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Effect of Cu on the microstructure and electrical properties of Cu/ZnO thin films

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ABSTRACT

The effect of copper layer on the microstructural and electrical properties of copper (Cu)/zinc oxide (ZnO) thin film structure on glass substrate, prepared by radio frequency (RF) magnetron sputtering have been investigated. Cu/ZnO thin film structures possess good microstructural and electrical properties which are correlated with Cu thickness. The crystal structure, elemental analysis, surface topography and electrical properties of the films were systematically investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM) with an energy dispersive X-ray spectroscopy (EDS) setup, atomic force microscopy (AFM) and four point probe analysis, respectively. The result showed that Cu/ZnO films exhibit high crystallinity with a very sharp intense XRD peak corresponding to lattice reflection plane (002) of a hexagonal wurtzite structure. Cu/ZnO film with higher copper thickness shows uniform grains which are densely packed and have distinct grain boundary. Cu/ZnO film with optimum copper thickness showed the lowest resistivity of 1.53×10^{-3} Ω-cm and sheet resistance of 5.06×10^{2} Ω/sq.

1. Introduction

Zinc oxide is an n-type semiconductor with a wide direct band-gap of ~3.37 eV and a large exciton binding energy of 60 meV [1–3]. Doped ZnO has received considerable attention due to its improved performance in electrical conductivity and optical transmittance in the visible region [4–6]. It has been widely used in optoelectronic applications such as flat panel displays, solar cells, light-emitting diodes, LCDs, and various other devices. As is well known, doping suitable elements in ZnO film offers an effective method to engineer their electrical and optical properties. Recently, many elements such as Al [7–9], Mg [10,11], Ga [12–15], S [16], Ag [17], Ti [18] and Cu [19] have been doped or alloyed into ZnO film and good properties have been obtained. Among the various types of doped ZnO thin films Cu has many physical and chemical properties that are similar to those of Zn. Cu doping has been reported to be able to change the electrical, optical and microstructure properties of ZnO thin films [20–22]. The catalytic effect of copper on the micro structural, electrical properties has been extensively reported in many works [23,24]. The incorporation of Cu can also change the resistive switching properties of ZnO films [25]. Therefore, the amount of copper is one of the key factors affecting the quality of the Cu/ZnO film. It is necessary to study the effects of copper in order to develop Cu/ZnO film with high quality and good performance.

In this article pure ZnO and Cu/ZnO thin films were deposited by radio frequency (RF) magnetron sputtering onto glass substrate. The catalytic effect of copper on the structural and electrical properties of Cu/ZnO thin film were investigated systematically by scanning electron microscopy (SEM) with an energy dispersive X-ray spectroscopy (EDS) setup, X-ray diffraction (XRD), atomic force microscopy (AFM) and four point probe analysis. In this investigation we discussed the influence of copper on the structural and electrical properties of Cu/ZnO thin films.

2. Experimental details

Cu/ZnO multilayer films were deposited on glass substrate (Corning 7059) by radio frequency magnetron sputtering using a sputtering target of Cu metal (99.99% purity) and ZnO powder (99.99% purity, Aldrich). The depositions of the film were carried out in a high vacuum chamber at room temperature. Before putting into the deposition chamber, the substrate glass slides were first washed with soap solution to remove any visible impurities. Then they were rinsed with distilled water. Organic impurities present in the substrate were removed by keeping the slides in freshly prepared chromic acid for 20 min. The slides were again rinsed with distilled water and were then cleaned by isopropyl alcohol. Cleaned glass slides were placed in the substrate holder parallel to the target. The distance between substrate and target was fixed at 5 cm. Before the deposition procedure to start the base pressure of the chamber was set approximately at 8×10^{-5} Pa. There was no break in vacuum at any stage during the preparation of the film. The copper buffer layer was deposited first with different concentration by controlling the sputtering time, and then a thin layer of ZnO was sputtered above it on a cleaned glass slide. The Cu and ZnO were sputtered at 1.5 Pa argon pressure with an RF power of 150 W. Bare ZnO films were also prepared under identical condition for comparison of properties. In this work the thickness of the copper buffer layer was changed by varying the exposure time like 5 min, 10 min, and 15 min and the thickness of the ZnO layer was kept constant by confining the exposure time to 30 min.

The crystalline structure and crystallographic orientation of all the films were characterized by X-ray diffraction by PANalytical 3 kW X'pert PRO X-ray diffractometer with λ of 1.54060 Å. The elemental constitutions and surface morphology of the

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films were analyzed by using a Hitachi SU6600 Variable Pressure Field Emission Scanning Electron Microscope (FESEM) with an EDS setup. EDS analysis involves the generation of an X-ray spectrum from the entire scan area of the SEM. Surface topography of the deposited films at nanometric scale was monitored Park XE-100 atomic force microscopy (AFM). The electrical resistivity and sheet resistance were measured using a Keithley 2400 four point probe data acquisition system.

3. Result and discussion

3.1. Elemental analysis

In order to confirm the presence of Cu in sputtered Cu/ZnO thin film, the EDS spectra of samples were recorded. Fig. 1 shows the EDS spectra of Cu/ZnO thin films deposited at different Cu thickness. In EDS spectra each element has characteristic peak positions corresponding to the possible transitions in its electron shell. The presence of copper, for example, is indicated by two K peaks at about 8.0 and 8.9 keV and a L peak at 0.85 eV. The atomic percentage of each element in the Cu/ZnO films is also shown in the Fig. 1. The weight percentage of copper sputtered for 5 min is 2.6%, 10 min is 4.4% and 15 min is 5.7%. The accuracy of EDS depends largely on the similarity of the standards and the specimen. For quantitative analysis, accuracy approaching ±1% (relative) is attainable [26] for major elements. From the EDS analysis, it is found that the concentration of O is greater than that of Zn and the concentration of Zn is lowering with respect to the Cu layer thickness. This lowering of Zn as compared to O shows the incorporation of Cu at the Zn sites. Similar type of observation was reported in ZnO/As thin films [27]. The EDS spectrum contains small amount of Au which was coated for SEM analysis, No other traces of impurity elements were distinguished in the spectra confirming the purity of thin film samples.

3.2. Microstructural analysis

XRD measurements were used to investigate the effect of Cu on the crystallinity and phase composition of Cu/ZnO thin films. Fig. 2 shows the XRD patterns of pure ZnO and Cu/ZnO thin film with different Cu thickness. All the films exhibit high crystallinity with a very sharp intense XRD peak corresponding to lattice reflection plane (002) of a hexagonal wurtzite structure [JCPDS Ref. Code 00-005-0664]. The presence of a single high intense XRD peak is an indication of crystalline nature of ZnO in the films. All the XRD patterns of the Cu/ZnO multilayered thin films show a polycrystalline nature. In the case of Cu/ZnO multilayered thin films, the peak at (111) plane due to Cu and (002) plane due to ZnO. The intensity of diffraction peak from buffer layer increases with buffer layer thickness [28], but the increase of Cu peak (111) intensity is not linear with Cu buffer layer thickness. It is evident from the EDS analysis that, as the Cu sputtering time increases the Cu concentration also increases. The diffraction peak (002) of ZnO is observed at 34.53°. It is clear from the Fig. 2 that the (002) diffraction peak of Cu/ZnO films is shifted to larger angle as compared to ZnO film. The shift increases with increasing Cu thickness suggesting a decrease in lattice parameter as a function of Cu layer thickness [29]. We observed a shift of 0.39° between Cu/ZnO and ZnO. Cu can assume a valency of +1 or +2 in the Cu/ZnO film. So the Cu^{+}, Cu^{2+} can substitute Zn^{2+} in ZnO matrix. As Cu^{2+} ions substitute Zn^{2+} ions at their lattice sites, resulted in the shift of (002) diffraction peak to larger angle. The shift to larger angle is due to the smaller radius of Cu^{2+} ions (0.072 nm) than the Zn^{2+} (0.074 nm) ions [30]. Similar observations are reported in ZnO:Cu films [31–33]. The average size of the crystalline grains in the films is estimated using the following Debye–Scherrer equation [34]

$$D_{hkl} = \frac{0.9\lambda}{\beta_{hkl}\cos(\theta_{hkl})} \quad (1)$$

Where λ is the X-ray wavelength, β_{hkl} is the full width at half maximum (FWHM) in radian of the main peak in the X-ray diffraction pattern and θ_{hkl} is the Bragg diffraction angle. The calculated values of average grain size for different film are in the range 28 nm to 53 nm listed in Table 1. The presence of Cu buffer layer induces change in the FWHM of the ZnO (002) diffraction peak.

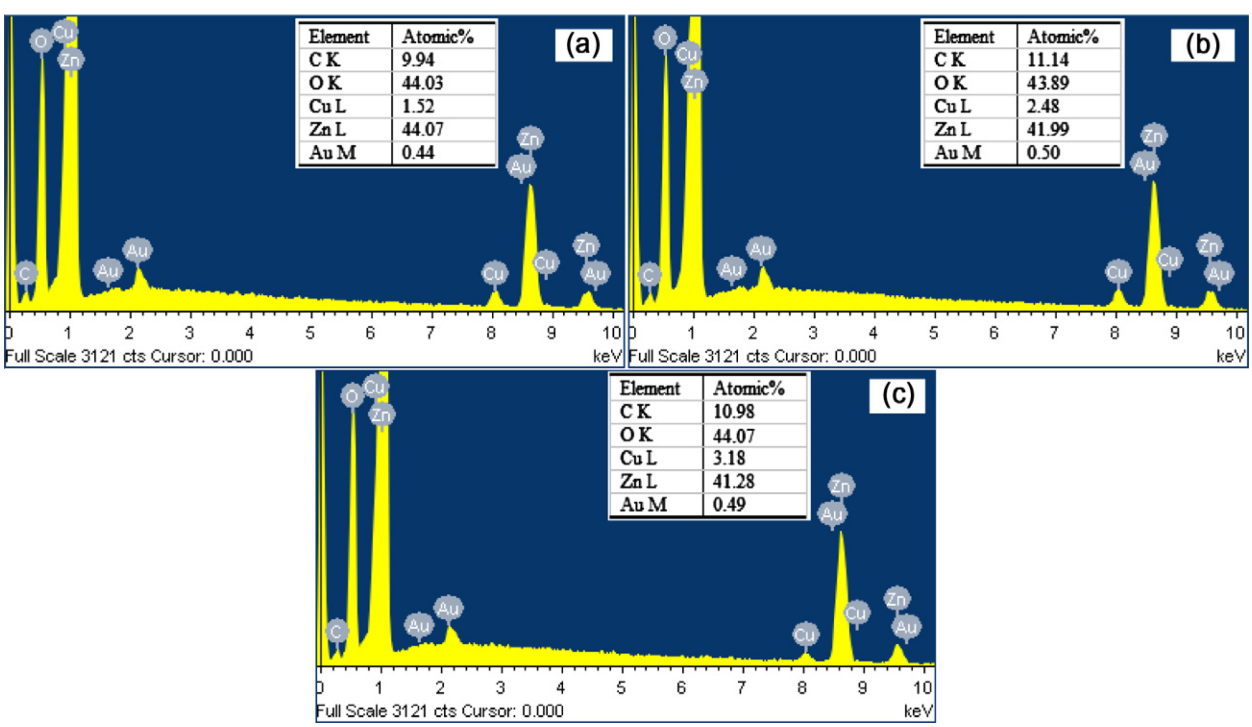

Fig. 1. EDS spectra of Cu/ZnO thin films deposited at different Cu thickness (a) Cu(5 min)/ZnO, (b) Cu(10 min)/ZnO and (c) Cu(15 min)/ZnO.