



Behavior of thin copper oxide on silver as an analogue for copper nanoparticles



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ABSTRACT

The behavior of a thin copper oxide (CuO_x) layer deposited on silver (Ag) was examined in order to clarify the process by which an interface is formed when Cu nanoparticles bond to an Ag adhesive. The results of X-ray photoelectron spectroscopy and atomic force microscopy revealed that an active interfacial reaction occurs between CuO_x and Ag when annealed in a reductive atmosphere at temperatures above 523 K. This reaction involves the migration of Ag atoms toward the surface, which is accompanied by the reduction of CuO_x to metallic Cu and the growth of newly generated elongated grains. As this reaction was limited in an inert atmosphere, it is concluded that annealing causes phase separation into Ag and Cu, which is then followed by the formation of an Ag–Cu solid solution. This suggests that interfaces are created through inter-diffusion between the Ag layer and a metastable metallic Cu surface layer formed on the surface of Cu nanoparticles by annealing in a reductive atmosphere.

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1. Introduction

The recent increase in demand for high performance hybrid electric vehicles has created a need for high performance power control units based on high current, high voltage and low-power-loss semiconductor devices. So far, Si-based devices have been used in such applications and shown great improvement, but there is still a physical limitation on efficiency. This has created a need for alternative power devices with greater efficiency, the most promising of which are based on SiC semiconductors [1]. These, however, need to be reduced in size to meet requirements for cheaper, smaller power control units, which is expected to increase their operating temperature to more than 473 K due to an increase in current density. This, in turn, means that any surrounding components need to have a high heat resistance.

One of the components that is most influenced by an increase in operating temperature is the bonding material used to affix a power device onto a substrate. Although Sn-based solders have generally been used for this purpose, their solidus line temperature is too low for exposure to operating temperatures greater than 473 K [2]. In the past, Pb-based solders were used in higher temperature applications, but the toxicity of Pb has resulted in the

development of various heat-resistant, Pb-free bonding methods such as: high-melting-point Pb-free solders [3–6], transient liquid phase bonding [7–9] and nanoparticle bonding [10–27]. The use of Cu nanoparticle bonding is of particular interest due to the advantages offered by copper in terms of its low cost, relative abundance, low electrical resistivity, high thermal conductivity and greater durability against ion migration when compared to Ag. Furthermore, the high surface energy of nanoparticles means that they can be processed at much lower temperatures than the melting point of the component material [28]. In a previous study, we developed a novel strategy for synthesizing Cu nanoparticles capped with fatty acids and amines, which allowed a high bonding strength to be achieved even at a low processing temperatures (573 K) [19]. However, this method generally requires an additional high-pressure process to ensure strong bonding, which only increases the cost and likelihood of defects associated with semiconductor device packaging. Subsequent research has revealed that a thin layer of Ni applied to the base materials allows for pressure-free bonding of Cu nanoparticles [23].

The strong interface that is formed when a Cu nanoparticle bonds to an Ag adhesive layer without additional pressure is the result of both the active self-diffusion of Ag atoms and an interaction between the Ag layer and Cu nanoparticles [27]. This interaction is considered to contribute to the final strength, because it produces rapid grain growth near the interface. Morisada et al. have also reported that mixing Ag nanoparticles with Cu nanoparticles

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further enhances the bonding strength [18]. Their analysis further revealed that there is no oxide phase at the interface between Cu and Ag, resulting in a nanoscale solid solution being formed. Furthermore, Ide et al. reported that Cu-to-Cu joints are produced by Ag nanoparticles, with no oxide layer being observed at the Ag/Cu interface [15]. However, the surface of Cu nanoparticles is usually covered with a surface oxide layer that can be preserved by organic molecules. Of the two species of copper oxide (CuO_x), Cu_2O is reported to be the more difficult to reduce by H_2 [29] and often exists on the surface of Cu nanoparticles [17,19]. It is therefore considered that the chemical state of Cu_2O on the surface of Cu nanoparticles is somehow altered when in contact with Ag.

In the case of Cu_2O on Ni, the valence of Cu is altered from monovalent to bivalent when it merges into the oxide layer on the Ni surface, and this reaction makes Cu easier to reduce [30]. However, a similar mechanism is unlikely in the case of Cu_2O on Ag because the most stable valence in this case is monovalent Ag_2O , which is much more thermodynamically reductive than CuO . This study therefore looks at the surface properties of a thin CuO_x layer deposited on Ag in order to clarify the process by which an interface is formed between Cu nanoparticles and an Ag adhesive layer. The effects of varying the annealing temperature and atmosphere on the chemical state and surface morphology of the CuO_x layer are also discussed.

2. Materials and methods

The specimens used for this study were prepared using RF-magnetron sputtering in a 2×10^{-3} Torr Ar atmosphere to deposit a 100 nm-thick Ag film onto Si(100) wafer substrates coated with a 100 nm-thick layer of thermally oxidized SiO_2 . During this process, the input power to the Ag target disk of 76.2 mm ϕ was 100 W, giving a deposition rate of 18 nm/s. Once the Ag layer was applied, the samples were immediately removed from the sputtering chamber and placed in air so as to replicate surface conditions typical of the Cu nanoparticle bonding process. The samples were then reloaded into the sputtering chamber and a layer of CuO_x was deposited by RF-magnetron sputtering in a 2×10^{-3} Torr atmosphere of Ar containing 3 vol% of O_2 . An input power to the 76.2 mm ϕ Ag target of 100 W was again used, which produced a deposition rate of 4.8 nm/s. Finally, the samples were annealed in an inert (N_2) or reductive (N_2 -3 vol% H_2) atmosphere at atmospheric pressure for 10 min at a temperature between 523 and 623 K.

The chemical state of the surface of each sample was analyzed by X-ray photoelectron spectroscopy (XPS) with Mg $K\alpha$ (1253.6 eV) radiation using a VG ESCALAB Mk-II. The pass energy for this analysis was configured to 20 eV and the binding energy of the spectra was corrected using that of the Ag $3d_{5/2}$ peak (368.2 eV). The spectra were then analyzed using peak fitting software (XPSPeak 4.0). The surface morphology was observed by tapping mode atomic force microscopy (AFM) using a Digital Instruments Nanoscope Dimension 3100. The images obtained were processed and analyzed using image processing software for scanning probe microscopy (WSxM 4.0 [31]).

3. Results

3.1. Surface chemical state

Fig. 1 shows the XP spectra of the CuO_x in an as-deposited state on the Ag film. The Cu $2p_{3/2}$ spectrum shown in Fig. 1(a) could be fitted by two components expressed by the Voigt function, with the higher binding energy (934.3 eV) component being derived from hydroxide ($\text{Cu}(\text{OH})_2$) [32,33]. The binding energy of the main peak

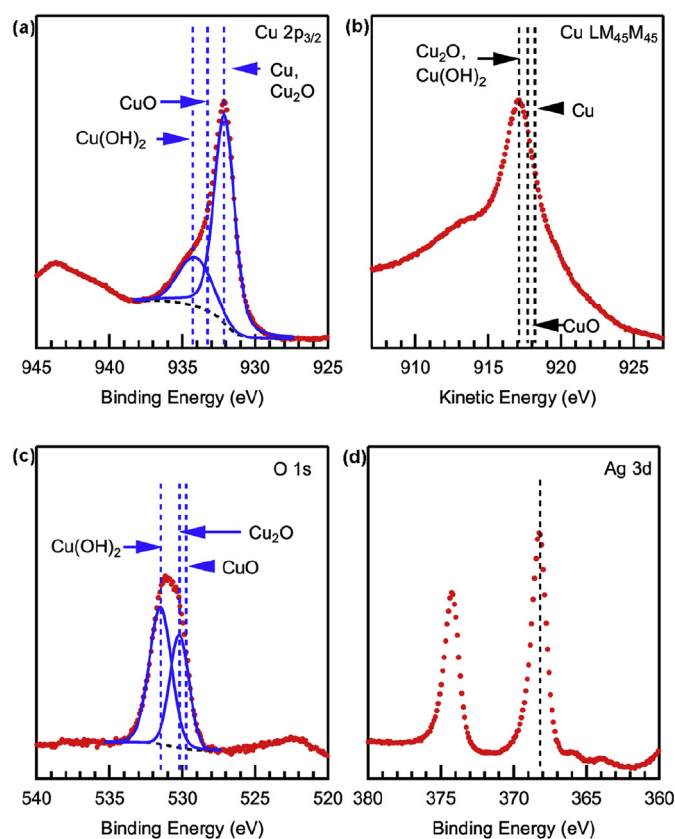


Fig. 1. XP spectra of as deposited CuO_x on Ag layer: (a) Cu $2p_{3/2}$, (b) Cu $\text{LM}_{45}\text{M}_{45}$ (Auger electron), (c) O 1s, (d) Ag 3d.

of the lower binding energy component was 932.3 eV, and the kinetic energy of the peak position of the Cu $\text{LM}_{45}\text{M}_{45}$ Auger electron spectrum in Fig. 1(b) was 917.1 eV. The major chemical state of Cu is therefore considered to be monovalent oxide (Cu_2O) based on its Auger parameter of 1849.4 eV [32–34]. The O 1s spectrum shown in Fig. 1(c) could also be fitted by two components, with a higher energy component explained by $\text{Cu}(\text{OH})_2$ and a lower energy component of Cu_2O , which is consistent with the Cu 2p spectrum. These results suggest that the chemical state of CuO_x on the Ag layer was a mixture of Cu_2O and $\text{Cu}(\text{OH})_2$. The Ag used as a substrate in this work was also detected, as shown in Fig. 1(d).

Figs. 2 and 3 show respectively the Cu $2p_{3/2}$ XPS spectra and Cu LMM Auger spectra of CuO_x on Ag after annealing. The peak energy and shape of the Cu $2p_{3/2}$ and Cu $\text{LM}_{45}\text{M}_{45}$ XPS spectra of the CuO_x layer annealed in an inert ambient barely changed following annealing in an inert atmosphere, as shown in Figs. 2(a) and 3(a), respectively. Contrary to this, it is evident in Fig. 2(b) that the relative peak intensity of Cu $2p_{3/2}$ decreased in CuO_x annealed in a reductive atmosphere even at the lowest annealing temperature used (523 K), and that no additional component was needed to obtain a fitting. This result indicates a decrease in the concentration of Cu at the surface and an absence of bivalent oxide (CuO) generation. Meanwhile, the binding energy of the peak exhibits a slight shift in the kinetic energy of the Cu $\text{LM}_{45}\text{M}_{45}$ Auger peak toward a higher energy, as shown in Fig. 3(b). This kinetic peak shift increased with annealing temperature to as much as 0.8 eV at 623 K, resulting in an Auger parameter of Cu (1850.2 eV) that lies between that of metallic Cu and Cu_2O . It is therefore considered that the chemical state of Cu in the sample annealed at 623 K is a mixture of metallic Cu and monovalent oxide (Cu_2O).

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