Cu is widely applied in electronic device integration or packaging due to low resistivity, high thermal conductivity, low cost. Usually, solder was used as intermeddle material for bonding in packaging. However, direct bonding technology is being studied and applied for some device fabrication to replace soldering bonding technology to achieve higher performance packaging.1–3 For Cu/Cu direct bonding, usually, high temperature should be required to achieve good mechanical performance for direct bonding. However, high temperature may cause some problems for some devices, such as performance degeneration and device damage.4–9 Cu is easy to be oxidized in air to Cu oxide on surface, which prevents Cu/Cu direct bonding at low temperature. In order to solve this problem, some surface treatment methods for Cu low temperature direct bonding were reported, such as Ar atom fast bombardment,4–5 hydrogen gas reduction6 and other chemical treatments.11,12 However, there are some disadvantages for these treatment methods, such as high cost, long time annealing, higher temperature.

Formic acid (HCOOH) is an organic acid with simple molecule formula. When formic acid exists as gas state, HCOOH molecule may adsorb and decompose to H(g), HCOO(g) on Cu surface at room temperature, and HCOO(g) decompose further to H(g), CO2(g) at the temperature about 200°C. H(g) generated from HCOOH decomposition can react with the oxide on Cu surface to produce CO2(g), H2O(g).13,14 According this theory, formic acid vapor may be used to treat Cu surface for low temperature (~200°C) direct bonding.15 And in formic acid and water solution, HCOOH may be ionized to H+, HCOO−. When Cu sample is immersed in formic acid solution, Cu oxide may react with H+, and is reduced to Cu. According formic acid vapor decomposition on Cu surface and HCOOH ionization in solution, two kinds of Cu surface treatment methods using formic acid vapor and formic acid solution were developed for low temperature Cu/Cu direct bonding to achieve reasonable bonding strength.

In this study, Cu film samples were treated using formic acid vapor and formic acid solution respectively. In Cu/Cu direct bonding, surface composition and surface morphology are very important for bonding quality. Therefore, after treatment, Cu film surface was studied. Surface morphology was observed using atom force microscopy (AFM), and surface composition was analyzed using X-ray photoelectron spectroscopy (XPS). For formic acid vapor treatment, effect of treatment time on Cu surface morphology and composition was studied. For formic acid solution treatment, effects of treatment time and concentration of formic acid solution on Cu surface morphology and composition also were studied. Finally, Cu/Cu low temperature bonding was performed after formic acid vapor/solution treatment. Treatment and bonding results were compared and discussed for these two different formic acid treatment methods.

Experimental

Cu film sample we used for treatment was prepared on Si chip using magnetron-sputtering method. The thickness of Cu film is about 600 nm. Two kinds of Cu film chips with 6 mm × 6 mm and 10 mm × 10 mm size were fabricated for treatment and bonding. For formic acid vapor treatment, Cu film was treated using thermal-compression bonding machine with formic acid vapor treatment process shown in Fig. 1, which includes formic acid vapor generation system and treatment/bonding chamber. Before treatment, Cu film sample was cleaned.

Figure 1. Schematic of formic acid vapor generation and Cu sample treatment/bonding machine.
using ultrasonic cleaning machine in acetone, ethanol, and pure water for 3 min, respectively. Then, Cu film was fixed on sample stage in treatment chamber. After sample setting, the chamber was vacuumed to about 5 Pa. The heater on stage was turned on, and sample was heated to 200°C. N2 was input to formic acid solution (98%HCOOH). Mixed gas of formic acid vapor (1%) and N2 (99%) was generated and filled in chamber to treat Cu sample on stage. For formic acid solution treatment, three kinds of formic acid solutions with different concentration (25%HCOOH, 50%HCOOH and 75%HCOOH) were made to treat Cu films. Cu films were immersed in different formic acid solutions to realize surface treatment. After formic acid vapor/solution treatment, Cu film chips were bonded together at 200°C using the bonder shown in Fig. 1.

Results and Discussion

**Formic acid vapor treatment for Cu film.** — At 200°C, formic acid vapor was introduced to chamber to treat Cu films for 10 min, 20 min, 30 min, respectively. After formic acid vapor treatment, Cu film surface composition was analyzed using XPS. Fig. 2 shows Cu2p spectra of Cu films treated by formic acid vapor with different times. Cu2p peak of Cu film without treatment is lowest. With treatment time increase from 10 min to 30 min, Cu2p peak becomes higher. Fig. 3 is O1s spectra of Cu films treated by formic acid vapor with different times. O1s peak of Cu film with 30 min treatment is lowest, and O1s peak of Cu film without treatment is highest. With treatment time increase from 10 min to 30 min, O1s peak becomes lower. It can be concluded that, formic acid vapor treatment may reduce Cu film surface oxide, and 30 min treatment may get best reduction results in this study.

AFM was used to observe and analyze Cu film surface after treatment. For formic acid vapor/solution treatment, the effect of different treatment time on Cu film surface morphology was studied. Surface morphologies of Cu film treated at 200°C by formic acid vapor with different treatment time were obtained by AFM, shown in Fig. 4. After formic acid vapor treatment, the change of surface morphology is not obvious. In order to get details of Cu film surface, surface roughness and Cu particle size for Cu films were studied. Fig. 5 shows the change of surface roughness and average particle size with formic acid vapor treatment time. After treatment, both surface roughness and average particle area were increased. With treatment time from 0 min increase to 30 min, surface roughness and average particle area were increased.
to 30 min, surface roughness increase from 1.33 nm to 2.03 nm, and average particle size increase from 9980 nm² to 104800 nm².

**Formic acid solution treatment for Cu film.**—Formic acid solution treatment for Cu films also was studied. In order to study the effect of different concentration solution on Cu film surface, 25%, 50%, 75% formic acid solutions were used to treat Cu films for 30 min, respectively. Fig. 6 is Cu2p spectra of Cu films treated by formic acid solution with different concentration. After formic acid solution treatments, Cu2p spectra are higher than that without treatment. Using the formic acid solution with 50% HCOOH, Cu2p peak is highest. Fig. 7 is O1s spectra of Cu films treated by formic acid solution with different concentration. O1s peak become lower after formic acid solution treatment. And the O1s peak of Cu film treated by 50% formic acid solution is lowest. In 25% formic acid solution, there are not enough H⁺ because HCOOH concentration is lower. And in 75% formic acid solution, formic acid solution is too high and H₂O is fewer, which restrains HCOOH ionization to generate H⁺. Therefore, 50% formic acid solution is optimal for enough H⁺ generation. Therefore, it can be concluded that Cu film surface oxide can be reduced by formic acid solution, and 50% formic acid solution is best for Cu film surface oxide reduction in this study.

Effect of treatment time of formic acid solution on Cu film surface composition also was studied by XPS. Cu film samples were treated by 50% formic acid solution for 10 mins, 20 mins and 30 mins, respectively. Fig. 8 is Cu2p spectra of Cu films treated by 50% formic acid solution for different treatment time. After treatments, Cu2p spectra are higher than that without treatment. With long treatment time, Cu2p peak becomes higher. Fig. 9 is O1s spectra of Cu films treated by 50% formic acid solution with different treatment time. O1s peak become lower after treatments. With treatment time increases, O1s peak becomes higher. And the O1s peak of Cu film treated for 30 min is lowest.

For formic acid solution treatment, effects of different concentration and different treatment time on Cu film surface morphology were studied by AFM. Fig. 10 shows Cu film surface morphology for different formic acid concentration and different treatment time. After treatment, Cu particle size on film surface becomes bigger obviously than that of untreated Cu film. Fig. 11 is the surface roughness and average area of Cu particles treated by 50% formic acid solution for different treatment time. With treatment time increases from 0 min to 30 min, surface roughness increases from 1.33 nm to 5.24 nm, and average area of Cu particles increases from 9980 nm² to 18100 nm² gradually. Fig. 12 shows the effect of the formic acid concentration on surface roughness and average area of particles on Cu film surface. With different concentration formic acid solution treatments, surface roughness and average particle size become bigger than that without treatment. Surface roughness and average particle size are biggest using 50% formic acid solution because Cu film surface was reduced enough using 50% formic acid solution.
Cu/Cu low temperature bonding.—In order to confirm the effects of formic acid vapor and solution treatments on Cu/Cu direct bonding, two pieces of Cu film samples treated by formic acid vapor and two pieces of Cu film samples treated by formic acid solution were used for bonding, respectively. For formic acid vapor treatment, Cu films were treated at 200°C for 30 min. And for formic acid solution treatment, Cu films were treated in 50% formic acid solution for 30 min. After treatments, every bonding was performed at 200°C under a load of 1500 N/30 min. Bonding strength was evaluated by tensile test after bonding. Fig. 13 shows the bonding strength using formic acid vapor treatment and formic acid solution treatment. For formic acid vapor treatment, the bonding strength is about 18.2 MPa. And using formic acid solution treatment, the bonding strength is about 11.5 MPa. Compared with formic acid solution treatment, formic acid vapor treatment may achieve higher strength for Cu low temperature bonding.

**Discussion**

For low temperature direct bonding, smooth and cleaning surface are beneficial to achieve high quality bonding. It is necessary to discuss effects of formic acid vapor and solution on Cu film surface further. Based on experiment results above, we compared and analyzed the effect of formic acid vapor/solution treatment on Cu low temperature direct bonding. Using formic acid vapor/solution treatment, Cu film surface can be reduced. And with treatment time increases, effect of
Cu film samples were treated using formic acid vapor and formic acid solution for Cu/Cu low temperature bonding. Effects of formic acid vapor/solution on Cu film surface were studied. Both formic acid vapor and solution treatment can reduce Cu surface oxide. And both formic acid vapor and solution treatment may cause surface roughness and particle size to increase. Using formic acid solution treatment, better surface reduction and rougher surface for Cu film were obtained. By contrast, using formic acid vapor treatment, surface reduction is not so good, but smoother surface was obtained. Considering surface reduction effect, formic acid solution treatment is superior to formic acid vapor treatment. However, for surface morphology, formic acid vapor can get smoother surface, which is better than formic acid solution treatment. For Cu/Cu bonding, the bonding strength using formic acid vapor treatment is stronger than that using formic acid solution treatment. Therefore, formic acid vapor treatment is more acceptable for high bonding strength in this study.

Conclusions

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