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Full Length Article

Low temperature de-oxidation for copper surface by catalyzed formic acid vapor

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ABSTRACT

This study investigated low temperature reduction of copper oxides using modified formic acid vapor treatment with Pt catalysts in terms of reaction kinetics and mechanisms. An *in situ* FTIR was adopted to monitor the evolution of organic ligands and oxidized copper surface under catalyzed formic acid vapor. 350 nm-thick Cu_2O can be perfectly and efficiently transformed to pure copper at 160 °C. Analytical results of electron paramagnetic resonance verify that HCOOH can be easily decomposed and forms hydrogen radicals through catalysis with Pt. An optimal catalytic temperature of 150 °C which generated the maximum amount of hydrogen radicals was suggested.

1. Introduction

The combination of excellent electrical and thermal conductivities makes copper a good choice for interconnect materials. However, copper suffers from easy oxidation in various atmospheres [1–5]. It is difficult to preserve fresh copper during storage and manufacturing, especially at high temperatures or harsh environment. Therefore, how to clean copper surface efficiently at low temperatures without using sophisticated vacuum processes is always an important topic. De-oxidation treatments for copper surface can be roughly categorized into wet and dry methods. With respect to wet treatments, acid solutions have been applied widely [6]. Koyama et al. [7] used three kinds of boiling organic acid solutions, *i.e.* formic acid, acetic acid and citric acid, to reduce copper surface and keep it fresh. It was found that formic acid exhibited the highest reductive rate but citric acid-treated samples can preserve un-oxidized state much longer in ambience.

Among dry treatments, $H_2/(He,N_2)$ mixed gases and H_2 plasma have been widely used as reductive atmosphere. To effectively reduce copper oxides at 250 °C or below, either high vacuum or high H_2 pressure is usually required [8,9]. No only remove oxide layer by ion bombardment, H_2 plasma can also reduce oxidized copper surface through the reaction shown in Eq. (1) [10].

$$Cu_2O + 2H \rightarrow 2Cu + H_2O \tag{1}$$

Without physical or electrical damage from Ar sputter cleaning, surface treatment for copper circuits using formic acid vapor developed by Ishikawa et al. [11,12] can efficiently clean Cu surface at about 200 °C, much lower than the temperature for thermal cleaning using H_2. It has good applicability particularly for narrow holes with high aspect ratio. Recently, this method attracted much attention due to the requirement for Cu to Cu direct bonding in 3D IC stacking [13–16]. Commercial Cu/Cu direct bonding is difficult to be realized practically in mass production because it needs to be performed at high temperatures (≧400°C) and high vacuum (e.g. 10^{-3}–10^{-4} torr) as well [17,18]. The development of formic acid vapor treatment plays the key role to achieve low temperature and atmospheric pressure Cu to Cu direct bonding [15–16].

Since Cu surface oxides can catalyze the decomposition of formic acid [19–21], the adsorption, dissociation and thus oxidation of formates can generate H_2O and take O atoms away from copper surface. As the surface temperature increases, the reaction varies from (2) to (3) below with a change in overall stoichiometry [19].

$$2HCOOH + O_{(a)} \rightarrow 2CO_2 + H_2 + H_2O \tag{2}$$

$$HCOOH + O_{(a)} \rightarrow CO_2 + H_2O \tag{3}$$

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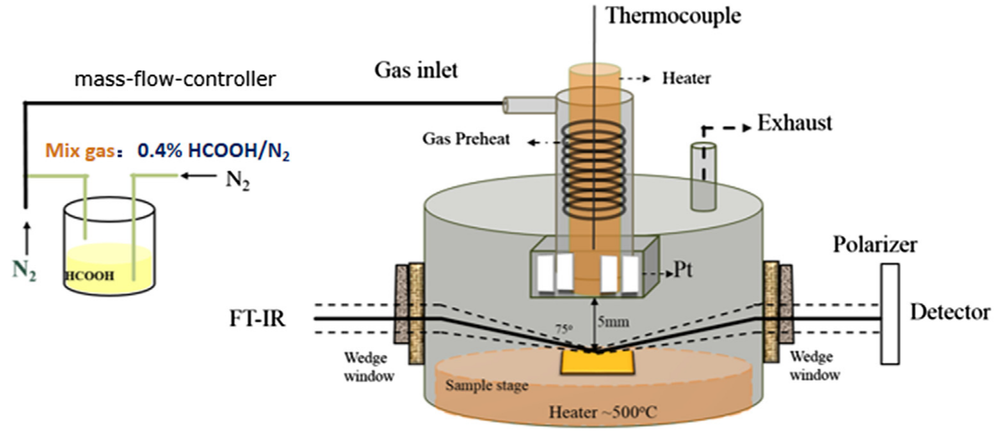

Fig. 1. Apparatus for real-time detection of the reaction between formic acid vapor and oxidized copper surface.

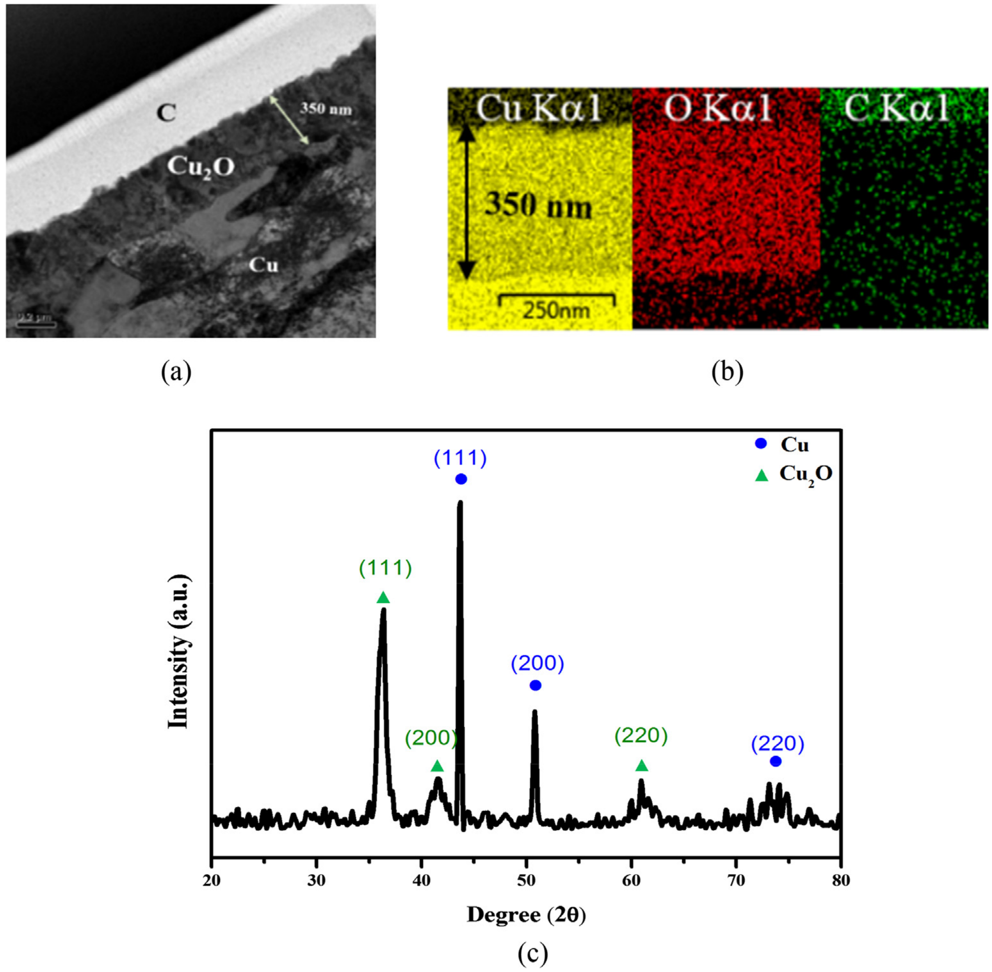

Fig. 2. Observation and identification of the copper oxide layer: (a) TEM bright field image and (b) EDS elemental mapping, (c) GIXRD pattern.

According to the examinations using TPD (Thermal desorption spectroscopy), STM (Scanning tunneling microscopy) [19,22,23] and FTIR (Infrared reflection absorption spectroscopy) [24,25], a series of reactions have been proposed. As given below, the acid protons of formic acid react with basic oxygen at the surface, which generates $H_{(a)}$ and $HCOO_{(a)}$ (Eq. (4)), and then $H_{(a)}$ links with $O_{(a)}$ atom to form $OH_{(a)}$. When the temperature is elevated at 177 °C and above, $HCOO_{(a)}$ becomes unstable and decomposes to yield $CO_{2(g)}$ and $H_{(a)}$ (Eq.(5)). The next step is the reaction between $H_{(a)}$ and $OH_{(a)}$to generate $H_2O_{(g)}$ (Eq. (6)). After that, Cu oxide reduction can be achieved by the extraction of O atom from the surface [19,22].

$$HCOOH_{(g)} \rightarrow HCOO_{(a)} + H_{(a)} \tag{4}$$

$$HCOO_{(a)} \rightarrow CO_{2(g)} + H_{(a)} \tag{5}$$

$$H_{(a)} + OH_{(a)} \rightarrow H_2O_{(g)} \tag{6}$$

In order to enhance the efficiency of organic acid vapor treatment, Suga et al. [13–16] proposed the dissociation of formic acid vapor using Pt as catalysts. By doing so, the process temperature for direct Cu bonding can be lowered further to 180 °C. However, there is still a lack