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Highly conductive copper films based on submicron copper particles/copper complex inks for printed electronics: Microstructure, resistivity, oxidation resistance, and long-term stability

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ABSTRACT

Submicron Cu particles mixed with Cu complex are used successfully to fabricate highly conductive Cu films for printed electronics. This study investigates the effects of Cu particle size on microstructure, conductivity and on the long-term stability of printed Cu films. In particular, the oxidation behaviors of printed Cu films at high temperatures are studied from the evolutions in microstructure and chemical composition. The submicron Cu particles are sintered efficiently due to the help of in-situ formed Cu nanoparticles from the decomposition of the Cu complex. Low resistivity of 5.8 μΩ cm is easily achieved. At temperatures of 140 °C and 180 °C, the printed Cu films prepared from 800 nm Cu particles are more stable than that from those 350 nm particles, which can be attributed to larger Cu particles possessing higher oxidation resistance. At 220 °C, the result becomes opposite because the loose structure with many large voids in the printed Cu films from large particles provides sufficient space for oxygen and accelerate the break of pathways between adjacent particles by the formation of Cu oxides layers. This indicates the long-term stability of printed Cu films is attributed to not only the intrinsic oxidation of Cu to Cu_2O but also the degradation of microstructures. At all events, the printed Cu films from submicron Cu particles with Cu complex exhibit excellent oxidation resistance and are superior to those from Cu nanoparticles. This presents significant potential and favorable prospects for the fabrication of highly reliable and cost-effective printed electronics.

1. Introduction

Conductive inks play an important role in printing high conductive electrodes and circuits onto flexible substrates and have received increasing attention due to their potential applications in low-cost and environmentally-friendly printed electronics [1–4]. Cu nanoparticle inks are highly expected to replace Ag-based inks because Cu has a high conductivity similar to Ag but the price is amazingly inexpensive at only 1/100 that of Ag [5–9]. However, Cu nanoparticles are very sensitive to oxygen resulting in oxidation [10,11]. The oxide layer on their surface will hinder the diffusion of Cu atoms between adjacent Cu particles and decrease the sintering efficiency, leading to a low conductivity [12–14].

To reduce the oxide layer, there strategies have been employed. The first strategy involves the use of a thick organic shell to avoid the oxidation of Cu nanoparticles during the synthesis process [8,12,14,15]. The second strategy is to perform the annealing of Cu nanoparticles in specific atmospheres such as vacuum, inert, or reducing atmospheres to reduce surface oxide on metal Cu [12,13,16,17]. The third one is using Cu complex inks, which transform into pure metallic Cu after heat treatment to overcome the oxidation during preparation and storage [18,19]. Although all of

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these strategies can achieve high conductivity Cu films, another drawback of using these Cu films is their poor long-term stability. The resistance of sintered Cu films increased rapidly to six times higher to the original value after a mere one week in an ambient atmosphere [20]. The poor stability of sintered Cu films seriously hinders their practical application in printed electronics.

To improve the stability of sintered Cu films, Paglia et al. [21] put forward a two-step deposition method to produce Cu films with a dense surface, which possibly prevents the penetration of oxygen into the underlying layer and thereby improving the long-term stability of sintered Cu films. However, the fabrication process is complicated and there is the fatal oxidation of the surface layer of the Cu films. On the other hand, compared with Cu nanoparticles, it is known that micro/submicron Cu particles have a stronger oxidation resistance [10] although sintering them at low temperature is difficult [22,23]. Therefore, both the sintering efficiency and long-term stability of Cu films should be considered simultaneously. Joo et al. [24] achieved a low sheet resistance Cu film by sintering the mixture of nano-Cu and micro-Cu particles, in which Cu nanoparticles played a role of nano-welders to connect those micro-Cu particles together. They also clearly stated that the existence of Cu oxide shell on these Cu nanoparticles was an obstruction for sintering Cu particles. Considering the size effect of nanoparticles in the sintering process, Yonezawa et al. [25] confirmed that the in-situ formation of small Cu oxide particles on the surface of large Cu particles assisted in the efficient sintering of large Cu particles at 200 °C in N_2-H_2 gas. This process typically demands a much higher temperature, greater than 300 °C. Very recently, to sinter large Cu particles by the in-situ formation of metallic Cu nanoparticles from Cu complex or stabilized sub-10-nm Cu particles were studied [26–29]. The fresh and active metallic Cu nanoparticles, once formed from the thermal decomposition of Cu complex, are quite suitable for immediate sintering provided that oxidation has been avoided. A high conductivity of 7.2 μΩ cm Cu film on flexible substrates can be easily obtained at only 140 °C [28]. However, the long-term reliability of printed Cu films fabricated from micro/submicron Cu particles has not been studied. Such studies of these printed Cu films are important and essential for their practical application in electronic devices. In the present study, two kinds of submicron Cu particle were used to fabricate Cu films. Our focus was on the microstructure, conductivity, and long-term stability of printed Cu films. The evolutions of microstructure and crystal phase of Cu films under high temperature environment were discussed according to oxidation behaviors.

2. Experimental

2.1. Preparation of submicron Cu particle/copper complex ink and printing Cu films

The standard fabrication process of the submicron Cu particle ink has been described in our previous study [27]. Briefly, 10.00 g Cu (II) formate tetrahydrate powder ($C_2O_4H_2Cu \cdot 4H_2O$, 98%, Wako Pure Chemical Industries Ltd) and 7.90 g 2-amino-2-methyl-1-propanol (AMP, $C_4H_{11}NO$, 98%, Nacalai tesque, Inc) were added to a sample cell and were stirred for 30 min at room temperature to get a Cu-amino complex. Then, 5.96 g submicron Cu particles (Mitsui Mining & Smelting Co., Ltd) were added and mixed with the Cu-amino complex by a hybrid mixer (HM-500, Keyence) for 30 min to obtain a homogeneous Cu particles/Cu complex ink. In this study, two kinds of Cu particles of 350 nm and 800 nm in average, respectively, were used to fabricate two kinds of Cu inks of Cu350 and Cu800. The inks were printed onto polyimide (PI) substrates of 77.5 μm thick by using mask-printing method and then sintered by a two-step method consisting of low temperature heating followed by flash light sintering [28]. The low temperature heating is conducted at 140 °C for 10 min in N_2 by using a reflow solder system (RSS-450-210, Unitemp GmbH). The flash light irradiation system used was PulseForge 3300 (Novacentrix, Austin, TX, USA) which covers a wide-energy band emission ranging from 200 nm to 1500 nm. The irradiation duration was fixed at 2000 μs and the electrical voltage was changed from 240 V to 300 V to supply optical energy from 1.7 J/cm^2 to 3.3 J/cm^2. The flash light sintering is conducted in air. The thicknesses of printed Cu films from Cu350 ink and Cu800 ink are about 6 μm and 8 μm respectively.

2.2. Characterization and reliability evaluation of printed Cu films

The thermal behaviors of Cu particles were investigated by thermogravimetric analysis (TGA 2000SE, NETZSCH) at a heating rate of 5 °C/min in air. The microstructure of sintered Cu films was observed by scanning electron microscopy (SEM, SU8020, HITACHI) and transmission electron microscopy (TEM, JEM-ARM200F, JEOL). The cross-sections of printed Cu films were cut using a Focused Ion Beam (FIB, FIB-2100, HITACHI) with a high-current beam (40 keV, 1.1–2.8 nA) followed by a low-current beam finish (40 keV, 0.3–0.6 nA). Electrical resistivity of sintered Cu films was measured by four probe analyzers (LorestaGP T610, Mitsubishi Chemical Analytech Co. Ltd.). Crystal phase analysis of sintered Cu patterns was performed by X-ray diffraction (XRD, Rigaku) using Cu Kα. The long-term stability of printed Cu films without any encapsulation was evaluated by exposing them to high temperatures of 140 °C, 180 °C, and 220 °C in air. The change of electrical resistance of printed Cu films during exposure was recorded. The oxidation behaviors of printed Cu films were studied by observing their resistivity change and corresponding microstructure. The qualitative evaluation of Cu, Cu_2O, and CuO in printed Cu films was performed by measuring the area under the peaks of Cu(1 1 1), Cu_2O(1 1 1), and CuO(1 1 1), respectively.

3. Results and discussion

A two-step sintering method was used to sinter the prepared submicron Cu particles/Cu complex inks for conductive Cu films [25]. During the first step, a low temperature heating of 140 °C can make a complete decomposition of Cu-amino complex into fresh metallic Cu nanoparticles, which cover the surface of submicron Cu particles. In the second step, these fresh and highly-active Cu nanoparticles can play a role of nano-welders to induce the efficient sintering of submicron Cu particles.

3.1. Microstructure evolution of printed Cu films

Fig. 1 shows the microstructure evolution of printed Cu films prepared from Cu350 ink. A low input energy of 1.7 J/cm^2 has resulted in local sintering between adjacent Cu particles although their surface does not show any significant change (Fig. 1a). The corresponding cross-section image also confirms that a weak network structure in small range is obtained (Fig. 1d). With the increase of input energy, the contact areas between adjacent Cu particles are clearly enlarged even though the interfaces between them are still clear (Fig. 1b and e). When the input energy increases to 3.3 J/cm^2, the interfaces between Cu particles seem to have disappeared and large necks between Cu particles can be observed (Fig. 1c). The cross-section also confirms that the grains are further grown to form a strong network structure (Fig. 1f).

In order to confirm the role of in-situ formed nano-welders (Cu nanoparticles), the interfaces between sintered Cu particles after 2.4 J/cm^2 irradiation were observed by TEM. As shown in Fig. 2a, the adjacent submicron Cu particles have been welded to one another