STUDYING THE STRUCTURE AND SOME PROPERTIES OF R.F. MAGNETRON SPUTTERED ZnO: Al FILMS

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Abstract: Structural, optical and electrical properties of Al-doped ZnO films, deposited by r.f. magnetron sputtering, have been investigated. The electrical and optical properties were found to depend on r.f. power and substrate temperature. The ZnO:Al films showed a resistivity in the range from 8.7×10^{-3} to 1.8×10^{-3} Ωcm at room temperature. The photoluminescence spectra at 11-300 K show emission bands related to neutral donor-bound exciton, donor-acceptor pairs and transitions from shallow donors to valence band.

1. Introduction

The application of zinc oxide films has increased for the last two decades due to their properties such as piezoelectricity, conductivity and optical absorption and emission [1-3]. These films have a better resistance against hydrogen and hydrogen plasma treatment, and do not degrade active solar cell materials owing to the interdiffusion of constituents as it occurs with indium tin oxide (ITO) or tin oxide (TO). Many efforts have been devoted to improve the electrical and optical properties of zinc oxide film. The electrical conductivity of zinc oxide films can be increased by doping with the group III elements. Doped ZnO films have been deposited by many techniques including chemical vapor deposition, magnetron sputtering, and electron beam evaporation. In this paper, we report the structural, electrical and optical properties of ZnO:Al films prepared by r. f. magnetron sputtering.

2. Experimental

The ZnO:Al films were prepared on glass substrate by r.f. magnetron sputtering. The target with a mixture of ZnO (99.9% purity) and Al2O3 (99.9% purity) was prepared by using conventional sintering process. The content of Al2O3 added to the used target was 3% in weight. The structural properties were determined with a Siemens D5005 X-ray diffractometer. Electrical resistivity was measured at room temperature using the standard four-probe. The optical transmittance measurements were performed with a UV-3001 spectrometer. Photoluminescence (PL) spectra were investigated by a spectrofluorometer FL3-22 Jobin-Yvon-Spex, using 450 W xenon lamp as an excitation source.

3. Results and discussion

The X-ray diffraction (XRD) patterns of the ZnO:Al films and the target are shown in Fig. 1. The X-ray diffraction shows only 002 peak indicating the strong preferred orientation, the c-axes of the grains are uniformly perpendicular to the substrate surface.

The energy dispersive X-ray spectroscopy (EDS) analysis shows that the films are composed of Zn, O and Al elements (Fig. 2).

The atomic force microscopy (AFM) observation indicates that all the films are very smooth and have similar morphology independent of the substrate temperature (Fig. 3)

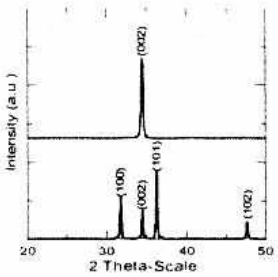

Fig.1. XRD patterns of ZnO: Al target and film grown on glass substrate

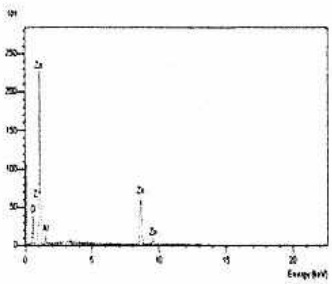

Fig.2. EDS spectrum of ZnO film

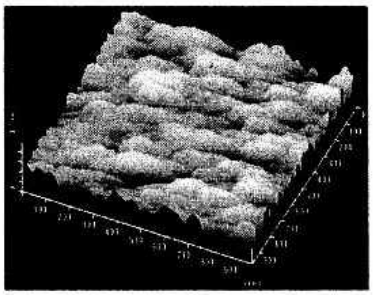

Fig.3. The AFM image of ZnO: Al film grown at 400°C

The resistivity of ZnO films shows very little dependence on temperature (Fig.4). It can be observed that the resistivity of ZnO: Al increases slightly with decreasing temperature. The weak temperature dependence of the resistivity confirms that the Al doped ZnO films are degenerate semiconductors.

The resistivities of the films depend on the composition of the target. Figure 5 gives the film resistivities as a function of Al_2O_3 contents in the target. For the Al-doped ZnO films, Al behaves as shallow level n-type dopant. Al atoms are incorporated in the samples substitutionally; creating more free electrons and making the samples become more conductive. However, when Al contents are more than the limit (here it is 3 wt. % for Al_2O_3), the excess Al atoms behaving as scattering centers in the films, reduce the mobility of charge carriers and, subsequently, increase the resistivity of the films.

Figure 6 gives the transmission spectra for three films which have transmission coefficient of over 80% in the wavelength range of 450-800 nm. The optical gaps were obtained by plotting $(\alpha h\nu)^2$ vs. $h\nu$ (α is the absorption coefficient and $h\nu$ is the photon energy) and extrapolating the straight-line portion of this plot to the energy axis. These plots yield band gaps of 3.50-3.60 eV.

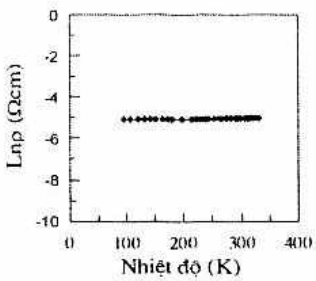

Fig.4. The plot of logarithm of the resistivity vs. temperature for ZnO: Al film

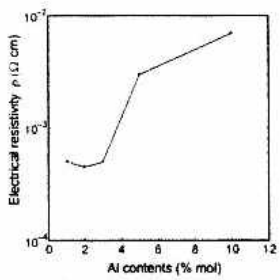

Fig.5. Electrical resistivities as a function of Al contents

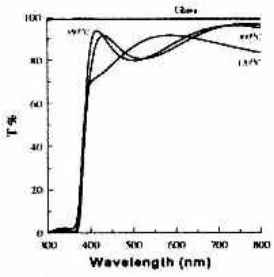

Fig.6. The optical transmission spectra for three highly conducting ZnO:Al films with different thicknesses

Figure 7 shows the dependence of the PL spectra of the ZnO:Al thin film, deposited on glass, on temperature in the range 11K – 300K with excitation wavelength 300nm. The photoluminescence spectrum of ZnO: Al at 11 K shows lines at 3.369, 3.315, 3.228 eV. It is

evident from the figure that the intensity of the sharp line observed at 3.369 eV is decreased rapidly and is shifted slightly to the low-energy side with increasing measuring temperature. At 100 K this line disappears, whereas the line at 3.315 eV is still maintained up to room temperature. This line is broadened and located at 3.26 eV at 300K. The wide line peaked at 3.228 eV is shifted to low-energy side with increasing temperature. At 100K this line is located at 3.046 eV, that is, the shift in energy is about 182 meV. Under such conditions a new line exhibits at 3.245 eV.

The investigation of the relationship between the integrated PL intensity vs. temperature shows that the temperature dependence of the intensity of the emission lines at 3.369 and 3.315 eV can be expressed by the equation: $I(T) = I0 / [1 + A \exp(- E / kBT)]$, where E is the activation energy of the thermal quenching process, kB is Boltzman constant, I0 is the emission intensity at 0 K and A is a constant. For the emission lines at 3.369 and 3.315 eV, E = 13.1 and 41.5 meV, respectively.

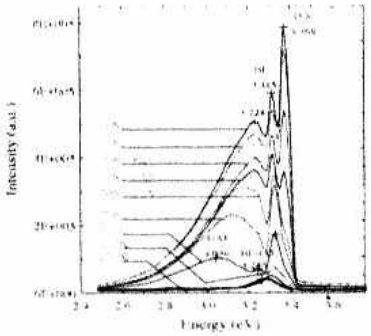

Fig.7. The PL of ZnO: Al films measured at temperature ranging from 11 K to 300K

The strong sharp line at 3.369 eV with linewidth of 20 meV probably corresponds to emission of a neutral donor-bound exciton (DoX). The value of 13.1 meV of the activation energy of the thermal quenching process for this line is close to the normal value of the binding energy of an exciton bound to a neutral donor. The line at 3.315 eV in our sample can not be interpreted as two-electron transition of exciton bound to neutral donor, because this line still remains at the temperatures, at which the bound exciton line disappears. The line at 3.315 eV can not be attributed to exciton bound to neutral acceptor because of the low binding energy for this complex. The excitons are thermally detached from these centers at low temperatures. The line at 3.315 eV with linewidth as narrow as the bound exciton line is not due to donor-acceptor pairs because in the last case, the transition energy strongly depends on the donor-acceptor distance and we should observe a broad emission line. In our opinion the line at 3.315 eV probably corresponds to recombination of a free carrier with a carrier bound on an impurity. In our case, it is possible that recombination of an electron bound on a donor with a free hole in valence band (BF). The line at 3.228 eV is due to donor-acceptor pairs (DAP). The line at 3.245 eV is assigned to a longitudinal optical (LO) phonon replica of BF emission, because their energy separation is found to be about 70 meV, which is close to the energy of the LO-phonon.

4. Conclusions

Good transparent conducting ZnO:Al films were prepared by r.f. magnetron sputtering. There is an optimum Al_2O_3 content with which the films have the highest conductivity. The photoluminescence spectra at 11-300K show emission bands related to the neutral donor-bound exciton, donor-acceptor pairs and transitions from shallow donors to valence band.

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