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Short Communication

FABRICATION AND CHARACTERIZATION OF Al DOPED ZnO THIN FILM BY PVD TECHNIQUE

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ABSTRACT

ZnO thin films were deposited onto quartz substrates at room temperature by dc sputtering of a ZnO target. Al was thermally evaporated onto the ZnO thin films in an evaporation chamber, with the thickness of the Al layer being monitored using a thickness monitor. To achieve Al doping, the Al coated ZnO thin films were then rapid thermal annealed at 773K for 1 minute. This helped in incorporating Al within the ZnO lattice. The amount of Al doping in the ZnO thin films was verified by energy dispersive x-ray analysis (EDAX). Scanning electron microscopy (SEM) of the Al doped ZnO (AZO) samples indicated excellent surface coverage with compact smooth film and x-ray diffraction (XRD) confirmed the hexagonal crystal growth with wurtzite structure. The optical transmittance of the thin films showed appreciable transparency of the thin films in the visible range. The optical constant and the thickness of the thin films were determined by a modified Kramers Kronig approach. Dark conductivity measurement indicated decrease in resistivity of the sample with the increase in Al doping, while the conductivity increased.

Keywords: ZnO, Al, Doping, Optical, Conductivity

1. INTRODUCTION

Al doped ZnO is an important transparent conducting oxide (TCO) material [1-3] with potential for application in transparent electronic, optoelectronic and sensor devices [4-6]. ZnO being a wide direct band gap material, having high excitonic binding energy of 60 meV, appreciable piezoelectric property, resistance to harsh environment, it is versatile enough by itself, to demand a lot of attention from researchers worldwide [7, 8]. However, with Al doping in ZnO, several properties including the conductivity of the ZnO samples can be modulated effectively according to requirement. Hence, AZO provides an attractive proposition for the TCO community to study in details [9-11]. Especially since Al is so easily available at relatively nominal cost but to put AZO into device application one has to have in-depth knowledge regarding the change in optical and electrical properties of ZnO caused by Al doping. In this communication, we report on the deposition of Al doped ZnO (AZO) by physical vapor deposition technique. Here, the ZnO layer is first deposited by dc sputtering technique onto quartz substrates. Then pre-determined thickness of Al was evaporated onto the ZnO thin film and was subject to rapid thermal annealing to dope the ZnO thin film with 1%, 3% and 4% of Al.

The Al doping in the ZnO thin films was verified by energy dispersive x-ray analysis (EDAX). The microstructure of the AZO thin films were examined by SEM and XRD, while the optical characteristics of the AZO films were studied by obtaining the transmittance trace at room temperature in the wavelength range of λ =300-800 nm using an UV-VIS-NIR spectrophotometer. From the transmittance spectra, the band gap, optical constants- including the refractive index (n), extinction coefficient (k) and the thickness of the thin films (d) were determined by a modified Kramers-Kronig model (KK model) [12]. The dark conductivity of the AZO thin films was also measured at room temperature to observe the change in conductivity of the films due to incorporation of Al.

2. MATERIAL AND METHODS

ZnO thin films were deposited onto quartz substrate at room temperature, by dc sputtering technique. Before the deposition, the sputtering chamber was evacuated to a base pressure of 10^{-6} mbar by rotary pump and oil diffusion pump combination. The target used was pure ZnO (Sigma Aldrich, 99.99% pure). The target to substrate distance was kept at 5 cm. Deposition was carried out in Ar plasma at a system pressure of 0.025

mbar. Before starting the actual deposition, the target was pre-sputtered with a shutter located in between the target and the substrate. Deposition was carried out for 30 minutes, with sequential 05 minutes deposition time and 02 minutes break to keep the substrate temperature within limit. The shutter was used to control the deposition time. The substrate temperature could be monitored by a copper-constantan thermocouple attached to the substrate holder. For the Al doping in the ZnO thin film, a very thin layer of Al was deposited on top of the ZnO nanowire sample by thermal evaporation technique. Pre deposition, the system was evacuated to a base pressure ~ 10^{-6} mbar. A quartz crystal oscillator was used to monitor the Al film thickness and evaporation rate. To incorporate 1% (sample Z2), 3% (sample Z3) and 4% Al doping (sample Z4), three different layers with thicknesses of 5nm, 8nm and 14nm of Al were deposited, respectively. Then the samples were subjected to rapid thermal annealing (RTA) at 773K for 1 min. Optical studies were performed by measuring transmittance in the wavelength region λ=300-800 nm using a UV-VIS-NIR spectrophotometer at room temperature. The films were also characterized by x-ray diffraction (XRD) using Cu Kα line (0.154 nm). Scanning electron microscope images were also obtained to characterize the film microstructurally. Energy dispersive x-ray analysis (EDAX) characterization was employed to verify the Al doping in the ZnO thin films. Dark conductivity was measured by standard two-probe technique to study the change in conductivity of the Z1 (undoped ZnO thin film), Z2, Z3 and Z4 samples with the change in Al doping by using a voltage source and a Keithley picoammeter.

3. RESULTS AND DISCUSSION

Figure 1 shows the representative SEM micrograph of 3% Al doped ZnO (Z3) thin film. From the micrograph it is evident that there was excellent substrate coverage. The film was compact with well-formed grains. This was found to be true for all the three films Z2, Z3 and Z4 of 1%, 3% and 4% Al doping, respectively. All the films had thickness of about 160 nm. EDAX analysis was used to verify the presence of Al doping in ZnO matrix. EDAX analysis indicated 1%, 3% and 4% Al doping in the ZnO thin film for 5nm, 8nm and 14nm evaporated Al layer thickness, respectively.

The XRD (not shown here) of all the samples (Z2, Z3 and Z4) indicated formation of hexagonal-ZnO (h-ZnO) with wurtzite structure as was evident from the XRD peaks arising due to diffraction from the (100), (002) and (101) planes of h-ZnO with wurtzite structure (JCPDS card no. 05-0664). No peak for Al was noticed in our XRD trace. The optical transmittance spectra measured at room temperature in the wavelength range of 300-800 nm is shown in figure 2. The trace (a) corresponds to undoped ZnO sample (Z1). From the transmittance trace it is evident that all the films had appreciable transparency (transmittance greater than 50%) in the visible wavelength range of 400-800 nm. However, the transmittance decreased for the films with the increase in Al doping percentage (Z2, Z3 and Z4).

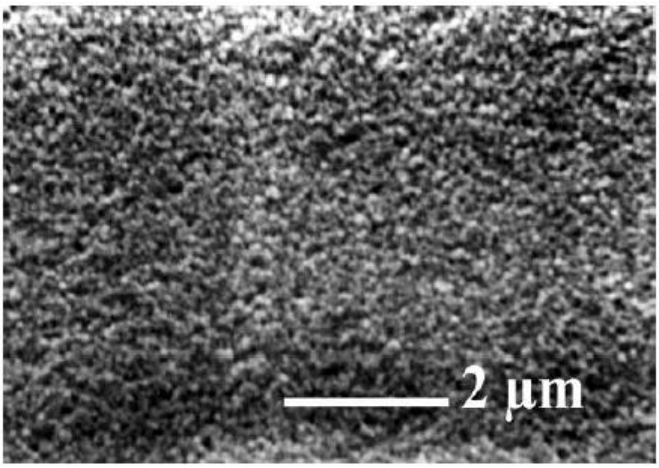

Fig. 1: SEM of representative AZO thin film

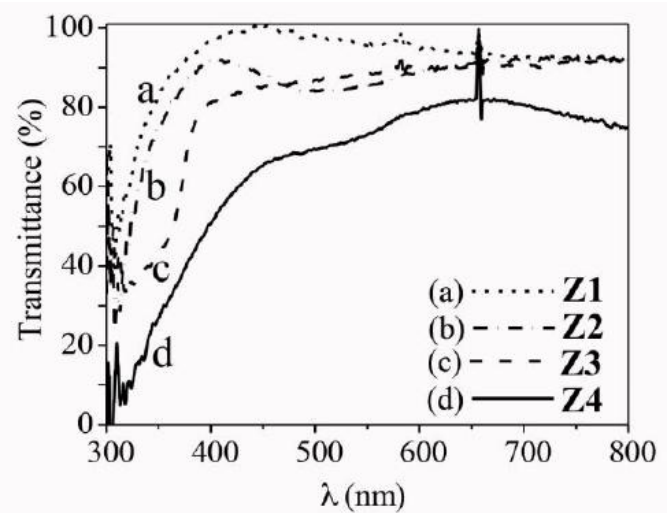

Fig. 2: Transmittance trace of undoped (Z1) and Al doped ZnO thin films (Z2, Z3, Z4)

From the transmittance trace, the bandgap (E_g) of the AZO samples could be calculated by obtaining the optical absorption coefficient α using the Beer's law. Then, α can be related to E_g as $\alpha h\nu = A (E_g - h\nu)^{1/m}$, where A = a

constant and m= 2 for direct transition and ½ for indirect transition. Hence plotting the $(\alpha h\nu)^2$ versus $h\nu$ and extrapolating the plot to $\alpha = 0$, one can calculate the bandgap of the material [13]. The bandgap for undoped ZnO thin film (Z1) was computed to be 3.25 eV, whereas Z2 (1 at % Al doped ZnO) was 3.32 eV, Z3 (3 at% Al doped ZnO) was 3.45 eV and Z4 (4 at% Al doped ZnO) was 3.57 eV, respectively. The increase in bandgap with the increase in Al doping % could be attributed to the Burstein-Moss shift [14]. The optical constants (n,k,d) were calculated for the undoped and Al doped ZnO thin films (Z1, Z2, Z3 and Z4) by a modified KK approach [12]. From the analysis, it was observed that both the n and k decreased with the increase in Al doping in ZnO thin film. Whereas the refractive index (n) was 2.24 for Z1 (undoped ZnO), it decreased to 2.18 for Z2 (1% Al doping), 2.13 for Z3 (3% Al doping) and 2.08 for Z4 (4% Al doping) at λ =400 nm. Similarly, the extinction coefficient (k) was 0.025 for Z1, 0.016 for Z2, 0.012 for Z3 and 0.009 for Z4 at λ =400 nm. The thickness (d) of the films was estimated to be 160 nm. The dark conductivity measured for the undoped and Al doped ZnO thin films by standard two-probe technique showed that the conductivity of the samples increased with the increase in Al concentration in the films. Expectedly, the resistivity of the AZO samples was found to decrease with the increase in Al doping in the ZnO thin films.

4. CONCLUSION

Undoped and Al doped ZnO thin films with Al doping of 1%, 3% and 4% were deposited by physical vapor deposition process. Initially, 160 nm thickness ZnO thin films were deposited by dc sputtering technique. Then, three different Al layers with thicknesses of 5nm, 8nm and 14nm of Al were deposited onto ZnO thin films by evaporation technique and the samples were rapid thermal annealed at 773K for 1 minute to achieve doping Al. SEM of the samples indicated thin films with excellent substrate coverage and compact, well-formed grains. EDAX analysis indicated doping percentage of 1% (sample Z2), 3% (sample Z3) and 4% (sample Z4) for 5nm, 8nm and 14nm evaporated Al layer thickness, respectively. XRD of the undoped (Z1) and Al doped (Z2, Z3 and Z4) samples indicated h-ZnO with wurtzite structure. No peaks for Al were observed. Optical transmission versus wavelength plot indicated that the transmittance decreased for the films with the increase in Al doping percentage. The bandgap calculated for the samples Z1 to Z4 indicated an increase in band gap from 3.25 eV for the Z1 (undoped ZnO) sample to 3.57 eV for the sample Z4 (4% Al doping). This change in bandgap was attributed to Burstein-Moss effect. Calculation of refractive index (n) and extinction coefficient (k) by a modified KK model indicated that both the n and k decreased with the increase in Al doping in ZnO thin film. The film thickness was determined to be 160 nm. The dark conductivity measurement of the samples Z1, Z2, Z3 and Z4 showed that the conductivity of the samples increased, whereas the resistivity decreased with the increase in Al doping in the ZnO thin films.

5. ACNOWLEDGEMENT

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