Reductive Kinetic Study of Oxidized Cu Surface by Catalyzed Formic Acid Vapor

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Abstract
The combination of excellent electrical and thermal conductivity properties makes copper a good selection for interconnect materials and packaging. However, the easy oxidation of copper surface causes the limit for manufacture. How to clean copper surface has been an importantly topic. In this study, the reduction of copper oxides at low temperatures can be achieved using catalytic formic acid treatment. An in situ FTIR was adopted to monitor the reductive reactions of the oxidized copper surface under catalytic formic acid vapor at different temperatures. Experimental results show that 350 nm-thick cuprous oxide (Cu₂O) on copper surface can perfectly reduce to pure copper at a reaction temperature down to 160°C. As the reaction temperature increased, the time for full reduction decreased. It is also verified that HCOOH can be easily decomposed to CO₂ and hydrogen radicals by using Pt as a catalyst. Analytical results of electron paramagnetic resonance suggest that a catalysis temperature of 150°C would generate the maximum amount of hydrogen radicals, which assisted the removal of Cu oxides more efficient.

1. Introduction
One of the main streams of the development of contemporary microelectronic packaging is 3D IC packaging, for which the Cu to Cu direct bonding is one of the key technologies for 3D chip stacking. However, Cu/Cu direct bonding needs to be performed at high temperature process (≥400°C), which may give rise to thermal mechanical stress and degeneration in device performance [1]. Easy oxidation of Cu surface is the main problem to be overcome for low temperature Cu to Cu direct bonding [2]. Ishikawa et al. [3] proposed that thermal reduction using a formic acid vapor treatment can efficiently clean Cu surface without physical damage.

According the studies using TPD (Thermal desorption spectroscopy), STM (Scanning tunneling microscopy) [4] [5] and FTIR (Infrared reflection absorption spectroscopy) [6], it has been proposed that Cu surface oxides can catalyze formic acid decomposition and thus the oxides are reduced. In the reaction process, the acid proton of formic acid reacts with basic oxygen at the surface, which will generate H₂O and HCOO⁻, and then H₂O contacts with O atom to form OH⁻. When the reaction is elevated at above 450K, HCOO⁻ become unstable and decomposes during the reaction process to yield CO₂ and H₂. The next step is the reaction between H₂ and O₂ to generate H₂O. Therefore, Cu oxide reduction can be achieved by the extraction of O atom from the surface [7].

Recently, Suga et al.[8,9] suggested that with formic acid treatment with Pt catalysts can generate H radical, which can clean Cu surface and thereby robust Cu to Cu direct bonding can be obtained at 200°C for 5 min. However, there is still a lack of systematic investigation on the reductive kinetics and the effect of Pt catalysis. In this study, the real-time observation of the copper oxide reduction at different reductive temperatures is carried out using in-situ FTIR. Electron paramagnetic resonance is also applied to study the effect of catalytic temperature.

2. Results and Discussion
Copper oxide layer for investigation was obtained by annealing fresh Cu surface at 200°C for 20min. As shown in the TEM cross-sectional image (Fig. 1(a)), the oxide layer well attached to the Cu substrate was about 350 nm in thickness. In combination with EDS elemental mapping (Fig. 1(b)) and chemical analytic results, the oxide phase was cuprous oxide, Cu₂O.

![Fig. 1 TEM observation of Cu₂O layer (a) bright field image and (b) EDS elemental mapping](image)

As the example given in Fig. 2(a), In situ FTIR was applied to observe the evolution of Cu₂O layer under the exposure of dilute formic acid vapor at different holding temperatures varied from 160°C to 225°C. As illustrated, the peak at 655-605 cm⁻¹ resulted from the absorption of the Cu₂O.
In the case of formic acid treatment at 200°C without Pt catalysis, as the exposure time increased the signal of Cu$_2$O layer decreased monotonically and reached almost zero at about 18 min.

Derived from the in-situ FTIR spectra, Fig. 2(b) summarized the reductive kinetic results. It can be found that with a higher reaction temperature the time for full reduction shrank. Pt catalysis can significantly accelerate reduction of oxide. It is interesting that catalytic temperature also played an important role. At each reaction temperature, the reaction with catalytic temperature of 300°C was the shortest. Notably, those catalyzed at 150°C was the runner-up when reacted at 160°C and 175°C.

![Image](image1.png)

Fig. 2 (a) A series of in situ FTIR spectra obtained during the exposure of 0.4% formic acid vapor without Pt catalysis when the sample was isothermally heated at 200°C (b) Relationship between reduction time and reaction temperature of Cu$_2$O layer, and the catalytic temperature

The fact that catalysis at 150°C showed excellent catalytic efficiency can be explained by the amount of H radicals (H). Fig. 3(a) displays electron spin resonance spectrum for the formic acid vapor catalyzed by Pt at 150°C, which shows a typical pattern of H trapped by DMPO [10]. The intensities for the cases with or without Pt catalysis at different catalytic temperatures are given in Fig. 3(b). It can be seen that the intensities did not differ too much without Pt catalysis, while those with Pt a catalytic temperature of 150°C apparently generate the most amount of H.

![Image](image2.png)

Fig. 3 (a) Electron spin resonance spectra of 0.4% formic acid vapor with Pt catalysis when the catalytic temperature was 150°C (b) Relationship between EPR intensity and catalytic temperature

According to the above results, it can be proposed that HCOOH would be directly decomposed to hydrogen radicals using Pt as catalyst and the direct combination between hydrogen radicals and adsorbed OH contributes to fast extraction of O and generation of H$_2$O. A higher catalytic temperature likely gave rise to a degradation of hydrogen radicals and formation of H$_2$. A fast reduction with a catalytic temperature of 300°C can be ascribed to the reaction of H$_2$ with oxide and the elevated vapor temperature promoted it.

**Conclusions**

The effect of Pt catalysis on Cu$_2$O reduction using formic acid treatment was studied. In situ FTIR observation demonstrates that Pt catalysis can significantly shorten the reduction time by formic acid vapor. It is demonstrated that a catalytic temperature of 150°C generated a maximum amount of the hydrogen radicals, which efficiently removed O atom and reduce copper oxides.

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**References**