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The growth of ZnO:Ga:Cu as new TCO film of advanced electrical, optical and structural quality

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A B S T R A C T

Because of having similarities in many physical as well as chemical properties to those of Zn, Cu has been strategically used as an effective dopant e.g., Al, Ga, F, etc., to change the optical, electrical and the micro-structural properties of ZnO thin films for obtaining its favorable opto-electronic performance as a transparent conducting oxide suitable for devices. Present study demonstrates the growth of transparent conducting ZnO:Ga:Cu thin films, by low power RF magnetron sputtering at a low substrate temperature (100 °C). Highly crystalline ZnO:Ga:Cu film with preferred *c*-axis orientation has been obtained demonstrating a high magnitude of transmission ~85% in the visible range and a high electrical conductivity ~40 S cm^{-1}, facilitated by large crystallite size (~29 nm), introducing reduced grain boundary scattering. XPS O 1S spectrum reveals the presence of a significant fraction of oxygen atoms effectively increasing the optical transparency. Incorporation of Ga and Cu ions into the ZnO matrix promotes violation of the local translational symmetry as suggested by the relaxation of Raman selection rules for the network, evident by the presence of strong (${B_1}^{high}$–${B_1}^{low}$) modes which are typically Raman inactive. The consequences of Cu doping has been compared with identically prepared ZnO and ZnO:Ga films.

1. Introduction

The ever-increasing demand of transparent and conducting oxide (TCO) thin films for a variety of applications e.g., in light emitting diodes (LEDs), flat panel displays, photovoltaics, and architectural windows, has inspired for pursuing research on numerous materials of the category. Wurtzite-type ZnO is an interesting material because of its wide band gap, high melting point and elevated exciton binding energy. ZnO thin films have received substantial attention for its prospective opto-electronic applications in the UV region [1–5]. Having high electrical conductivity and good visible transmittance together, superior to those of several transparent conducting oxide (TCO) e.g., SnO_2 [6–8], ITO [9,10] and other oxides [11,12], the ZnO films are enormously useful in the fabrication of devices like solar cells [13,14], particularly being highly stable within H_2 plasma and non-hazardous in nature [15,16]. Various elements e.g., Al, Ga, F, etc have been used as suitable dopants of ZnO films [17–19]. Among many other elements, compared to Cu, Ag is expensive while Al is more sensitive to oxygen. Cu has many properties similar to those of Zn which could be strategically used to change the optical, electrical and the micro-structural properties of ZnO thin films for obtaining its favorable opto-electronic performance [20–23]. Cu, being a group Ib element can have a valency of either +1 or +2 depending on its specific chemical configuration, for example in the composite materials like Cu_2O and CuO, respectively. Being in the same Ib group, the radii of Cu^+(~98 pm) and Cu^{2+}(~80 pm) ions are analogous to that of Zn^{2+} ion (~74 pm) [24]. It is likely that Cu atoms can restore either interstitial or substitutional Zn atoms from the ZnO lattice [25,26]. It has been reported that an energy level of the Cu^{2+} atoms exist < 0.2 eV below the conduction band edge when Cu atom is substituted at the Zn site [27,28]. Further Cu doping has been reported to introduce an acceptor (Cu^+) level in ZnO above its valence band [29,30].

A variety of growth techniques are involved in the development of ZnO films, such as chemical vapour deposition (CVD) [31], vapour phase epitaxy (VPE) [32], pulsed laser deposition (PLD) [33], electro-deposition [34], etc. Among all these radio frequency magnetron sputtering provides a number of different advantages. It can maintain excellent uniformity of growth over large area, good adhesion, moderate deposition rate and high chemical purity of ZnO [35,36]. In addition, reasonably good material properties are obtainable at sufficiently low substrate temperatures which are needful for manufacturing of the devices and for successful integration in industrial applications.

The development of ZnO:Ga:Cu films with simultaneous low

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resistivity and high transmittance in the visible range has been studied by using magnetron sputtering at low RF power. A systematic investigation has been made as an effect of changing the growth temperature on the optical, electrical and micro-structural properties of ZnO:Ga:Cu thin films, supported by the chemical state of zinc, oxygen and copper. The consequences of Cu doping has been compared with identically prepared low-temperature (100 °C) grown ZnO and ZnO:Ga films. Ga and Cu-doping promoted marginally for band gap widening, while Cu-doping of the ZnO:Ga films further enhanced the electrical conductivity, simultaneously facilitating the superior TCO activity of the ZnO films, compatible for device application.

2. Experimental

Cu doped ZnO:Ga films were grown by RF magnetron sputtering by using a 2% Ga doped high purity ZnO target of 3 in. in diameter partially covered by two high purity 5 mm wide Cu strips placed perpendicularly across the centre, and using Ar (~3.3 sccm) as the sputtering gas. The RF power and the gas pressure were kept fixed at 50 W and 20 mTorr, respectively whereas the substrate temperature (T_S) was varied from 100 to 300 °C. A base vacuum of ~9×10^{-7} Torr was attained in the sputtering chamber before the deposition of ZnO:Ga:Cu films on Corning® Eagle2000™ glass substrates placed on a heated holder rotated at 10 rpm for maintaining a good homogeneity and uniformity. A typical thickness of ~400 ± 50 nm was maintained for the samples, as estimated by Dektak 6 M profilometer.

The optical transmission data was obtained by a double-beam spectrophotometer (Hitachi 330). The X-ray diffraction analysis was carried out by a Bragg diffraction setup (Seifert 3000 P) with Cu-Kα X-ray radiation (λ ~1.5418 Å) source. The surface morphology of the films was studied by atomic force microscope (Veeco di CP-II). Four-probe method was used to measure the room-temperature electrical conductivity. Raman spectra of the samples were taken by 514 nm excitation wavelength with a power density of ~2 mW cm^{-2} from an air-cooled Ar^+ laser source of a Renishaw inVia Raman Microscope. The X-ray photoelectron spectra were obtained from the XPS instrument (Omicron Nano Technology 0571), using a focused Al-Kα X-ray source (1486.8 eV).

3. Results

The optical transmission of the films increased systematically at higher substrate temperature (T_S), as evident in Fig. 1(a). In all cases a convincingly high transmission ~80–95% was attained in the visible to NIR range, at around 550–1900 nm. Increasing transmission at higher T_S resulted from increased oxidation of Cu within the ZnO:Ga:Cu network. ZnO being a direct band gap semiconductor, the optical band gap (E_g) of the films was calculated from the very standard Tauc plot. It was identified as the energy where the extrapolation of the linear portion of $(\alpha{\cdot}E)^2$ vs E plot intersects the energy axis, α being the absorption coefficient of the material. E_g was estimated to 3.47 eV at T_S=100 °C. With increase in T_S, E_g gradually reduced to 3.39 eV at 300 °C. The comparison of optical band gap of the ZnO:Ga films without Cu and with the inclusion of Cu at different substrate temperature, has been shown in Table 1, from similar data of Tauc plot on identically grown films obtained by our earlier studies [37]. It has been identified that the optical band gap (E_g) increases with the decrease in substrate temperature in both cases, with and without Cu inclusion. It may be noted that Cu inclusion enhances the optical band gap at each temperature; however, the widening in E_g arising due to the lowering in deposition temperature of the ZnO films reduces in case of inclusion of Cu, as a dopant into the network.

Urbach tail is the absorption edge at which the fundamental absorption increases exponentially [38] according to: $\alpha(E) = \alpha_0 exp(E/E_0)$, where α_0 is a constant. The Urbach energy (E_0) indicates the width of localized states within the optical band gap. In

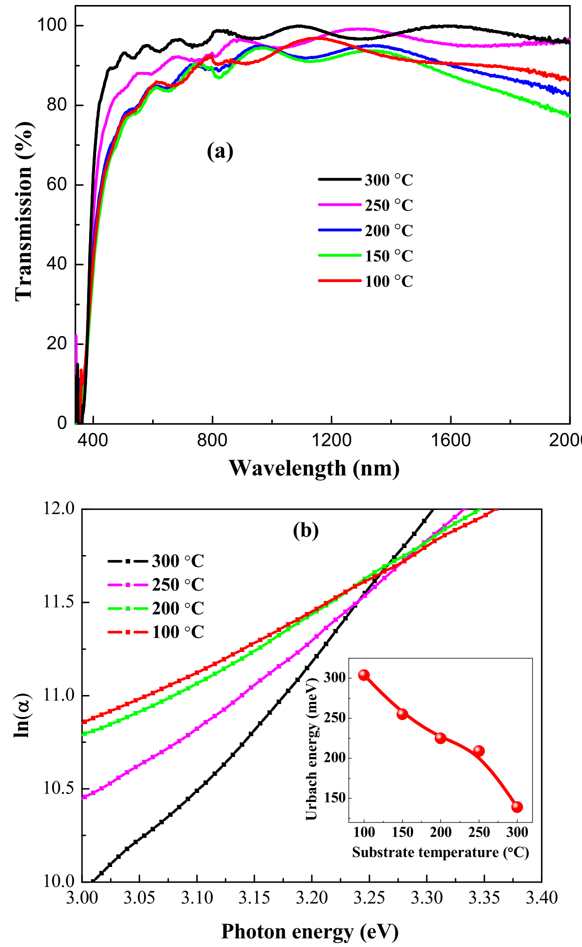

Fig. 1. (a) Optical transmission spectra of the ZnO:Ga:Cu films grown at different T_S. (b) ln (α) versus E plots of ZnO:Ga:Cu films. Inset presents the change of Urbach energy with the applied substrate temperatures.

Table 1
Comparison of the optical band gap of ZnO:Ga films without Cu and with the inclusion of Cu.

T_S (°C)	100	200	300
E_g (eV) (Without Cu)	3.45	3.42	3.3
E_g (eV) (With Cu)	3.47	3.45	3.39

order understand about the defects in the network, ln(α) vs E has been plotted for all the samples just below the band edge ($E < E_g$) and E_0 has been assessed from the inverse of the slope obtained from the linear section of respective ln(α) vs E curves. At T_S=100 °C, the corresponding E_0 is convincingly high, ~304 meV and that decreases sharply with increase in T_S and attains the value 139 meV with further increase in T_S to 300 °C as shown at the inset of Fig. 1(b).

Fig. 2(a) shows the nature of variations in the X-ray diffraction spectra for the ZnO:Ga:Cu films with substrate temperature. The traces of a number of peaks have been identified at 2θ=31.7°, 34.4°, 36.2° and 62.9° which are associated to the < 100 > , < 002 > , < 101 > and < 103 > crystallographic planes of ZnO, respectively; however, < 002 > and < 101 > are the two most significant peaks available. The films appear to be dominantly *c*-axis oriented both at lower and higher growth temperature. Fig. 2(b) shows the comparison between two ZnO:Ga samples prepared without and with the addition of Cu, grown at identical conditions at T_S=100 °C.

The intensity ratio $I_{<002>}/I_{<101>}$ of ZnO:Ga:Cu films grown at different T_S is presented in Fig. 3. Evaluation on similar data for ZnO:Ga films grown at T_S=100 °C demonstrates that inclusion of Cu