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Enhanced photoluminescence properties of Cu-doped ZnO thin films deposited by simultaneous RF and DC magnetron sputtering

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ABSTRACT

Copper (Cu)-doped ZnO thin films were grown on unheated glass substrates at various doping concentrations of Cu (0, 5.1, 6.2 and 7.5 at%) by simultaneous RF and DC magnetron sputtering technique. The influence of Cu atomic concentration on structural, electrical and optical properties of ZnO films was discussed in detail. Elemental composition from EDAX analysis confirmed the presence of Cu as a doping material in ZnO host lattice. XRD patterns show that the films were polycrystalline in nature with (002) as a predominant reflection of ZnO exhibited hexagonal wurtzite structure toward c-axis. From AFM analysis, films displayed needle-like shaped grains throughout the substrate surface. The electrical resistivity was found to be increased with increase of Cu content from 0 to 7.5 at%. Films have shown an average optical transmittance about 80% in the visible region and decreased optical band gap values from 3.2 to 3.01 eV with increasing of Cu doping content from 0 to 7.5 at% respectively. Furthermore, remarkably enhanced photoluminescence (PL) properties have been observed with prominent violet emission band corresponding to 3.06 eV (405 nm) in the visible region through the increase of Cu doping content in ZnO host lattice.

1. Introduction

Transparent semiconducting oxides are active materials for their massive applications in the field of optoelectronic devices. Among the transparent semiconducting oxide materials, zinc oxide (ZnO) with space group of $P6_3mc$ (186) received a considerable attention for device applications based on its intrinsic properties such as non-toxicity, wide direct band gap energy of 3.37 eV, exciton binding energy (60 meV) higher than room temperature thermal energy (26 meV) and excellent chemical and thermal stability. Owing to these desirable features in ZnO, it has been widely used as an active material for potential applications in luminescence, UV light emitting diodes, solar cells and photodetectors [1–4]. Physical properties of pure ZnO films can be significantly enhanced by doping of some active transition metals. In the past, a wide variety of transition metals have been used as dopants in ZnO, such as Mo [5], Ni [6], Co [7], Ti [8], Cu [9] and V [10] using several deposition techniques at desired doping concentrations. Although various deposition methods were carried out to produce doped ZnO, the dopant concentration effect on ZnO host lattice is still not clear and challenging. Among the high variety of transition metal to be used as dopants in ZnO, copper (Cu) has great interest due to Cu behaves like a fascinating luminescence activator modifies the luminescence behavior of ZnO through creating a localized impurity levels in ZnO host lattice [11]. Additionally, Cu in its Cu^{2+} ionic state (0.072 nm) has similar ionic radius compared to Zn^{2+} (0.074 nm) and the similarities in their electronic shell structure allows Cu^{2+} ions substitution easily into the ZnO host lattice. So far, numerous attempts have been performed to fabricate the Cu-doped ZnO films for specific applications in the field of optoelectronics through various deposition techniques, such as spray pyrolysis [9,12], RF sputtering [13–16], DC sputtering [17], simultaneous RF and DC magnetron sputtering [18], low-temperature aqueous solution route [19], pulsed laser deposition [20] and co-reactive magnetron sputtering [21]. However, among these, we focused on simultaneous RF and DC magnetron sputtering technique which enables here for better adhesion, tunable dopant concentration and controllability of structural and optical properties by independently doping of dopant element into host lattice.

In the present work, we report the results of Cu-doped ZnO films by co-sputtering process that designates here simultaneous RF and DC magnetron sputtering of ZnO and Cu respectively. It was found that enhancement of the violet emission photoluminescence (PL) with increasing of Cu doping concentration in ZnO host lattice. Moreover, the physical properties of the deposited films will have a dependence on deposition technique and process parameters, such as oxygen partial pressure prevailed in

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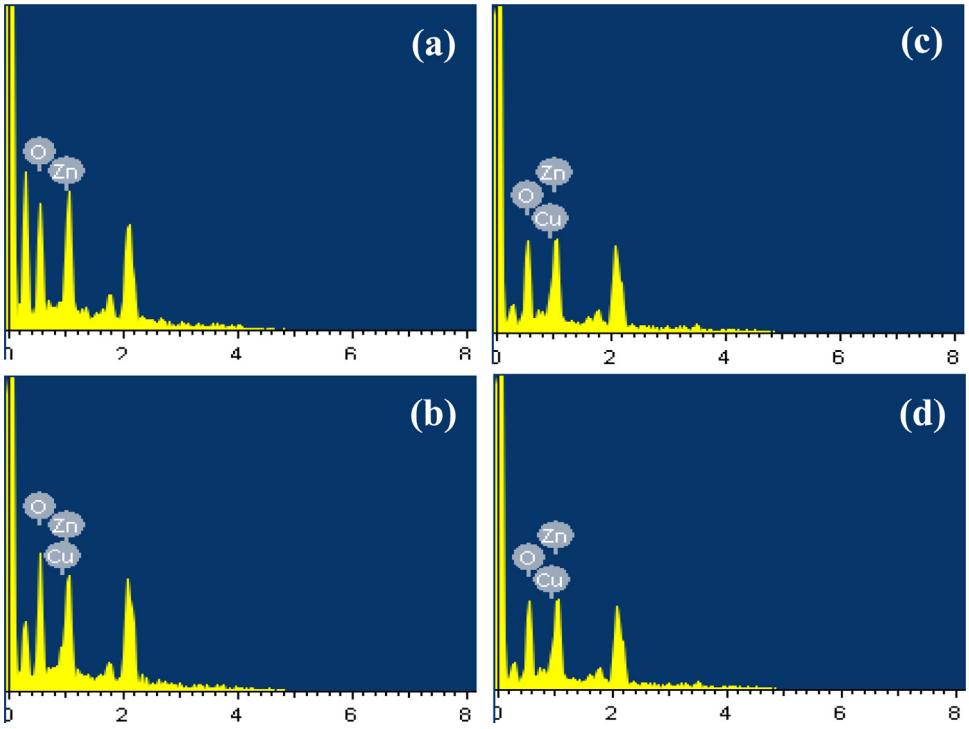

Fig. 1. EDAX spectra of Cu-doped ZnO films formed at: (a) Cu 0 at% (b) Cu 5.1 at% (c) Cu 6.2 at% and (d) Cu 7.5 at%.

the chamber, working pressure, substrate temperature and target to substrate distance, dopant concentration, sputter power and substrate bias voltage. Among these several factors, we focused on the variation of Cu dopant concentration in ZnO host lattice using simultaneous RF and DC magnetron sputtering technique.

2. Experimental

Cu-doped ZnO thin films for various doping concentrations of Cu (0, 5.1, 6.2 and 7.5 at%) have been deposited on glass substrates using simultaneous RF and DC magnetron sputtering technique. ZnO (99.999% purity, 2″ dia. and 7 mm thick) and Cu (99.99% purity, 2″ dia. and 7 mm thick) were employed as source materials. All the RF depositions were performed at a fixed RF sputter power of 150 W to the ZnO target using 13.56 MHz RF generator. In order to produce Cu-doped ZnO samples having different Cu concentration (ranging from 0 to 7.5 at%), the DC sputter power was varied from 0 to 8 W (0 W, 4 W, 6 W and 8 W). All the sputter depositions were performed at room temperature. The glass substrates were ultrasonically cleaned in acetone and distilled water for 10 min, then blown with purified nitrogen gas and finally dried on the hot plate at 100 °C for 5 min before insert into the deposition chamber. The rotating substrate holder was fixed to a distance of 15 cm from the sputter targets. Argon as a sputtering gas introduced into the sputter chamber at a flow rate of 30 sccm through fine mass flow controller. The base pressure in sputter chamber evacuated to 6.6×10^{-4} Pa using rotary and turbo molecular pump combination and the working pressure was set as 2.6 Pa under pure argon ambient for the duration of 40 min. Prior to film deposition, the pre-sputtering process was carried out for 10 min in argon atmosphere in order to remove other contaminants present on the target surface. Detailed deposition conditions for the preparation of Cu-doped ZnO films are tabulated in Table 1.

Table 1
Deposition conditions maintained for the growth of Cu-doped ZnO thin films.

Sputter targets	ZnO (99.999% purity, 2″ dia. and 7 mm thick), Cu (99.99% purity, 2″ dia. and 7 mm thick)
Target-to-substrate distance	15 cm
Base pressure	6.6×10^{-4} Pa
Working pressure	2.6 Pa
Deposition temperature	Room temperature
Deposition time	40 min
Sputter power (ZnO)	150 W
(Cu)	0, 4, 6 and 8 W
Film thickness	60, 110, 140 and 330 nm

Various characterization techniques have been performed to study the influence of Cu doping on ZnO films. Thicknesses of the deposited films were measured by using a surface profiler (Tencor, Alpha-Step 500). The chemical composition of the Cu-doped ZnO films was determined by energy dispersive X-ray analysis (EDAX) attached to the field emission scanning electron microscope (FESEM, HITACHI, S-4800). Structural characterization studies have been performed by X-ray diffractometer (XRD, X'Pert Pro MPD, PANalytical) with monochromatic CuK_{α} radiation ($\lambda = 1.5406$ Å) as X-ray source. The surface microstructures were obtained by atomic force microscopy (AFM, Digital instruments, Veeko). The electrical resistivity was measured with standard four probe technique. Optical transmission spectra of the films were recorded over a specific wavelength range from 300 to 850 nm using UV–vis spectrophotometer (UV–vis, HITACHI, U-3900). Whereas, room temperature photoluminescence (PL) measurements were carried out using IK Series He-Cd Laser attached to the Dongwoo Optron Co. monochromator (Model DM 501) at an excitation wavelength of 325 nm.

3. Results and discussion

3.1. Elemental analysis

The Cu atomic concentration present in the Cu-doped ZnO films has been identified by EDAX analysis attached to the field