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Preparation and Optical properties of undoped and Nitrogen doped ZnO thin films by RF sputtering

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Abstract : ZnO and ZnO:N thin films were deposited on plane glass substrate using RF sputtering method. The crystalline structure and surface morphology of the films were investigated using XRD, EDAX, SEM and AFM. ZnO thin film has largest crystalline orientation for the (002) peak and shows wurtzite structure. The transmittance and absorbance of ZnO thin films were measured using UV-VIS-IR spectrophotometer in the wavelength range 200 nm-800 nm. The band gap of ZnO film was 3.3 eV calculated by Tauc's plot method. Photoluminescence property was also investigated at the excitation wavelength 325 nm. Current-voltage characteristics show the p-type conductivity in N doped thin films. The study demonstrated that ZnO and ZnO:N thin films fabricated by RF sputtering method can be used in electronic and optoelectronic applications due to high transmittance in visible region and large bandgap.

Keywords: RF Sputtering, X-Ray diffraction, Band gap, Photoluminescence, p- type conductivity.

Introduction

Zinc oxide (ZnO) is a direct wide-band gap (3.37 eV) compound semiconductor with large excitation binding energy (60 meV) at room temperature^{1,2}. As a II-VI semiconductor, ZnO is a promising candidate in various technological applications, especially for optoelectronic short wavelength light emitting devices, solar cells and chemical sensors³⁻⁵. To realize the light-emitting devices, an important issue is the fabrication of p-type ZnO with a high hole concentration and low resistance. ZnO is natural n-type semiconductor and has the low solubility of the dopants⁶. It is very difficult to obtain p-type ZnO due to compensation effect of native n-type carrier with dopants and the low solubility of the acceptor dopants⁷. In spite of these difficulties there are some reports of p-type conductivity in doped ZnO with different doping such as, Nitrogen (N)⁸, Phosphorus (P)⁹, Arsenic (As)¹⁰, Antimony (Sb)¹¹ and Lithium (Li)¹². It has been believed that nitrogen in group Vth is a better dopant element for p-type Conductivity in ZnO, which have smallest ionization energy and does not form the N_{Zn} antisite¹³. Undoped and doped ZnO thin films were prepared by different techniques such as chemical vapor deposition (CVD)¹⁴, pulsed laser deposition (PLD)¹⁵, molecular beam epitaxy (MBE)¹⁶, metal organic chemical vapour deposition (MOCVD)¹⁷, RF magnetron sputtering^{18,19} and sol-gel technique²⁰. Among these techniques RF magnetron sputtering is an attractive technique for obtaining films since it has the advantage of easy control of film composition and fabrication of film over a large area at low cost²¹.

In this work, high quality undoped and N-doped ZnO thin films on glass substrate were deposited and were investigated, their structural, optical and electrical properties.

Experimental details

ZnO powder (Loba chemical, 99.99 % purity) was used to prepare the ZnO target for preparing the thin films by RF sputtering. 25 gm of ZnO powder was taken in disc and compressed with 10 ton pressure using palletize machine. The prepared target was sintered at 450°C for 5 h. The sintered target was used for synthesis of thin films deposited by RF sputtering coating unit (planer magnetron sputtering unit modal: 12" MSPT). Argon (Ar) gas of high purity was used as sputtering gas. The ultrasonically cleaned glass substrates were used for coating in sputtering chamber. The sputtering chamber was first pump down from atmospheric pressure to a base pressure of 5×10^{-6} Torr, then Ar gas was introduced into the chamber. When the pressure of the chamber reached $\sim 5 \times 10^{-2}$ Torr, RF power supply was switched ON and hold the power at 160 W for 30 min. The thin films were deposited on the glass substrate. For N doped thin films N₂ gas was used with Ar gas.

X-ray diffraction (X'pert Pro) was used to analyze crystalline structure of films and crystallite size. EDAX was used for element detection. SEM & AFM (EVO-40 ZEISS) were used for the surface morphology and UV-VIS-IR spectrophotometer (Schimadzu-3600) was used for transmittance and absorption of thin films. The band gap of the sample was determined using Tauc's plot method. The Hall (HL-5500 PC) system was used to measure Hall mobility, resistivity and carrier concentration. Keithley 4200 SCS was used for I-V measurements of the films.

Results and discussion

X-Ray diffraction (XRD)

Fig.1 shows the X-ray diffraction of undoped and N doped ZnO thin films deposited at room temperature on glass substrate with different N₂ concentration. It is evident that only (002) diffraction peak is indexed as the hexagonal wurtzite crystal structure of ZnO (JCPDS card no. 36-1451)²². No XRD peak was observed for 10 SCCM of N₂. Therefore, the structure transforms to amorphous at high nitrogen concentration from crystalline due to the internal defects of ZnO. As seen from figure, the diffraction angle of the (002) peaks shift towards small angle. The Crystallite size increases with N₂ concentration of these films as estimated by Scherer's formula (Equation 1).

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where, K is the constant taken to be 0.94, λ is the wavelength of X-Ray used ($\lambda_{\text{Cu}\alpha} = 1.54 \text{ \AA}$) and β is full width half maxima (FWHM).

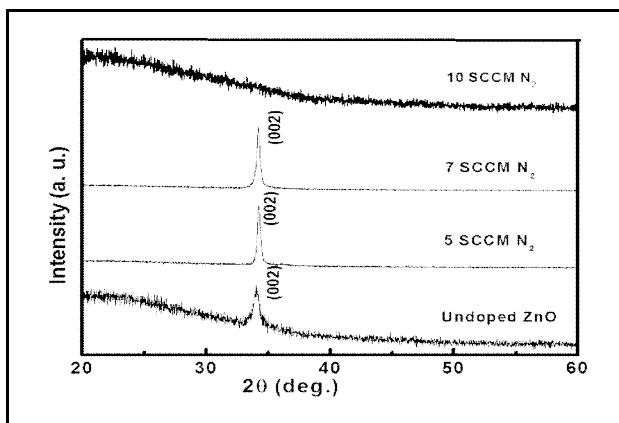


Fig. 1 X-ray diffraction profile of ZnO thin films.

The crystallinity of ZnO film decreases with increase in the N₂ volume from 5 SCCM (standard cubic centimeter per minute) to 7 SCCM. The shrinkage of doped lattice caused by the defects formed by the replacement of smaller oxygen ions and the filling oxygen vacancies by the bigger nitrogen ions in the lattice²³.

Surface Morphology

Fig. 2 shows the EDX analysis of the undoped and doped ZnO thin film. EDX indicates that the products consist of zinc and oxygen elements in undoped films, while N is observed for doped films. No other impurity peak was detected in the EDX results of undoped and doped ZnO films.

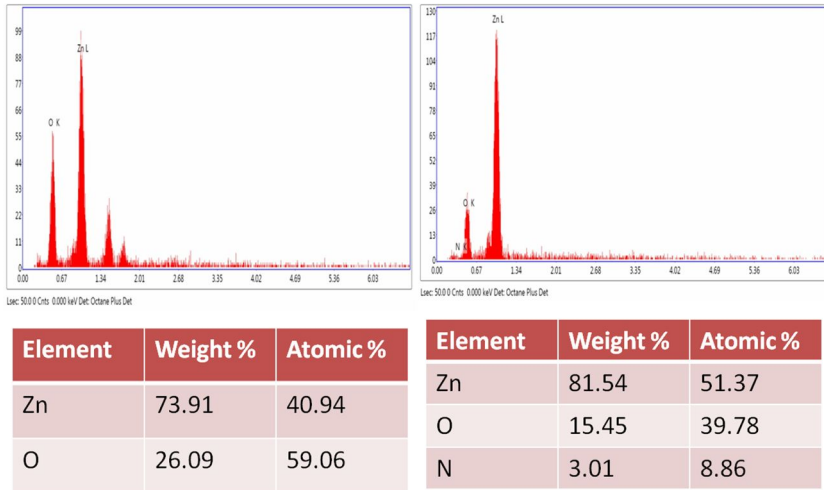


Fig. 2 EDAX analysis of undoped and doped ZnO thin films.

SEM image of undoped and doped ZnO thin films with different N₂ concentration are shown in fig.3. The samples show hierarchical nanostructure. The films consist of closed packed grains with an average size of approximately 50 nm. The grain sizes exactly correspond to those of XRD spectra.

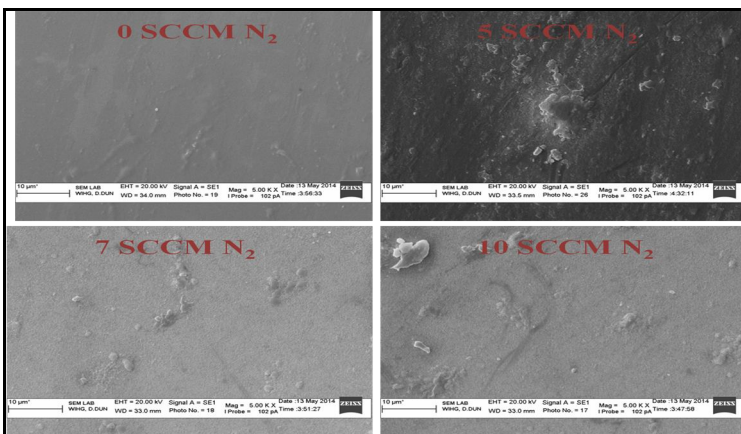


Fig. 3 SEM image of undoped and doped ZnO thin films.

AFM images of undoped and doped ZnO thin films with different N₂ concentration are shown in fig.4. The films consist of closed packed grains.

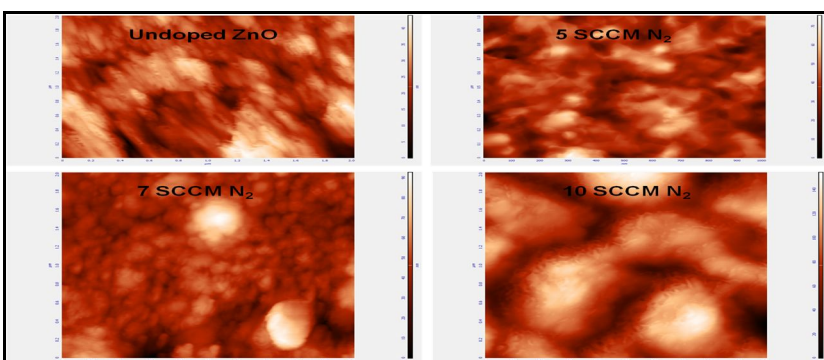


Fig. 4 AFM image of undoped and doped ZnO thin films.

Optical Study

The wavelength dependent optical transmission spectra of undoped and N doped ZnO thin films deposited at different nitrogen volume are shown in fig.5. The films show an average transmittance of about 80%, indicating that they are transparent in the visible region. The maximum transmittance is observed for undoped ZnO thin film and it decreases with doping concentration. The optical interference pattern in transmittance spectra shows a good smooth thin films.

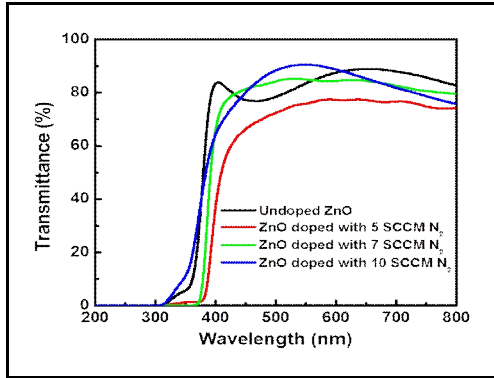


Fig. 5 Transmittance spectra of undoped and doped ZnO thin films.

The optical energy band gap of the film was calculated from fundamental absorption edge of the films. For the allowed direct transition, the variation of α with photon energy ($h\nu$) obeys Tauc's plot method²⁴.

$$(\alpha h\nu)^2 = A(h\nu - E_g) \quad (2)$$

where A is the constant for direct transition, E_g is the energy gap, h is Planck's constant and ν is the frequency of incident radiation. The curve between $(\alpha h\nu)^2$ vs. $h\nu$ is shown in fig.6. The optical bandgap of the films change between 3.32 eV and 3.14 eV. The change in bandgap can be explained in term of Bursten-Mass (B-M) shift theory²⁵. According to the B-M effect, in heavily doped semiconductors the donor electrons occupy states at the bottom of the conduction band. Since Pauli principle prevents states from being doubly occupied and optical transitions are vertical, the valence electrons require an additional energy to be excited to the higher energy states in the conduction band to conserve linear momentum.

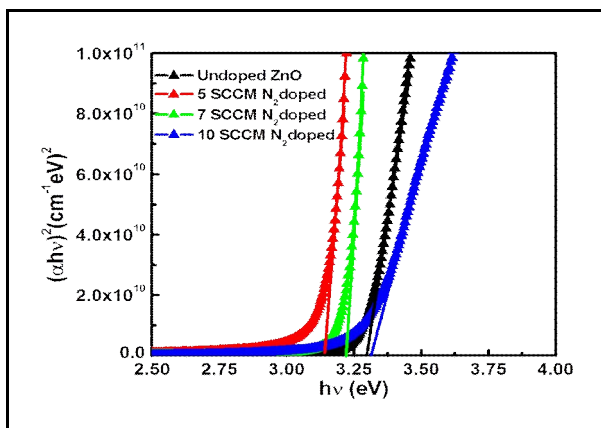


Fig. 6 Band gap calculation using Tauc's plot method.

The PL spectrum of the undoped and doped ZnO films is shown in fig.7. ZnO exhibits two types of emission; UV and visible emission due to band emission and deep level defects²⁶. Generally, ZnO have six kind of defects, namely oxygen vacancy (V_o), oxygen interstitial (O_i), oxygen antisite (Zn_o), zinc vacancy (V_{zn}), zinc interstitial (Zn_i) and zinc antisite (O_{zn})²⁷. The intensity of the defect level emission (DLE) depends on the concentration of the corresponding defects. In these films, we found band to band emission as well as defect related emission. The intensity of PL emission decreases after codoping due to decrease in the crystallinity.

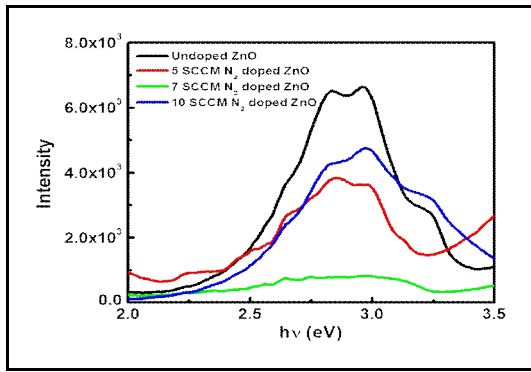


Fig. 7 Photoluminescence spectra of undoped and doped ZnO thin films.

Electrical characterization

The effect of doping ratio on the resistivity, carrier concentration and mobility are shown in fig. 8. The resistivity decreases from 2.235 Ω cm to 1.561 Ω cm with N doping as shown in Table 1. The Hall results showed that the undoped ZnO film have a n-type conductivity, while N doped ZnO film shows weak p-type conductivity with minimum resistivity 1.240 Ω-cm. The increased carrier concentration is attributed to the free electron/hole denoted by doping ions in ZnO²⁸.

Table1. Effect of doping on resistivity, carrier concentration and Hall mobility of ZnO thin films

Sample	Carrier concentration (cm ⁻³)	Hall Mobility (cm ² / Vs)	Resistivity (Ω cm)	Type
ZnO Undoped	-8.42e+18	1.2	2.235	n
ZnO:N 5 SCCM N ₂	2.4e+16	1.51	1.240	p
ZnO:N 7 SCCM N ₂	2.32e+18	1.39	1.561	p
ZnO:N 10 SCCM N ₂	1.06e+19	1.08	2.135	p

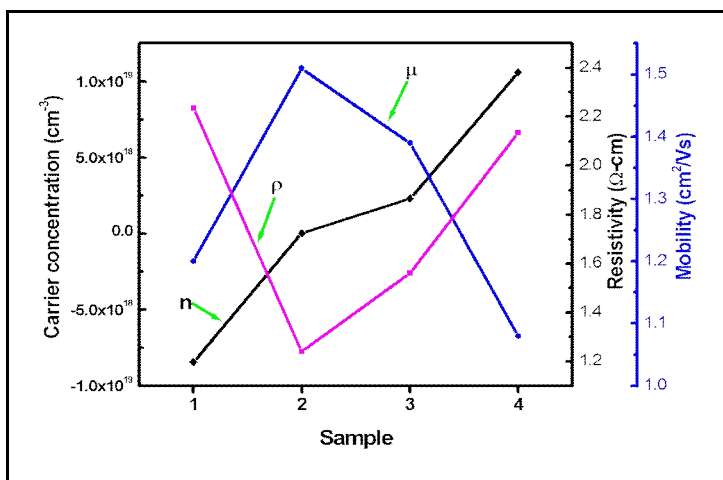


Fig. 8 Hall Probe Effect of doping on resistivity, carrier concentration and mobility of ZnO thin films.

To confirm the carrier type of thin films, current voltage characteristics were carried out using semiconductors characterization system (SCS-4200, Keithley). The effect of doping on I-V results of ZnO films is shown in the fig.8. The ohmic behavior is confirmed by the fairly linear I-V curve for all thin films. The

symmetry of I-V characteristics with ZnO structure shows that ZnO film has n-type conduction as shown by Hall measurement results. On the other hand the I-V measurements of doped film show consistent polarity with low resistance which confirms p-type conductivity²⁹. It is obvious that conductive type of ZnO thin films depends on N₂ atoms concentration.

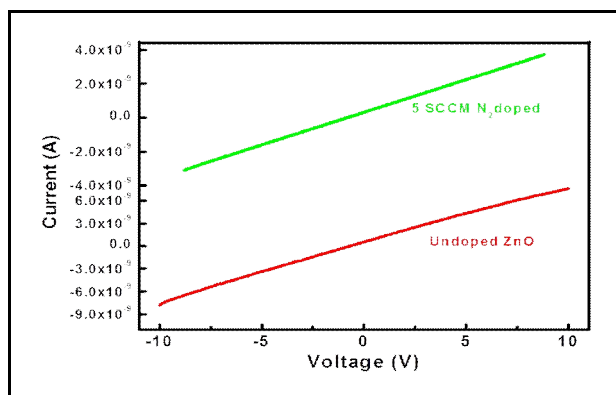


Fig. 9 Current-voltage characteristics of undoped and doped ZnO thin films.

Conclusion

N doped p-type ZnO films were successfully synthesized by RF sputtering. The structure of the film was wurtzite hexagonal crystalline structure. The crystallinity of thin films decreases with increase in N₂ concentration. The transmittance of the film is 80% on an average with respect to air and the band gap decreases on N₂ doping. The minimum resistivity is observed to be 1.240 Ω-cm for N and Al codoped ZnO films. The current voltage characteristics of doped films show consistent polarity with low resistance which confirms p-type conductivity. These highly transparent and conducting p-type ZnO thin films can be used as a window layer in solar cells as well as in other optoelectronic devices.

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