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Sol-gel-derived ZnO/Cu/ZnO multilayer thin films and their optical and electrical properties

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ABSTRACT

Sol-gel preparation of transparent conducting ZnO/Cu/ZnO multilayer thin films has been investigated. CuO thin films were deposited on glass substrates via a dip-coating method. The CuO thin films were further subjected to reductive annealing in hydrogen to form highly conductive Cu thin films with sheet resistances as low as 10 Ω/□. ZnO/Cu/ZnO multilayers were successfully prepared in a similar way by reducing ZnO/CuO/ZnO. The sheet resistance of the ZnO/Cu/ZnO multilayer thin films is about 10 kΩ/□, which is much higher than that of the pure Cu thin films. The formation of large discrete Cu crystallites in the multilayers explains the poor electrical conductivity of the sol-gel-derived ZnO/Cu/ZnO multilayers.

1. Introduction

Flexible thin films of transparent conducting oxide (TCO) are among the most important components in developing various optoelectronic devices including solar cells, touch screens, liquid crystal displays, and organic light emitting diodes [1–3]. Recently, thin metal films sandwiched between two oxide films, i.e., oxide/metal/oxide (O/M/O) multilayers, have been studied to develop a transparent composite electrode with the desired electrical conductivity [4–10]. Although metals have high reflectivity, very thin films (<15 nm) show moderate transmittance in the visible region and the dielectric layers can suppress the reflection from the metal layer in the visible region and produce a selective transparent effect. These advantages render a higher figure of merit of O/M/O multilayers than that of a traditional single-layer TCO film [11].

Fabrication of O/M/O multilayer thin films mainly relies on expensive and inefficient high-vacuum physical vapor deposition techniques such as sputtering [12–15], thermal evaporation [16–18], and electron-beam evaporation with ion-beam-assisted deposition [19,20]. Alternative solution processes have been endeavored due to their low cost and facile film deposition. For example, solution-processed WO_3 has been achieved in the WO_3/Ag/WO_3 multilayers by Jeon et al., despite the fact that the thin Ag layer is thermally evaporated [7]. In this work, we report the preparation of ZnO/Cu/ZnO multilayer thin films by all solution process of sol-gel method. The optical and electrical properties of the ZnO/Cu/ZnO multilayers have been systematically investigated.

2. Experimental procedures

The preparation of ZnO/Cu/ZnO multilayer thin films is shown in Scheme 1. ZnO/CuO/ZnO multilayers were prepared by sol-gel method, which were subsequently subjected to reductive annealing to form ZnO/Cu/ZnO. The preparation details of the precursor sol for ZnO can be found elsewhere [21]. For the preparation of 0.2 M precursor sol for CuO, 0.02 mol of copper acetate monohydrate was dissolved in 0.1 L of absolute ethanol in a 250 mL conical flask. After vigorously stirring for 30 min, diethanolamine (DEA) was slowly added while stirring. The molar ratio of DEA/Cu^{2+} was fixed at 1. The solution became bluish and homogeneous after stirring for about 20 min. This solution was continually stirred overnight before final use for thin film coating.

Multilayer thin films were prepared on glass substrates via a dip-coating method. The cleaned substrates were dipped in the sol and then drawn upward at a constant rate of 1.0 mm/s, which produced a uniform film of the desired thickness. After each dip coating, the wet films were directly annealed at 400 °C in a furnace in air for 10 min. This process was repeated to increase the film thickness and/or fabricate the multilayers. After coating, thin film

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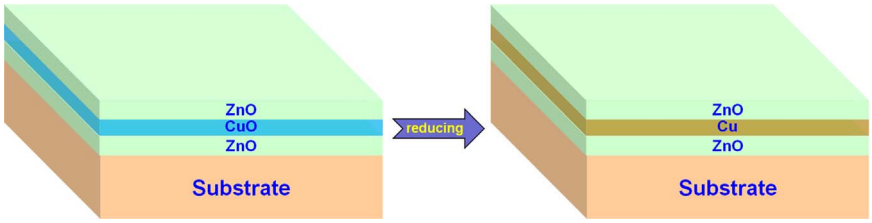

Scheme 1. Schematic illustration showing the preparation of ZnO/Cu/ZnO multilayer thin films by reductive hydrogen annealing of ZnO/CuO/ZnO.

samples were subjected to a two-step heat treatment, i.e., annealing first in air at 400 °C in a box furnace and followed by reductive annealing in H_2 at 400 °C in a tube furnace. The temperature-increasing rate and annealing duration for each treatment step were fixed at 5 °C/min and 1 h, respectively. The gas flow rate of H_2 for reductive annealing was 0.2 L/min. Cu thin films were prepared by reducing CuO, and ZnO/Cu/ZnO multilayers were prepared in a similar way.

Structural characterization of the thin film samples was carried out using an X-ray diffractometer (XRD, Bruker AXS D8 Advance) with Cu Kα radiation. Sample morphology was examined by a JEOL JSM-7001F field emission scanning electron microscope (SEM) operated at 15 kV. The sheet resistance and optical transmittance of the films were measured by a four-point probe method (RTS-9) and a double beam UV−vis spectrophotometer (Shimadzu UV2550), respectively.

3. Results and discussions

Fig. 1(a) shows the XRD patterns of the as-prepared CuO and Cu thin films. Rather weak diffraction peaks are observed for the CuO thin films, which could be readily identified as monoclinic CuO (JCPDS No. 48-1548). On the other hand, no apparent peaks appear in the XRD pattern of the Cu thin films, indicating the poor crystalline or amorphous nature of the as-prepared Cu thin films. Upon reduction in H_2 at atmospheric pressures, a direct transformation from CuO to Cu occurs [22]. This is consistent with our observation that no intermediate phase Cu_2O is formed. Fig. 1(b) plots the XRD patterns of the ZnO/Cu/ZnO multilayer thin films. Mixed reflections related to the hexagonal ZnO and cubic Cu are monitored, implying the successful preparation of the ZnO/Cu/ZnO multilayers by sol-gel technique.

Before studying the properties of the multilayer thin films, the optical and electrical properties of the CuO and Cu thin films are investigated. As illustrated in Fig. 2(a), the optical transmittance of two-layer CuO thin films decreases monotonically from 90% at 800 nm to about 20% at 360 nm. As the film thickness increases, the optical transmittance of CuO is further reduced. The average transmittance in the range of 400−800 nm for six-layer CuO thin films is ca. 35% (obtained by integrating the curve and dividing by Δx 400). CuO typically possesses a narrow band gap of 1.3–2.1 eV [23,24]. However, no obvious absorption edge could be identified in Fig. 2(a). This result is possibly due to the poor crystallinity of the CuO thin films as revealed by the XRD measurement (Fig. 1(a)). As CuO is hydrogen-reduced to Cu, significant change in the spectral shape is observed (Fig. 2(b)). Notably, a characteristic transmittance peak appears at 563 nm for all Cu thin films. This transmittance peak is enhanced as the Cu film thickens, leading to an increased transmittance of the films. The transmittance peak at 563 nm can be ascribed to the excitation of plasma resonances and is a characteristic property of the metallic Cu [25]. This abnormal increase in transmittance has been monitored in ZnO/Cu/ZnO multilayers deposited by sputtering, where the Cu-related transmittance peak is enhanced with increasing film thickness of Cu

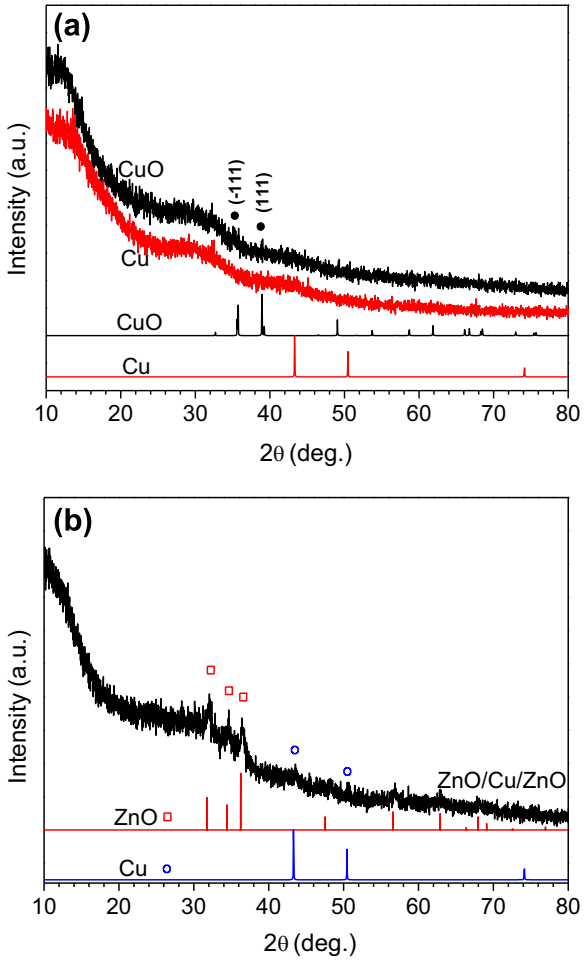

Fig. 1. XRD patterns of CuO, Cu (a) and ZnO/Cu/ZnO (b) thin films. Standard XRD patterns of CuO, Cu and ZnO have been included for comparison.

from 8 to 14 nm [26]. It is proposed that the island structure of the Cu film formed initially on ZnO can cause scattering of the incident light and thereby reduction of the transmittance [26].

Fig. 3 shows SEM images of the CuO and Cu thin films. As illustrated in Fig. 3(a), the CuO thin films consist of crystallites with 50–100 nm widths. Furthermore, CuO with poor crystallinity is observed between the crystallites. After reduction, the result is a semi-continuous Cu film, and gaps are visible between cluster-like Cu particles as shown in the magnified image (Fig. 3(b)). The film thickness of six-layer Cu thin films is about 90 nm as determined from the cross-sectional SEM observation (inset of Fig. 3(b)).

Sheet resistances of the CuO and Cu thin films as a function of film thickness are plotted in Fig. 4. Two-layer CuO thin films are nearly insulating (2000 MΩ/□), which decreases monotonically to 30 MΩ/□ as the number of the coating layer approaches six. No sheet resistance is recorded for two-layer Cu thin films, possibly due to the disconnected Cu particles in the films. Three-layer Cu thin films exhibit a sheet resistance of 8000 Ω/□, which is further