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# Investigation of the optical and electrical properties of ZnO/Cu/ZnO multilayers grown by atomic layer deposition

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ABSTRACT

Transparent conducting oxides (TCOs) with ZnO/Cu/ZnO sandwich structure grown by atomic layer deposition (ALD) were investigated. The optical and electrical properties of the ZnO/Cu/ZnO multilayers with different Cu thickness were studied by optical spectrometry and four-point probe measurements, respectively. The structural properties were investigated using x-ray diffraction and high resolution tansmission electron microscopy. The experiment results indicated that the thickness of copper has a significant influence on the photoelectrical properties of films. A average transmittance of over 65% at visual wavelength and low resistivity of ~$3.05 \times 10^{-4}\ \Omega\cdot$cm were obtained when the thickness of Cu was 14 nm. The obtained results inspire us that ALD method is one of candidates for preparing high quality TCO films with high transmittance and low resistivity.



## 1. Introduction

Transparent conducting oxide (TCO) films exhibit good electrical conductivity as well as high optical transparency in visible and near-infrared spectral regions [1]. These properties make TCO films useful for extensive applications including solar cells, organic light emitting devices, thin film transistors, photovoltaic cells, electrochromic devices, and flat-panel displays [2–8]. The conventional TCO film is indium tin oxide (ITO) which has excellent electrical (resistivity $\leq 10^{-3}\ \Omega\cdot$cm) and optical (light transmittance ≥80% in visible region) properties [9,10]. However, indium being a high-priced rare metal makes ITO so expensive to meet the growing demands of the rapidly expanding market [11]. Recently, zinc oxide (ZnO) based films have attracted much attention because of its outstanding properties such as inexpensive, stable in hydrogen plasma, and wide bandgap (~3.37 eV) [12–16]. Unfortunately, the doped ZnO films are limited in their conductivity by ionized impurity scattering [17]. It was then suggested to improving the performance of TCOs by inserting a thin metal layer between ZnO films to form ZnO/metal/ZnO sandwich structure [18–20]. For example, the intermediate noble metals provide high density of free electrons and effective path for their conduction. This kind of sandwich structure can greatly increase the conductivity of the TCO films. As a matter of fact, a lot of studies have demonstrated that these ZnO/metal/ZnO films exhibit favorable optoelectrical characteristics, which are expected to take the place of the current commercial TCO material ITO [21–26].

In the ZnO/metal/ZnO sandwich structure, the most commonly used metals are gold (Au), silver (Ag), aluminum (Al) and copper (Cu) due to their low resistivities [27,28]. However, the metal Ag is high-priced and prone to oxidation, which makes it imperfect in practical application. Another kind of metal Al is more sensitive to oxygen. Accordingly, the metal Cu becomes one of potential candidates for its lower price and better oxidation resistance relative to the metal Ag. In recent years, ZnO/Cu/ZnO films have been extensively studied to obtain low resistivity and high transmittance. It has been reported that the sheet resistance can be decreased by increasing the metal thickness [29]. However, this causes a

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decrease in the transmittance since photons are strongly absorbed by the high density of charge carriers [20]. The excellent conductivity and high optical transparency are mutually exclusive properties. In other words, it is a considerable challenge in the film growth to obtain a high quality TCO film with high conductivity and transparency.

As is well known, the optical and electrical properties of the thin metal layer in the ZnO/metal/ZnO structure depend significantly on its thickness and deposition conditions. The intermediate metal layer should be thin, uniform, and continuous. Thermal evaporating and magnetron sputtering are common methods to prepare the ZnO/Cu/ZnO sandwich films [30]. Atomic layer deposition (ALD) has recently emerged as an excellent film growth technique which is based on self-limiting surface reactions of two different precursor chemicals. High quality stacked films have been prepared by ALD with high conformality, uniformity and precise thickness control at atomic scale. However, ZnO/metal/ZnO sandwich thin films grown by ALD method has been rarely studied because its difficulty in growing high quality metal layers. In this work, ZnO/Cu/ZnO multilayer were grown by ALD method. The effect of Cu layer thickness on the structural, electrical, and optical properties of the ZnO/Cu/ZnO sandwich structure was investigated in details. The mechanisms behind the change of the conductivity and transparency in the multilayers were discussed in this study. A average transmittance of over 65% at visual wavelength and low resistivity of ~$3.05 \times 10^{-4}$ Ω·cm was obtained through process optimization.

## 2. Experimental

ZnO/Cu/ZnO multilayers, with different copper thickness, were sequentially deposited on Si(100) and quartz substrates in a BENEQ TFS200 ALD system. The samples grown on quartz were used to characterize the electrical properties and optical transmittance. Prior to deposition, the silicon wafers were cleaned by a standard RCA process followed by a de-ionized (DI) water rinse. Both the top and bottom ZnO thin films were grown with 150 cycles using diethylzinc ($Zn(C_2H_5)_2$), DEZn) and DI water as Zn and O precursors, respectively. The middle Cu layer were deposited by ALD using alternating exposures to Cu (II) hexafluoroacetylacetone [$Cu(hfac)_2$] and DEZn. Various ALD Cu cycles of 0, 15, 30, 45, 60, 75, 90, 105, 120 were used to grow nominal 0–16 nm thick Cu thin films. The growth temperature during ALD process was 200 °C. After the deposition, the structural properties and crystal orientation of these films were determined by X-ray diffraction (XRD, D8 Advance, Bruker, Germany) with Cu Kα radiation (40 kV, 40 mA, λ = 1.54056 Å) from 20 to 65° at 2θ scale. Meanwhile, the high resolution tansmission electron microscopy (HRTEM, JEOL JEM2010) was employed to characterize the microstructure and morphology of Cu layer in the early growth stage. Electrical properties such as resistivity and sheet resistance were measured using four-point-probe method. Besides, the optical transmission spectra were obtained using a UV spectrophotometer (UV-3100) in a wavelength range of 200–800 nm at room temperature in air.

## 3. Results and discussion

The crystalline structures of different multilayers were determined by XRD measurements. Fig. 1 shows the XRD patterns of ZnO/Cu/ZnO multilayers on quartz with different Cu thickness. All the films are polycrystalline with a ZnO hexagonal wurtzite type. As can be seen, three XRD characteristic peaks of ZnO in hexagonal phase (100), (002), and (101) were detected. The pure ZnO film exhibits a preferred orientation of (100) at 2θ = 31.7°. When an ultrathin Cu layer was inserted into ZnO thin films, the ZnO (002) peak gradually becomes dominant and the (100) peak turns to be

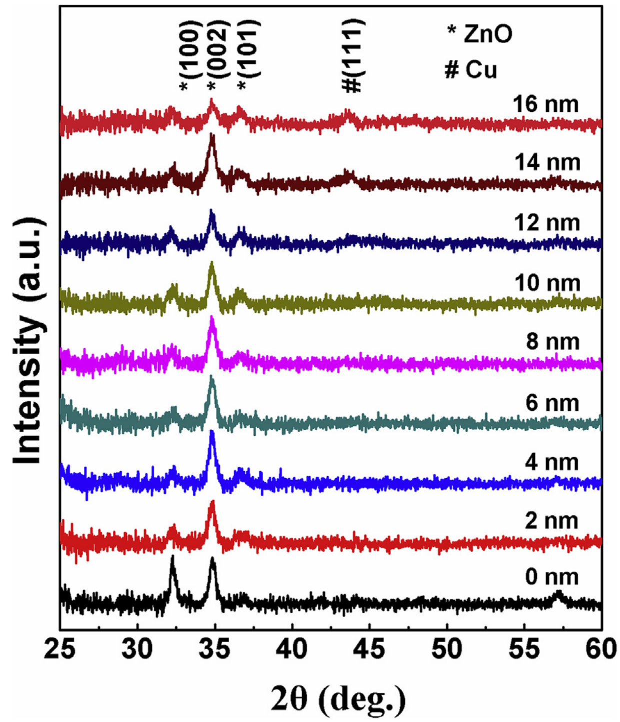


**Fig. 1.** XRD patters of ZnO/Cu/ZnO films with various Cu layer thickness.

weaker. It is well known that the (002) plane of ZnO consists of alternate planes of $Zn^{2+}$ and $O^{2-}$ and thus is charged positively or negatively, depending on surface termination. On the other hand, the (100) plane is a charge neutral surface consisting of alternate rows of $Zn^{2+}$ and $O^{2-}$ ions on the surface. The layer-by-layer growth during ALD will cause the Cu ions to disturb the charge neutrality of the (100) plane, thereby affecting its surface energy and causing its preferential growth [31]. In addition, no peaks related with crystalline Cu or Cu oxides are observed in these films when the thickness of Cu layer is thinner than 12 nm.

To obtain the profile the ultra thin Cu layer in the ZnO films, the cross-section view of the ZnO/Cu/ZnO film with 4 nm Cu layer is shown in Fig. 2 (a). To examine well the microstructure of the ZnO/Cu/ZnO layers, a high resolution TEM image is also shown in Fig. 2(b). ZnO grains appear separated into two regions and a Cu layer is located at the interfaces between the ZnO regions, the Cu layer is in the form of poorly connected islands and there are lots of voids intersperse among the well-isolated Cu nanoparticles. With the increase of the thickness, the continuity and uniformity of the Cu layer is improved. A peak belong to Cu (111) is observed for the film with the Cu thickness of 12 nm. The intensity of the peak increases with the increase of the Cu thickness. These results indicate that the preferential growth is strongly affected by the variation of the Cu thickness.

Fig. 3 shows the variation in resistivity and sheet resistance of the prepared ZnO/Cu/ZnO samples as a function of the thickness of the Cu layer. The resistivity and sheet resistance of the as-deposited ZnO films are 54 Ωcm and $1.07 \times 10^3$Ω/sq., respectively. When Cu layer inserted in the ZnO film, the resistivity of the ZnO/Cu/ZnO structure decreases drastically from 54 Ω·cm for pure ZnO film to $2.06 \times 10^{-4}$ $\Omega \cdot cm$ for the film with 16 nm thick Cu layer. On the other hand, the sheet resistance also decreases from $1.07 \times 10^3$ Ω/sq. to 31 Ω/sq. Besides, it can be seen from Fig. 3 that the resistivity curve shows two regions with different slopes. In the region of Cu thickness less than 12 nm, a rapid drop of resistivity is