6. Variation in the work of adhesion (W_{ad}) with Al atomic concentration.

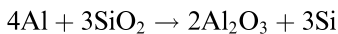
3.3. Diffusion at the interfaces

Fig. 7 shows the microstructures and composition alterations at the Cu/SiO_2 (a), Cu–5at.%Al/SiO_2 (b) and Cu–15at.%Al/SiO_2 (c) interfaces. An interdiffusion of Cu and Si occurs at the Cu/SiO_2 interface. With the addition of Al to Cu, the accumulation of Al and the formation of an aluminum–oxygen (Al_xO)-rich layer were identified at the Cu–Al/SiO_2 interfaces (see also X-ray spectrum in Fig. 4(b)). However, the interdiffusion between Cu and SiO_2 does not seem to be inhibited by the presence of this Al_xO-rich layer. Examination of the SiO_2 surfaces beneath the Cu–Al drops reveals that the reaction products are not dense but in the form of small particles with numerous fine cracks or pits (see Fig. 4(b)) as a result of volume shrinkage due to SiO_2 transformation to Al_2O_3 [9]. Obviously, these defects serve as channels for the further diffusion and penetration of Cu into SiO_2.

4. Discussion

The results obtained in this study show that at high temperature (e.g., 1473 K), the addition of Al to Cu mildly promotes the wettability, yet fails to substantially enhance the adhesion of Cu to SiO_2 and effectively impede the diffusion of Cu into SiO_2, which is in contrast with the behaviour observed in the low-temperature annealing studies [2–4,6] of the Cu–Al thin films on the SiO_2 substrates, as we described in the introduction.

It is not surprising that Al concentrates at the Cu–SiO_2 interfaces, as shown in Fig. 7(b) and (c), since the reduction of SiO_2 by Al



$$4Al + 3SiO_2 \rightarrow 2Al_2O_3 + 3Si$$

$$\Delta G^0_{298} = -595.22\ \mathrm{kJ\ mol^{-1}}\ [11] \qquad (2)$$

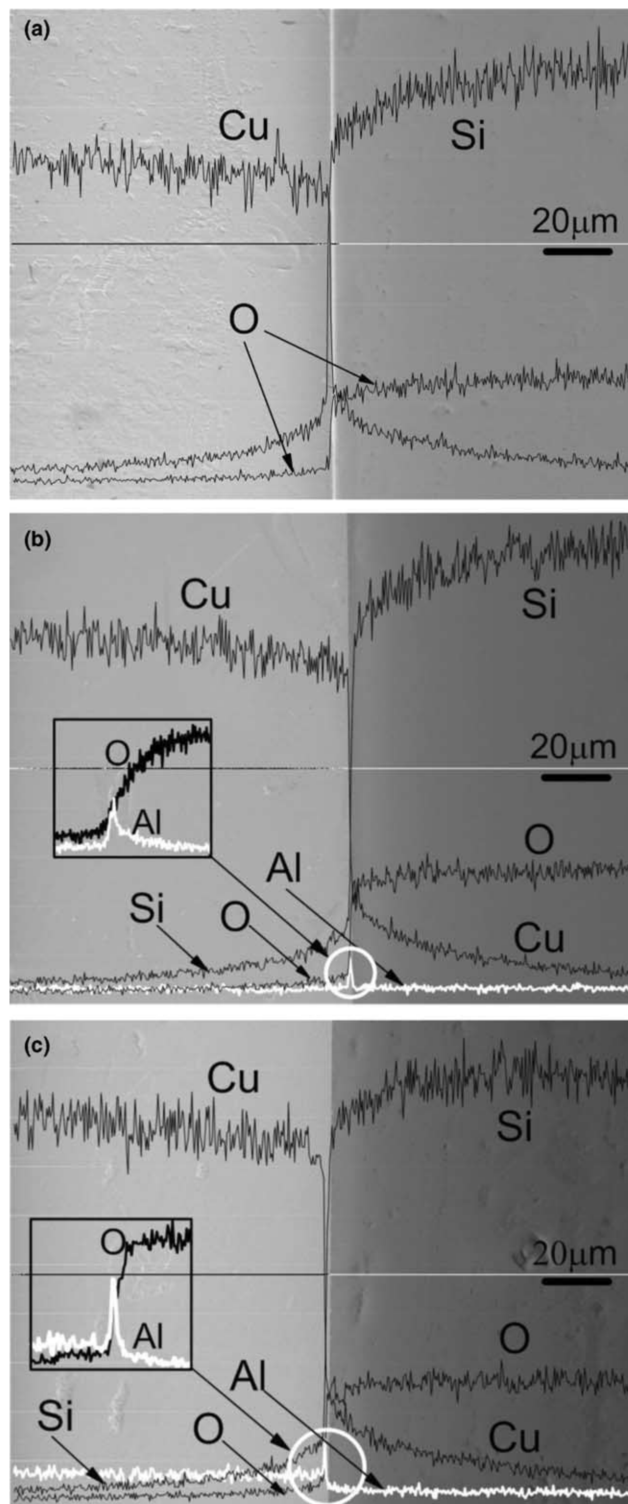


Fig. 7. Microstructures and composition alterations at (a) pure Cu/SiO_2, (b) Cu–5at.%Al/SiO_2 and (c) Cu–15at.%Al/SiO_2 interfaces.

is strongly favored from the viewpoint of thermodynamics. Also, it is reasonable to conjecture that the promotion of the wettability results from the strong affinity of Al for SiO_2 and the reaction-induced alter-

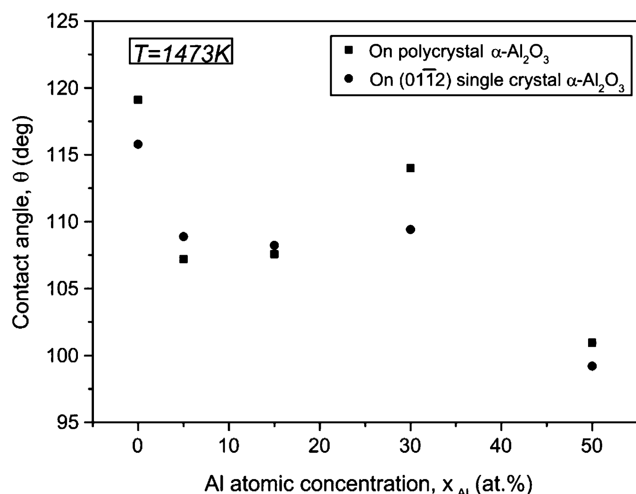


Fig. 8. Variation in the contact angles for the Cu–Al alloys on the polycrystalline (R_a = 100 nm) and single crystalline (R_a = 3 nm) α-Al_2O_3 substrates with Al atomic concentration.

ation in the interfacial chemistry (such as formation of the Al_xO phase). In order to better understand to what extent the wettability could be improved by the reaction, we examined the wettability of α-Al_2O_3 substrates by the same compositions of the Cu–Al alloys. Fig. 8 shows the contact angles obtained from both the polycrystal (R_a = 100 nm) and $(01\bar{1}2)$ single crystal (R_a = 3 nm) α-Al_2O_3 substrates. As compared with Fig. 3, the contact angles for the Cu–Al alloys on the α-Al_2O_3 substrates are only about 5–10° smaller than those on the SiO_2 substrates. According to the viewpoint of Eustathopoulos [12] that the wetting in reactive systems is determined by the final interfacial chemistry rather than by the intensity of the reaction, this result indicates that the wetting improvement in the Cu–Al/SiO_2 system by the chemical reaction and formation of the Al_xO-rich phase (e.g., alumina) at the interface is essentially limited. In this context, the significant adhesion enhancement by the addition of Al to Cu found in the low temperature (473–673 K) annealing studies [2–4,6] of the Cu–(Al) thin films on the SiO_2 substrates may result more from the removal of the hydroxyl groups on the SiO_2 surface, as a result of the reaction between Al and SiO_2, than from the formation of the thin alumina layer at the Cu–SiO_2 interface. It has been reported that the hydroxyl group can significantly weaken the adhesion between Cu and SiO_2 [13,14], while robust adhesion of a Cu thin film does occur on the moisture-free SiO_2 surface [13].

5. Conclusions

The effect of Al addition on the wettability, adhesion and diffusion properties of the Cu/SiO_2 system at 1473 K was investigated. The results show that at high temperature, Cu alloyed with Al mildly promotes the wettability, yet fails to enhance the adhesion and impede the thermal diffusion between Cu and SiO_2, in contrast to the behavior observed in the low-temperature annealing studies. The promotion of the wettability results from the strong affinity of Al for SiO_2 and the chemical reaction-induced alteration in the interfacial chemistry. The decrease in the surface tension with the increase in Al concentration partially offsets the function of the increase in the wettability, thus hardly improving the adhesion. The failure in impeding the Cu diffusion into SiO_2 is mainly due to the reaction product layer at the interfaces being porous.

Acknowledgments

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