

Growing hydrophobicity on a smooth copper oxide thin film at room temperature and reversible wettability transition



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ABSTRACT

The thin CuO film is acquired by a quick dip of copper in H₂O₂ solutions at room temperature. The CuO film appears smooth and exhibits superhydrophilic nature. The composition change cannot be verified by X-ray photoelectron spectroscopy but can be manifested by the water contact angle. In the ambient condition, the thickness of the oxidized layer and the surface hydrophobicity grow gradually, while the chemical composition of the overall oxidized film remains essentially unchanged. In the vacuum, the growth rate of the hydrophobicity is significantly elevated, revealing deoxidation on the upmost surface. Our results indicate that growing hydrophobicity on the CuO film is spontaneous and the reversible wettability transition can be observed by H₂O₂ oxidation and vacuum deoxidation.

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For nanoscale integrated circuits manufacturing technologies, copper has become a primary focus for replacing aluminum as the internal connection metal owing to its higher electrical and thermal conductivity, higher melting temperature, and better resistance to electron migration features [1–3]. During the fabrication steps such as chemical mechanical planarization (CMP), large amounts of contaminations will leave on the wafer surface, such as abrasive particles, metal oxide residues, and organic residues that might affect the yield performance. Consequently, aqueous cleaning processes including post CMP clean and post etch clean have been employed to remove unwanted residues after contamination steps. The wet cleaning steps often involve soaking the wafer in an aqueous solution containing hydrogen peroxide (H₂O₂) such as the first step in RCA clean [4]. Due to the exposure to oxidant H₂O₂, a thin oxidized layer on the copper surface is formed and the relevant properties are altered. For example, the presence of copper oxide would cause the device high resistance and reliability issues.

It is known that copper has three different oxidation states: Cu⁽⁰⁾ (metallic copper), Cu^(I) (cuprous oxide, Cu₂O), and Cu^(II) (cupric oxide, CuO) and these oxidation states exhibit different wettability.

When exposed to air, a mixed layer of cuprous oxide, cupric oxide, cupric hydroxide (Cu(OH)₂), chemisorbed water, and carboxylate species was formed on the surface of the copper film [5–7]. The characterization of the copper surface layers is generally carried out by X-ray photoelectron spectroscopy (XPS) [5,8,9]. However, the sampling depth of XPS is known to be at least 50–100 Å and thus it is rather difficult to perform surface chemical analysis on the top layer of the surface by XPS. In addition, high-resolution XPS spectra are too comprehensive to distinguish the chemical compositions of the copper oxide layer accurately. For example, the Cu 2p_{3/2} binding energies and peak shapes of Cu₂O and Cu⁽⁰⁾ are essentially identical. Moreover, the binding energies of Cu₂O and Cu(OH)₂ are overlapped in Cu LMM transition.

The surface of metallic oxide generally exhibits the hydrophilic character because of the presence of hydroxyl groups M–OH. Such chemical groups on surfaces can undergo dissociation or interact with H⁺ and OH[−] ions from solutions. They can ionize to yield M–O[−] at high pH, or the lone pair on oxygen can hold a proton to yield M–OH₂⁺ at low pH [10]. Consequently, the surface of CuO shows hydrophilic feature and the CuO powders can be easily dispersed in water. On the contrary, the Cu₂O powders are very difficult to mingle with water and often float on the water surface by surface tension. Thus, it is believed that the surface of Cu₂O is somewhat hydrophobic [11].

The wetting behavior of a surface is generally characterized by the contact angle (CA), which depends on the chemical nature of the top layer and roughness of a solid surface. For a smooth,

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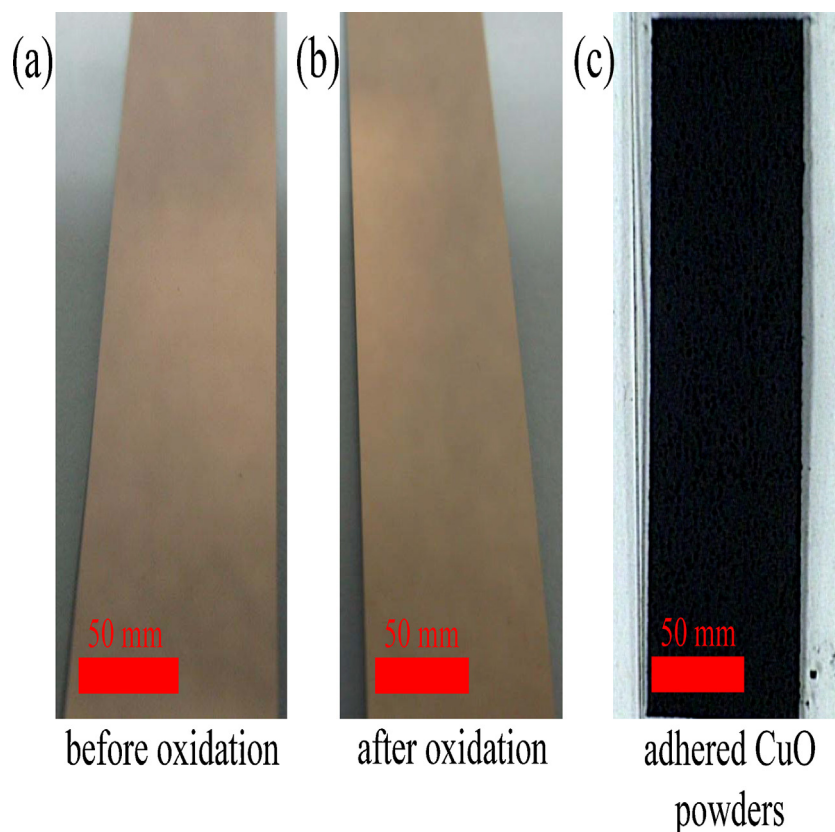


Fig. 1. Photos of CuO films. (a) Cu wafer before oxidation, (b) after oxidation by H_2O_2 , (c) micron-size CuO powders adhered on the conductive carbon tape.

heterogeneous surface composed of two types of homogeneous patches that have different solid–fluid interfacial tensions, the Cassie–Baxter model showed that the apparent contact angle (θ_a) is given by $\cos \theta_a = f_1 \cos \theta_1 + f_2 \cos \theta_2$, where f_i and θ_i represent the surface area fraction and the CA of patch i , respectively. When the wettability of the composition 1 is different from that of the composition 2, the contact angle measurement can be a simple yet direct approach to analyze the chemical composition of the top layer of the substrate. For example, if the apparent contact angle on a surface containing both CuO and Cu_2O is 70° , then the composition of hydrophilic CuO with its intrinsic CA 20° is 0.46 and that of hydrophobic Cu_2O with its intrinsic CA 100° is 0.54 [12,13].

Recently, thick (black) CuO films with nanowires [11] or microflowers/nanoneedle arrays [14–16] are able to show superhydrophobic ($\theta > 150^\circ$) characteristics. Moreover, subject to annealing in air at 350°C or oxygen plasma treatment, the transition from superhydrophobicity to superhydrophilicity ($\theta < 10^\circ$) can take place. An explanation based on the origin of interfacial tension has been proposed for hydrophobicity of CuO [11]. Since the environment around Cu atoms at the interface is distinctly different from that in the bulk, the CuO structure is thermodynamically stable in the bulk but not at the interface. By annealing at 100°C , partial deoxidation of the upmost layer of the CuO surface results in a hydrophobic Cu_2O -like structure, $2\text{CuO} \rightarrow \text{Cu}_2\text{O} + (1/2)\text{O}_2$. Because the proposed mechanism involves only one or two layers, the composition change cannot be verified by XPS but can be manifested by the water contact angle. In addition to the surface composition, the multiscale roughness is believed to play an essential role for increasing hydrophobicity. In this work, to alleviate the influences of roughness and temperature, the smooth CuO thin film is employed to explore the growing hydrophobicity behavior on the CuO surface.

The thin copper oxide film (less than 100 \AA) can be acquired at room temperature by the oxidation of the copper film. The latter was deposit on silicon wafer by physical vapor deposition (PVD) with a film stack of Cu 1 k \AA /Ta 250 \AA /TEOS 5 k \AA /Si substrate. The surface roughness of the copper film determined by AFM is less than 5 \AA . The copper coupon was immersed in 31% H_2O_2 solution for 10 s and then it was dried by nitrogen. Such a short time treatment in peroxide can yield a thin, superhydrophilic CuO layer with the contact angle (CA) less than 10° but avoid the formation of serious surface roughness. The CA is determined by sessile drop measurement, where a water droplet is placed on the surface of Cu coupon, and the value is obtained by the KRÜSS drop shape analysis system DSA10 Mk2 carried out in an air environment at room temperature.

According to ellipsometry (JA Woollam M-2000), the thickness of the oxide layer was about 60 \AA right after immersion. Fig. 1 demonstrates the photo of the thin film acquired by oxidation. Different from the typical black appearance of CuO, the reddish color of the underlying Cu substrate can be clearly seen, revealing the thin and smooth characteristics of the CuO layer. Fig. 2 shows the images of transmission electron microscopy (TEM, FEI Tecnai G2 F20) for the oxide layer, of which the thickness varies from 41 to 97 \AA . Moreover, the analysis by atomic force microscope (AFM) reveals that the roughness was 67.8 \AA . This result is consistent with that of TEM. Since the peroxide solution etches neither copper nor copper oxides according to our dissolution experiments of Cu and CuO powders, the roughness arises mainly from the inhomogeneous oxidation.

The composition of the oxidized thin film was characterized by XPS (Thermo Scientific Microlab 350 X-ray photoelectron spectroscopy system equipped with an Al $K\alpha$ source). Fig. 3 illustrates the Cu 2p XPS spectra of the freshly oxidized copper. The characteristic shake-up labeled with S peaks in 942 and 962 eV have proved

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