

Optical Tailoring of RF Magnetron Sputtered ZnO Thin Films

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Abstract. Pure and N₂ doped ZnO thin films of thickness ranging ~300-500nm with 5,10,15,20,25, and 50 sccm inflow ratios of N₂ are deposited on soda-lime glass by means of RF magnetron sputtering system, and observed the dependence of optical properties of ZnO by the function of doping with the help of spectroscopic ellipsometer. And found that the N₂-inflow highly affects the optical properties of ZnO thin films. Even the high transmittance of about 97% is achieved and absorbance graph also shows that slight variation in N₂ inflow affects the absorbance, which is maximum with in UV region. Optical conductivity of ZnO is also observed high with the increase of N₂ inflow. With 25sccm N₂ inflow conductivity rose to the maximum value of about $1.4 \times 10^7 \Omega^{-1} \text{cm}^{-1}$, with 15sccm inflow of N₂ conductivity value is $2.0 \times 10^6 \Omega^{-1} \text{cm}^{-1}$ in the visible region. This is a strong contribution towards next generation photovoltaic devices.

Keywords: TCO, ZnO, RF magnetron sputtering, spectroscopic ellipsometer, optoelectronic.

1. Introduction:

transparent conductive oxide thin films (TCO's) are currently gain much interest of researchers worldwide^[1], because of their intense penetration in the field of optoelectronic devices^[2], photovoltaic^[3], and semiconductors lasers^[4] and modern LED's^[5]. The efficiency of transparent conductive oxides (TCO's) can be judged by examine their transmittance and resistivity, which is a core issue in this era. Transmittance and resistivity of different transparent conductive oxides (TCO's) materials (CdO^[6], ITO^[7], FTO^[8], ZnO^[9], SnO₂ and In₂O₃^[10]) have been investigated and found that material having high transmittance with low value of resistivity is the need of time these days^[1]. CdO regards first transparent conductive oxide (TCO) material been investigated with resistivity of $1.4 \times 10^{-4} \Omega \text{cm}$. However, the toxicity and narrow band gap of CdO limits its practical applications ^[6]. ZnO based transparent conductive oxides (TCO's) attracted much interest in this regards because of its multiple advantages over all other transparent conductive oxide (TCO's) materials, such as its wide and direct band gap of ~3.37eV, high value of binding energy ~60meV at room temperature and high transparency as well ^[9]. Thin films of ZnO based transparent conductive oxides (TCO's) are being



prepared by different deposition techniques, such as spray pyrolysis [7], pulsed laser deposition [8], sol-gel method [6], molecular beam epitaxy [9], chemical vapor deposition [10].

Doping of different dopants (Al, N₂, Cu, K, Na, Sn, Pb and Bi) in ZnO based transparent conductive oxides is also intensively studied to enhance the optical properties of ZnO based transparent conductive oxides [11]. Among all other dopants N₂ is supposed to be the best candidate due to its quite similar radii with Zn atoms and with non-toxic and environment friendly behavior. The p-type behavior of doped ZnO thin films is a key issue in this regards, some researchers claims that, but it is not be considered as large scale production[12].

In current work, we investigated the optical properties of N₂-doped sputtered deposited ZnO thin films via RF magnetron sputtering system, and characterized them with the help of spectroscopic ellipsometer (M-2000FI).

2. Experimental Details:

N₂-doped ZnO thin films on glass substrate are deposited with different N₂-inflow ratios varies from 0-50sccm inflow. Before deposition, the glass substrate are cleaned firstly with detergent, and then given ultrasonic bath of acetone and IPA for 15-20mins, after that dry them with N₂. ZnO target of 99.99% purity is used. Sputtering was carried out in the environment of (Ar +N₂) at room temperature and 10⁻⁵ Pa of pressure. Distance between target and substrate surfaces was maintained 72mm. Film thickness and optical parameters were investigated using spectroscopic ellipsometer (M2000-FI.J.A Woollam, USA).

3. Results & Discussions:

Figure.1 (a) exhibits the transmittance spectra of 7 samples. All the samples show high

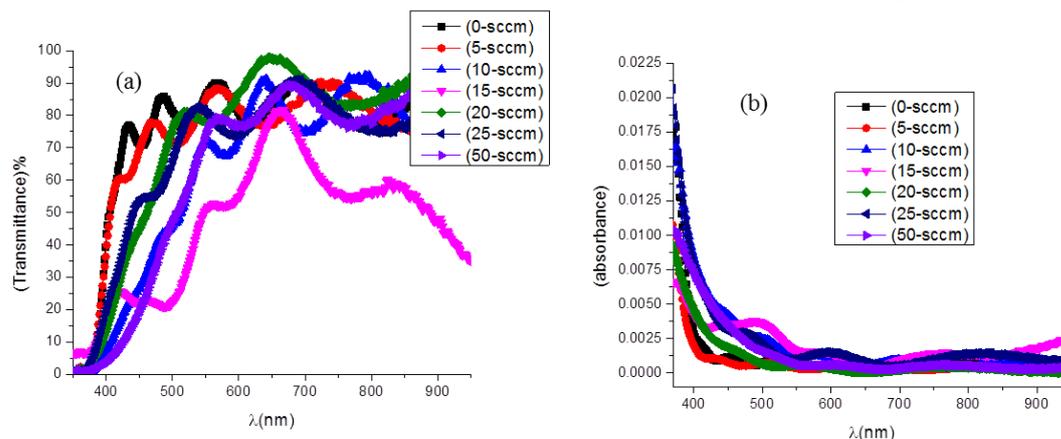


Figure 1: undoped & doped (a) transmittance spectra (b) and Absorbance spectra of ZnO thin films with different N₂ inflow ratio as a function of wavelength.

transparency of >80% in visible region which drops to 0% at 350nm wavelength and it can be seen that with the increase of N₂-inflow transmittance increases generally, with 20sccm flow of N₂ the maximum transmittance of about 97% is observed which is high value reported till now. The reason behind this can be the substitution of N₂ atoms in ZnO are in perfect ratio to overcome the lattice mismatches and defects. Clear variations in transmittance spectra with slight change of N₂ inflow reminds that doping highly affect the transmittance of ZnO, and with doping concentration one can easily control the transmittance of ZnO. This is quite easy and affordable way [13].

The coefficient of absorption “ α ” can be calculated using Eq.1

$$\alpha = -\frac{\ln T}{d} \dots\dots\dots (1)$$

“T” is transmittance and “d” denotes thickness which calculated by Eq (1) .The absorbance of ZnO thin films is also affected by N₂ doping.

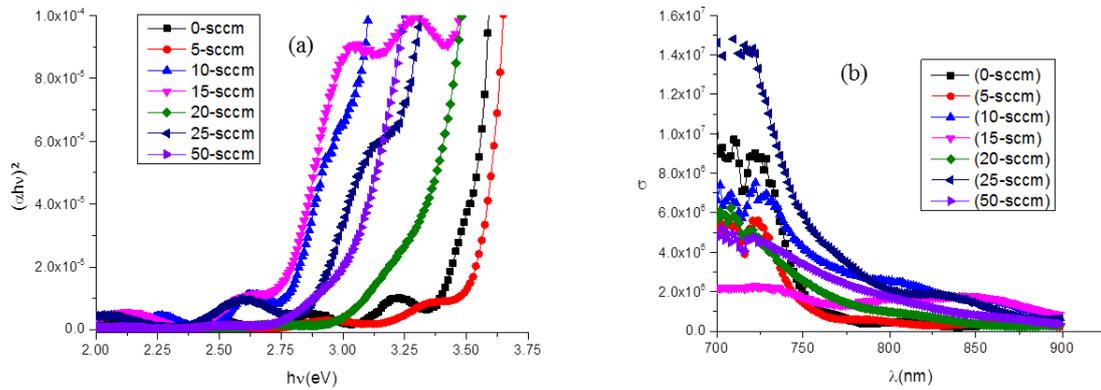


Figure 2: (a) (αhv) 2 vs photon energy plot of undoped & doped ZnO thin films (b) variation of optical conductivity vs wavelength with different inflow ratio of N₂.

Figure.1 (b) show that in UV region the absorbance is high and in visible spectrum it is found very low and goes to zero from infrared region and onward. A clear shift in absorbance edge is observed with the function of doping concentration, which shifts the absorbance edge into visible region. With 50sccm inflow of N₂ the absorbance edge falls on 440nm wavelength. And in pure ZnO thin films it falls on near 400nm wavelength. It concludes that the high doping of N₂ made ZnO thin films very good UV absorber. Which can be used as UV filters [13].

Band-gap of direct band-gap semiconductors can be evaluated by the following Eq.2

$$\alpha hv = A(hv - E_g)^{1/2} \dots\dots\dots (2)$$

“A” is proportionality constant; “hv” is photon energy calculated in “eV” and “E_g” refers to the band-gap of the material. Linear exploration of the photon energy “hv” vs (αhv)² also describes us about the band-gap of that specific material.

Figure.2 (a) shows the decreasing trend of band-gap with increase in the N₂-inflow ratio, the variation of band-gap depend upon many factors like film thickness, fabrication process, doping type and concentration. Present work is the strong evidence of theoretical models, which suggest the decrease of band-gap with increase in doping concentration.

The optical conductivity of any material is an important parameter in order to check its optoelectronic properties, because it gives the healthy information about the band structure of materials, more general it tells how the electronic state are disturbed when optical radiations strikes the surface of that material. It is related strongly with the well-known “moss Burstein effect”. The following formula is helpful to calculate optical conductivity

$$\sigma = \frac{\alpha n c}{4\pi} \dots\dots\dots (3)$$

Here “α” is coefficient of absorption, “n” is refractive index and “c” is speed of light in free space which is constant [13]. The optical conductivity of ZnO thin films is also analyzed and results are found in such a way with 25sccm N₂ inflow the conductivity rose to the maximum value of about 1.4 × 10⁷Ω⁻¹cm⁻¹, with 15sccm inflow of N₂ the conductivity value is 2.0 × 10⁶Ω⁻¹cm⁻¹ in the visible region after that it is decreasing exponentially in figure 2 (b).

The high value of optical conductivity in the visible region of electromagnetic spectrum with doping of N₂ made a great contribution to leads the future optoelectronic devices.

Conclusion:

In short, we examined that the optical properties of ZnO thin films can be perfectly tailored by introducing N₂ contents. The results show the precise control of doping concentration on each optical parameter. As the doping level increases the enhancement in optical parameters can be seen. And it is also observed that the doping of N₂ highly affects the optoelectronic properties of ZnO thin films. In fact, the transmittance of ZnO thin films increased up to 97%, while absorbance is also high in the UV region, and the increase in optical conductivity due to N₂ doping made ZnO thin films a perfect alternate of ITO thin films for high efficiency solar cells of modern era.

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