PREPARATION OF TRANSPARENT CONDUCTING *ZnO : Al* FILMS ON GLASS SUBSTRATES BY *r.f* MAGNETRON SPUTTERING

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Highly transparent conducting *Al*-doped *ZnO* films with good adherence and low resistivity have been prepared on glass substrates by *r.f* magnetron sputtering. Mechanically stable polycrystalline conductive *ZnO* : *Al* films had a preferred orientation with the (002) planes parallel to the substrate surface. The *ZnO* : *Al* films showed a resistivity in the range from 8.7×10^{-3} to $1.8 \times 10^{-3}\Omega$ cm, a carrier density in the range $(0.2 - 3.1) \times 10^{20} cm^{-3}$ and a Hall mobility between 7 and 17 $cm^2V^{-1}s^{-1}$. The average transmittance in the visible range exceeded 89 % for a $1.9\mu m$ thick film. The films showed a band-edge photoluminescence. The origin of the observed near-UV lines was identified in terms of bound exciton complexes, bound electron with free hole recombination and donor - acceptor pairs.

1. Introduction

Transparent conducting zinc oxide films have been extensively studied in recent years, because of their low material cost, relatively low deposition temperature and stability in hydrogen plasma compared to ITO and SnO_2 films [1]. These advantages are of considerable interest for solar energy conversion applications.

ZnO is a *n*-type wide bandage semiconductor with wurtzite crystal structure. Non-stoichiometric undoped zinc oxide thin films have usually shown a low resistively due to oxygen vacancies and zinc interstitials [2]. Hence, low resistivity films can be obtained by controlling these native defects. Nevertheless, many attempts have been made to reach low resistivity by doping with group-III elements such as aluminium [3], because it has been remarked that extrinsic donors due to the dopant atoms are more stable than the intrinsic donors due to the native defects. Comparing with undoped *ZnO*, *Al* - doped *ZnO* films have lower resistivity and better stability. A decrease in resistivity resulting from an increase in carrier concentration from 10^{20} to 10^{21} cm^{-3} was obtained as the impurity content doped into the *ZnO* films increased [4]. However, this increase in carrier concentration resulted in a decrease in mobility as well as optical transmittance in the near - IR range [5].

In this paper, the structural, optical and electrical properties of *ZnO* : *Al* films prepared by *r.f* magnetron sputtering have been investigated in detail, together with the effects of heat treatment in air and hydrogen.

2. Experiment

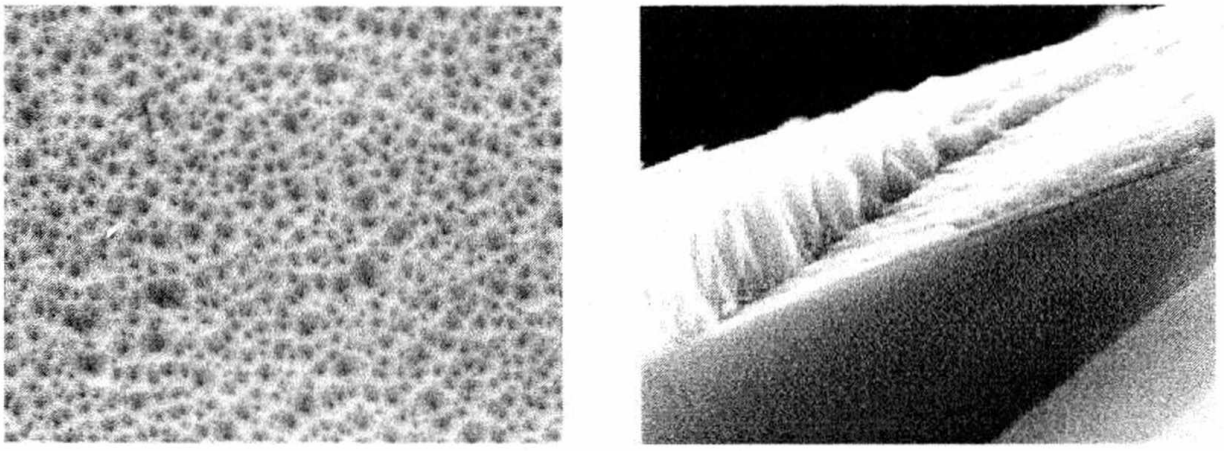
The films were deposited on glass substrates by sputtering a 75 mm diameter ZnO : Al target in a conventional $r.f$ magnetron sputtering system (Univex - 450 system of Leybold Coorp.) with 10^{-6} Torr basic pressure. A power supply operated at a crystal - controlled frequency of 13.56 MHz. The target with a mixture of ZnO (99.9 % purity) and Al_2O_3 (99.9 % purity) was employed as source material. The target was prepared by using conventional sintering process. The content of Al_2O_3 added to the used target was 2 % in weight. The distance between target and substrate was about 6 cm. The sputtering gas Ar with 99.9 % purity was controlled via a crystal controlled high frequency power source. A heater under the substrate table was used to change the temperature of the substrate for some samples.

Controlled parameters were varied systematically in order to obtain optimum quality films (low resistivity, high transmission and good adhesion to the substrates).

The following parameters were found to be suitable and were used in film preparation: the content of Al_2O_3 in the used target was $2wt.\%$, the input power was from 100 W to 360 W and the Ar pressure was 9×10^{-3} Torr. Under these conditions, the deposition rate was about $12nm\,\mathrm{min}^{-1}$.

The sheet resistivities were measured by a four - point probe instrument. The thickness of the films was measured using a α-step X30 surface - profile measured system. The Hall measurement was made at room temperature. The optical transmittance measurement was performed with a UV-3001 spectrophotometer. The structural properties were determined with a Siemens D5005 X-ray diffractometer, which used a CuK_α radiation. The growth morphologies were observed by using JSM 5410 LV scanning electron microscopy (SEM).

3. Results and discussion



a) *b)*

Fig. 1. SEM surface (a) and cross - section (b) micrographs of a ZnO:Al film on glass substrate at r.f power 350 W and argon pressure 8.8\times$10^{-3}$ Torr

X-ray diffraction (XRD) spectra and SEM micrographs indicate that the films grow strongly textured in columnar structure with the hexagonal c-axis perpendicular to the substrate surface. Typical SEM images are shown in Fig.1. When the columnar structure appeared, the dominant XRD peak was the (002) reflex at 34.4^0 (Fig. 2).

Fig. 1b shows the vertical cross-sectional view of the $ZnO : Al$ film of nearly $2\mu m$ thick on glass substrate. The columnar growth of the film is clearly seen from the figure; that is indicative of a strong c-axis orientation of the film. The SEM observation shows also that the films deposited at low $r.f$ powers exhibit a "toothed structure" on the top layer with fine vertical line patterns (Fig. 3). The compactness of the coating increases with the $r.f$ power (Fig. 1a). Composition of the films was analyzed along surface by energy dispersion spectrum (EDS) (Fig. 4). It is seen from the figure that oxygen, zinc and aluminium compositions in the films were rather alike distributed.

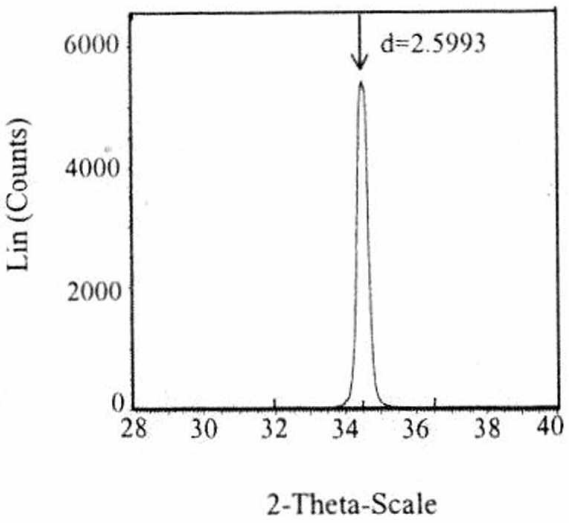


Fig. 2. X-ray diffraction pattern of a ZnO:Al film deposited on glass substrate

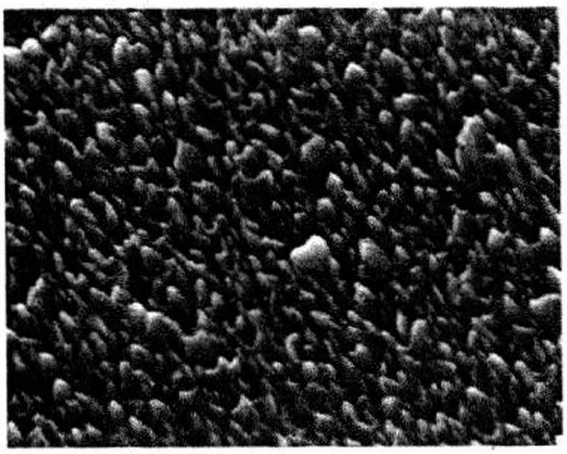


Fig. 3. SEM of ZnO:Al film deposited on glass substrate at r.f power 100 W and argon pressure 8.8×10^{-3} Torr

Electrical measurements showed that at room temperature the $ZnO : Al$ films showed a low resistivity value of $(1.8 - 8.7) \times 10^{-3} \Omega$cm, a carrier concentration of $(0.2 - 3.1) \times 10^{20}$ cm^{-3} and a Hall mobility of $(7 - 17) cm^2 V^{-1} s^{-1}$.

The transmittance spectrum of a $ZnO : Al$ film grown at $r.f$ power 350 W and argon pressure 8.8×10^{-3} Torr is presented in Fig. 5. As can be seen from the figure, average transmitance in the visible region is about 89 %.

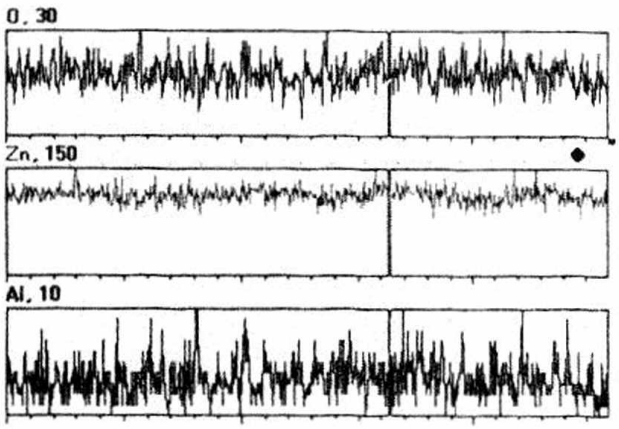


Fig. 4. Compositions of ZnO:Al films along surface

The optical absorption coefficient α can be described by the relation for parabolic bands:

$$\alpha h\nu = A(h\nu - E_g)^{1/N}, \tag{1}$$

where A is the constant, $h\nu$ is the photon energy, E_g is the band gap of the semiconductor. N depends on the type of the electron transition [6].

For direct allowed transitions to an empty parabolic conduction band N is to be set to 2. The energy band gap E_g was calculated by extrapolating the square of the absorption coefficient given in Eq.(1) versus the photon energy curve, as an insert in Fig. 5. The estimated energy band gap E_g was 3.60 eV.

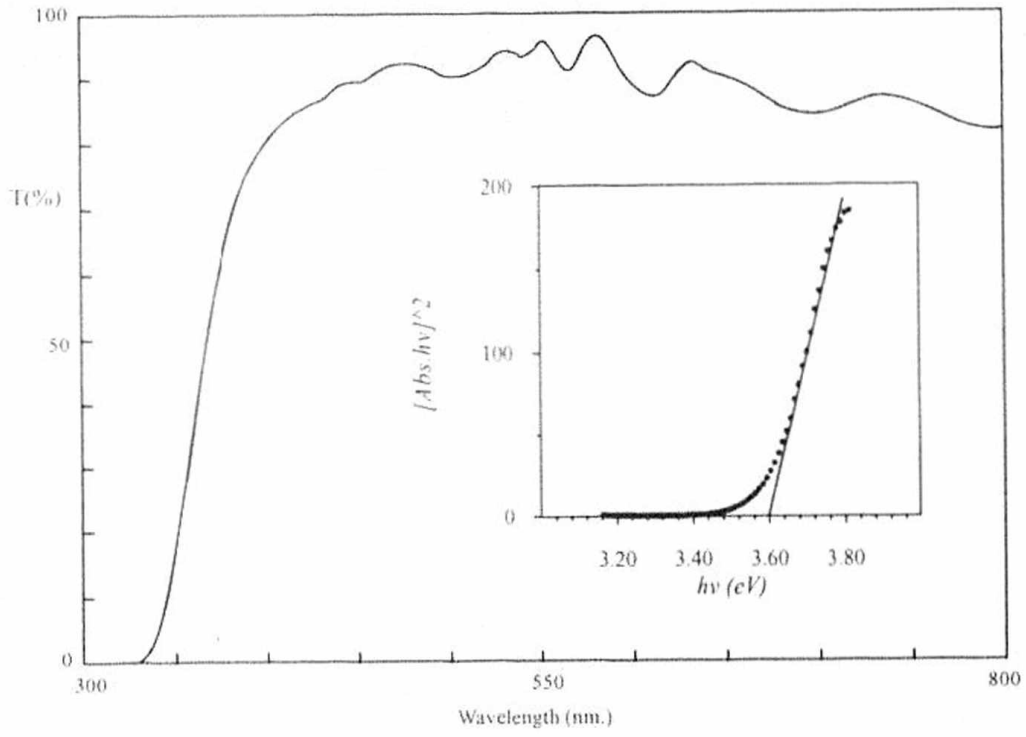


Fig. 5. Optical transmittance of a ZnO:Al film deposited on glass ubstrate at r.f power 350 W and argon pressure 8.8 x 10^{-3} Torr.

Photoluminescence (PL) spectra of $ZnO : Al$ films were measured in the temperature range from 11 K to room temperature with excitation wavelength 300 nm. Typical PL spectra at 11, 100, 270 K are shown in Fig. 6. The PL spectrum at 11 K exhibits three emission lines with maxima at 368 nm (3.368 eV), 374 nm (3.314 eV), and 384 nm (3.228 eV). As can be seen in the figure, the PL spectrum measured at 11 K is dominated by emission line at 368 nm (Fig. 6a).

The intensity of PL lines decreases and their relative intensity changes with increasing temperature. The intensity of the 368 nm line fast decreases and at 50 K it can not be observed, while the 374 nm line almost does not change in position until 200 K. Above 200 K the 374 nm line is broadened and slightly shifts to the long wavelength side and it is located at 379 nm (3.271 eV) at 270 K. In contrast to the 374 nm line, the little broad line peaked at 384 nm shifts to the long wavelength side with increasing temperature even from 50 K and it is located at 407 nm (3.046 eV) at 100 K, at the temperatures higher than 150 K this line will be extinct. Under such conditions a new emission line at 382 nm (3.245 eV) can be revealed (Fig. 6b). At 270 K, in the PL spectrum the only emission line located at 379 nm can be observed (Fig. 6c).

The 368 nm line can be assigned to neutral-donor-bound-exciton (D^0X) complexes; the 374 nm line is due to radiative recombination of electrons bound to donors and free

holes in valence band (BF). The energy separation between the 374 nm and 382 nm lines is 69 meV, which agrees well with the longitudinal optical phonon energy in *ZnO*. So, the 382 nm line is regarded as a phonon replica of the 374 nm line (BF-LO). The broad line at 407 nm can be interpreted as result of the donor - acceptor pairs (DAP) radiative transitions.

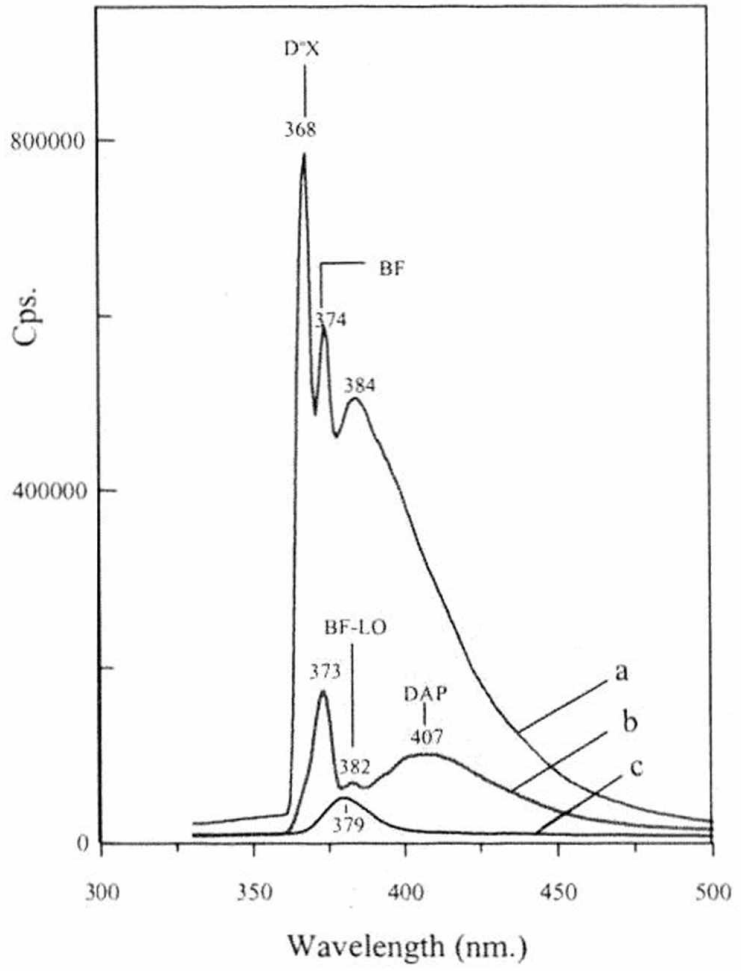


Fig. 6. PL spectra of ZnO:Al films with excitation wavelength 300 nm at different temperatures: a) 11 K, b) 100 K, c) 270 K

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TẠP CHÍ KHOA HỌC ĐHQGHN, Toán - Lý, T.XVIII, Số 2 - 2002

CHẾ TẠO MÀNG BÁN DẪN TRONG SUỐT *ZnO : Al* TRÊN ĐẾ THUỶ TINH BẰNG PHƯƠNG PHÁP PHÚN XẠ MAGNETRON

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Màng bán dẫn *ZnO* pha *Al* có độ truyền qua cao, độ bám dính tốt, điện trở thấp đã được chế tạo trên đế thuỷ tinh bằng phương pháp phún xạ magnetron. Màng bán dẫn *ZnO : Al* đa tinh thể có hướng ưu tiên với mặt (002) song song với bề mặt đế. Điện trở của các màng *ZnO : Al* đã chế tạo nằm trong khong $(1,8-8,7)\times 10^{-3}\Omega$cm, nồng độ hạt tải trong khoảng $(0,2-3,1)\times 10^{20} cm^3$, độ linh động Hall có giá trị nằm giữa $7-17 cm^2V^{-1}s^{-1}$. Độ truyền qua trung bình của màng có độ dầy $1,9\mu m$ là 89 % trong miền nhìn thấy.