Extended Abstracts of the 2015 International Conference on Solid State Devices and Materials, Sapporo, 2015, pp78-79

# *In situ* FTIR Spectroscopic and Kinetic Studies of Cu Surface Reduction by Using Formic Acid Treatment with Pt catalysts

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**Abstract**

**The combination of excellent electrical and thermal conductivity properties makes copper a good selection for interconnect materials and packaging. Because the copper surface is easily oxidized, it causes the limit for manufacture. Therefore, 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 formic acid treatment. An *in situ* FTIR was adopted to monitor the reactions between formic acid vapor and the oxidized copper surface at difference temperatures. The results show that cuprous oxide on copper surface can perfectly reduce to pure copper at the temperature down to 160ºC. With the assistance of Pt catalysts, the removal of Cu oxides was 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 $H_{(a)}$ and $HCOO_{(a)}$, and then $H_{(a)}$ contacts with $O_{(a)}$ atom to form $OH_{(a)}$ (eq. (1)). When the reaction is elevated at above 450K, $HCOO_{(a)}$ become unstable and decomposes during the reaction process to yield $CO_{2(g)}$ and $H_{(a)}$ (eq. (2)). The next step is the combination of desorbed $H_{(a)}$ to form $H_{2(g)}$ (eq. (3)) or the reaction between $H_{(a)}$ and $OH_{(a)}$to generate $H_2O_{(g)}$ (eq. (4)). Therefore, Cu oxide reduction can be achieved by the extraction of O atom from the surface [7].

$$HCOOH_{(a)} + O_{(a)} \rightarrow HCOO_{(a)} + OH_{(a)} \quad (1)$$
$$HCOO_{(a)} \rightarrow CO_{2\,(g)} + H_{(a)} \quad (2)$$
$$2H_{(a)} \rightarrow H_{2(g)} \quad (3)$$
$$H_{(a)} + OH_{(a)} \rightarrow H_2O_{(g)} \quad (4)$$

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 200ºC for 5 min. However, there is still a lack of in-depth investigation on the kinetics as well as the mechanism. In this study, the real-time observation of the copper oxide reduction at different temperature is carried out using in-situ FTIR. The effect of Pt catalysts on reaction kinetics is the main issue. Forming gas ($N_2$-5%$H_2$) is also adopted for comparison.

## 2. Results and Discussion

Copper oxide layer for investigation was obtained by annealing fresh Cu surface at 200ºC for 20min. According to GIXRD (Grazing Incidence X-ray Diffraction) analytic data, the copper oxide phase can be identified to be cuprous oxide, $Cu_2O$.

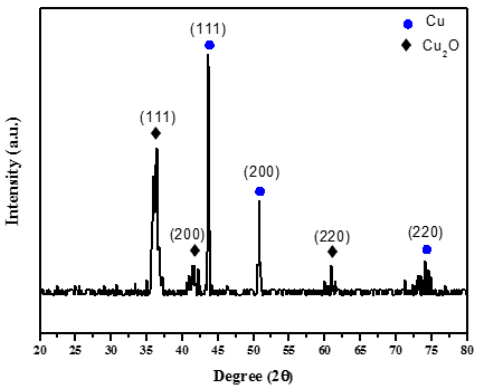


Fig. 1 X ray diffraction pattern of the oxide layer for investigation.

*In situ* FTIR was applied to observe the evolution of $Cu_2O$ layer under the exposure of dilute formic acid vapor at different holding temperatures varied from 160ºC to 225ºC. Fig. 2 shows the case reacted at 200ºC without using Pt catalyst. The appearance of the peak at 655-605 $cm^{-1}$ resulted from the absorption of the $Cu_2O$. As the exposure time increased, the signal of $Cu_2O$ layer decreased monotonically

and reached almost zero at about 18 min.

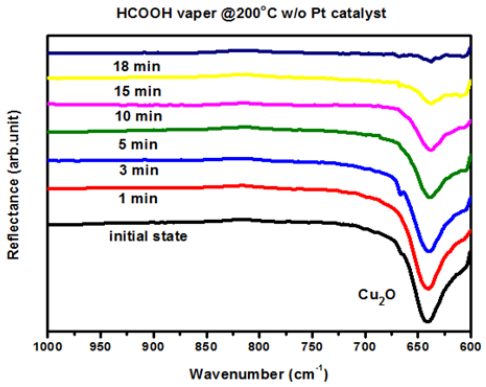


Fig. 2 A series of *in situ* FTIR spectra obtained during the exposure of 0.4% formic acid vapor without Pt catalyst when the sample was isothermally heated at 200°C

Derived from the in-situ FTIR spectra, Fig. 3 illustrates the decrease of $Cu_2O$ layer as a function of reaction time. In Fig. 3(a), it can be found that cuprous oxide can be perfectly reduced to metallic copper under 0.4% formic acid vapor in 18 min at 200°C and 45 min at 160°C. With Pt catalysts (Fig. 3(b)), the reaction kinetics can be effectively accelerated, *i.e.* 5 min at 200°C and 27 minutes at 160°C.

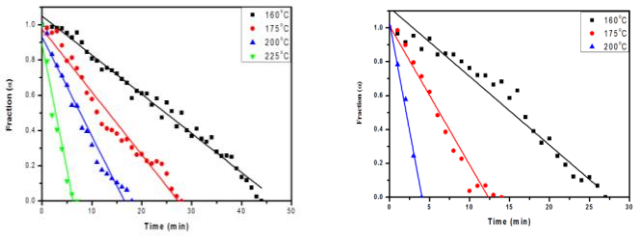


Fig. 3 The evolution of copper oxides with increasing formic acid reaction time: (a) without Pt catalysts (b) with Pt catalysts

## 3. Conclusions

The effect of Pt catalyst on $Cu_2O$ reduction using formic acid treatment was studied. The *in situ* FTIR observation demonstrates that Pt catalysis can significantly shorten the reduction time. At 160°C, it takes 27 min for complete removal of Cu oxide, while at 200°C it needs only 5 min.


## Acknowledgements

This work was supported by Ministry of Science and Technology of R.O.C. through the contract No. NSC 101-2628-E-005-001-MY2. The authors also thanks for the financial support from Taiwan Comprehensive University System.


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