

Morphological, Structural and Optical Properties of W Doped-ZnO Films Grown by Pulsed Laser Deposition onto Different Glass Substrates

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Abstract Tungsten-doped zinc oxide thin films were prepared by ablating a target containing 1 wt% WO₃ with XeCl excimer laser ($\lambda=308$ nm). The films were grown onto different glass substrate at a repetition rate of 10Hz, pulse energy of 100 mJ and irradiation time of 20 min. The structural and optical properties of the films are found to be strongly dependent on the nature of the substrate. The X-ray Diffraction (XRD) results show that all the films are preferentially C-axis oriented. The room temperature photoluminescence (PL) spectrum shows a dominant near-band-edge emission peak for the film deposited on borosilicate and GGG substrate. The average transmittance was found to be in the range of 84-90%. The absorption coefficient exhibits a direct bandgap feature with some band tailing effects.

Keywords: laser ablation, nucleation, band gap, ZnO nanomaterial, glass substrate

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1. Introduction

Transparent Conducting Oxide (TCO) films have found extensive applications in optoelectronic devices (for example, solar cell, liquid crystal displays, heat mirrors and multiplayer photo thermal conversion system). Zinc Oxide has attracted attention as a transparent conducting oxide because of its large band gap, high conductivity, ease in doping, chemical stability in hydrogen plasma, thermal stability when doped with IIA group elements, abundance in nature and nontoxicity. In addition to potential use as transparent conducting oxide in optoelectronic devices, ZnO thin films also find application as gas sensors, because of their high electrical resistivity [1,2].

For applications in the ultraviolet spectral range, besides GaN based materials, ZnO and its alloys have become the focus of attention in the last years, due to the possibility of using excitonic effects at room temperature. Band gap engineering can be achieved using ZnO and its related alloys. The structural and optical properties of ZnO thin films depend on the deposition and post-deposition treatment conditions as these properties change significantly with film deposition temperature and desorption during annealing treatment [3,4,5].

Several deposition techniques are used to grow ZnO thin films. These include Chemical Vapour Deposition (CVD), Chemical bath deposition [6], Flame transport

synthesis [7], Magnetron Sputtering, Spray Pyrolysis and Pulsed Laser Deposition (PLD) [8]. In comparison with other techniques, PLD has many advantages such as the composition of the films grown by PLD is quite close to that of the target, the surface of the films is very smooth. Good quality films can be deposited at room temperature due to high kinetic energies (>1eV) of atoms and ionized species in the laser produced plasma.

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In the present study, we have investigated the effect of the nature of the substrate on the morphological, structural and optical properties of tungsten-doped zinc oxide thin films deposited by pulsed laser deposition. The purpose of this work is to determine the conditions that can produce highly conducting and transparent films for optoelectronic applications.

2. Experimental Details

W-doped ZnO thin films were deposited on Borosilicate, Gd₃Ga₅O₁₂ and Float-Glass by focussing a XeCl (308 nm) laser on to a target rotating at 15 rpm. The ZnO (99,999% purity) target was un (01) centimeter diameter and was doped with 1 Wt% of WO₃ (99,99%)

pressed at $1.91 \cdot 10^9 \text{ N.m}^{-2}$ and sintered in oxygen atmosphere at $1200 \text{ }^\circ\text{C}$ during 2 hours. For all experiments, repetition rates of 10Hz and energy laser 100 mJ were used. The laser pulsed duration was 20 ns. The distance between the target and the substrate was maintained at 30 mm for all the depositions. The films were deposited by ablating the target for 20 minutes. The deposition cell was initially evacuated to the pressure of order of $4 \cdot 10^{-5}$ mbar and the film deposition was done at $3 \cdot 10^{-1}$ mbar of oxygen pressure. The substrate temperature was fixed at $300 \text{ }^\circ\text{C}$. The structural investigations was carried out by means of X-Ray Diffraction technique with a Cu $K\alpha$ radiation ($\lambda=1.54056\text{\AA}$).

The film thickness and composition was carried out by Rutherford Backscattering Spectroscopy (RBS). To investigate the optical properties of the samples, photoluminescence (PL) measurement was carried out using a HeCd laser line at 325nm as the excitation source. The room temperature PL spectra were dispersed by a

grating spectrometer and detected by a photomultiplier tube. The transmission through the sample, referenced to air, was measured from 200 to 900 nm with a Cary 5E UV-Vis spectrophotometer at normal incidence.

3. Results and Discussion

3.1. Morphology and Structural Analysis

The X-Ray Diffraction (XRD) analysis is performed to determine the structure of the materials. From the XRD pattern (Figure 1), it is observed that the W-doped ZnO films formed at $300 \text{ }^\circ\text{C}$ onto different substrates are crystalline having a wurtzite structure. Only one peak around 34.4 ° is observed which is due to the Bragg reflection from the (0002) plane of ZnO according to the JCPDS-ASTM No 01-1136. The (0002) peak is more intense for the film deposited on the borosilicate substrate.

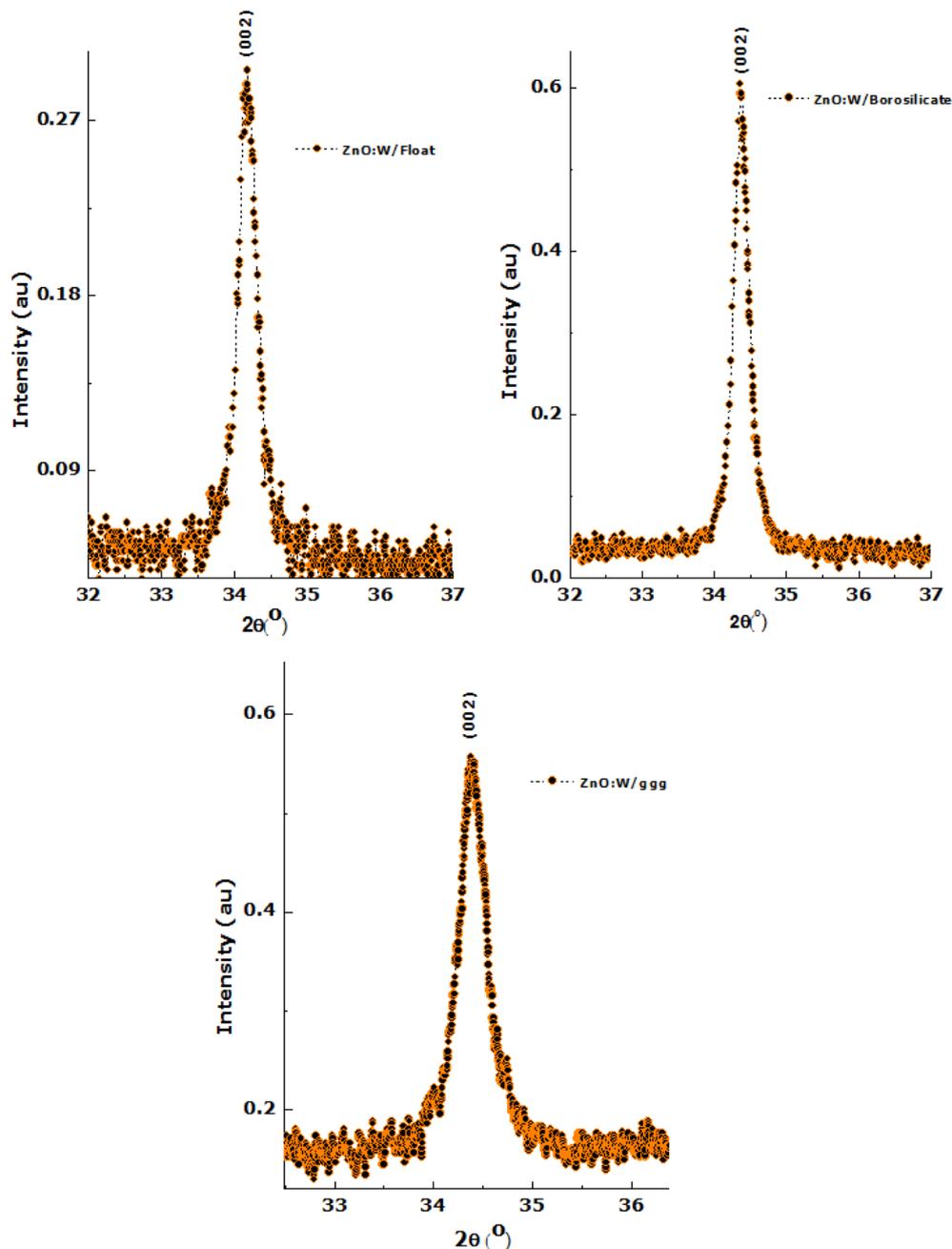


Figure 1. XRD pattern of a ZnO:W thin film deposited onto glass different substrates

The FWHM value listed in Table 1 calculated from the (0002) peak was 0.26° , 0.32° , 0.48° for Borosilicate, Float-Glass and $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ substrates respectively. The increase of the intensity and the decrease of the FWHM of the diffraction peak (0002) rocking curves for the sample deposited on borosilicate substrate are related to a better crystalline quality improvement of the crystal quality of the ZnO films.

Table 1. lattices parameters and FWHM₀₀₂ of ZnO:W onto different glass substrates

Samples	$d_{002}(\text{Å})$	C(Å)	FWHM ₀₀₂ (degrees)
ZnO :W/Float	2.62	5.24	0.32
ZnO :W/Boro	2.60	5.20	0.26
ZnO :W/GGG	2.60	5.20	0.48

The d values listed also in Table 1, which is the inter-planar spacing of (0002) planes of the films are evaluated from the position of (0002) peak from the XRD data by using the following relation:

$$\lambda = 2 d_{hkl} \sin\theta \quad (1)$$

The d_{hkl} values of the film are 2.60 Å , 2.60 Å , 2.62 Å respectively for the Borosilicate, $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ and Float Glass substrates. The variation of d value with the substrate nature is due to the stress developed in the films.

The lattices constants for the hexagonal structure of the pulsed laser deposited W-doped ZnO thin films are determined by the following relations:

$$d_{hkl} = \frac{a}{\sqrt{\frac{4}{3}(h^2 + k^2 + hk) + l^2 \frac{a^2}{c^2}}} \quad (2)$$

The values of "c" calculated are 5.24 Å for Float Glass and 5.20 Å for Borosilicate and $\text{Gd}_3\text{Ga}_5\text{O}_{12}$, which are found to be slightly different from the one of pure ZnO which is 5.176 Å according to the JCPDS-ASTM No 01-1136.

The rough surface morphology of W-doped ZnO consisting of crystallites is found to depend on the substrate as shown by Figure 2.

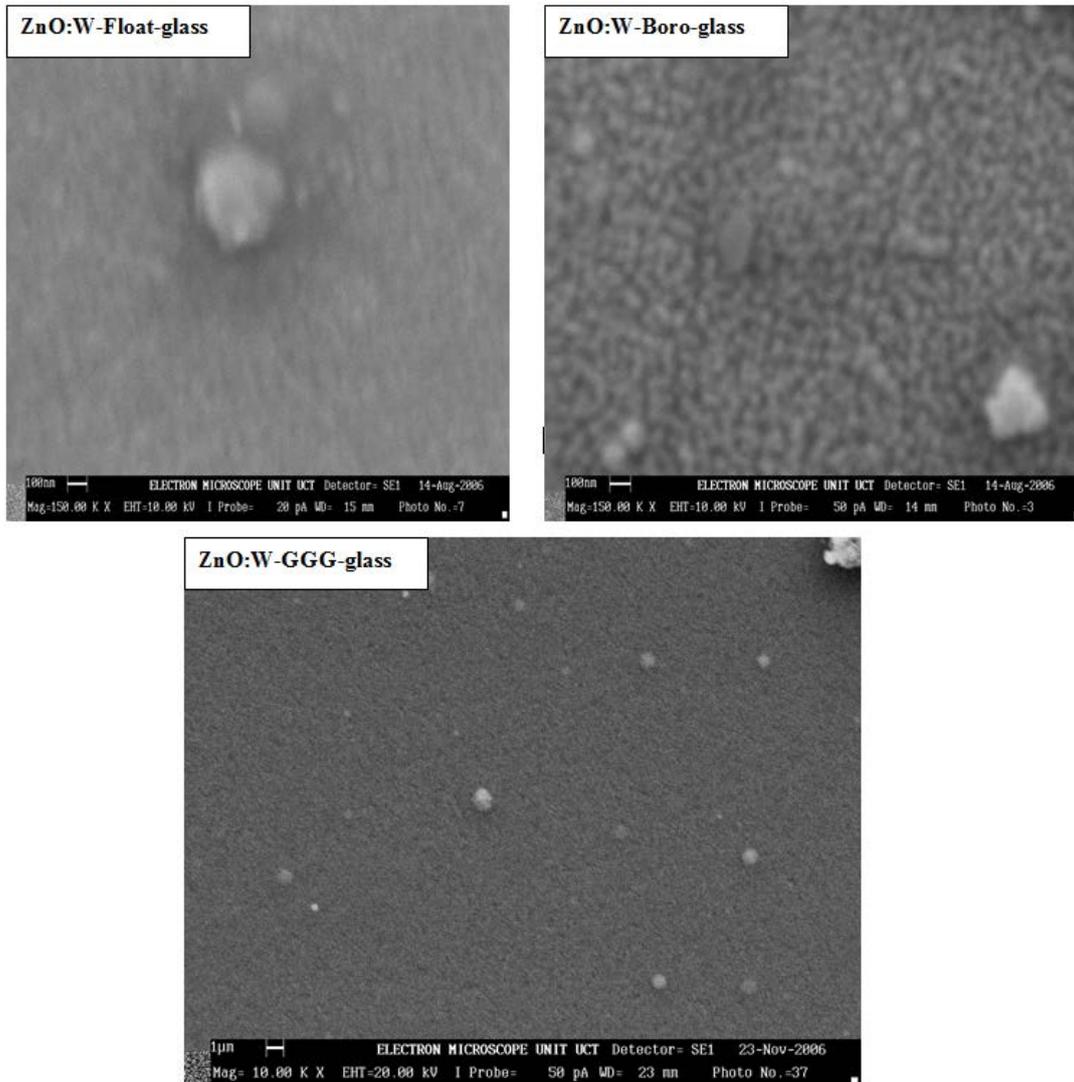


Figure 2. RBS of a ZnO:W thin film deposited onto different glass substrates

The SEM images obtained show that the thin films grown on the borosilicate have a granular surface with grains sizes larger. The thin films grown on GGG

substrate are smoother. This confirms the previous results that are to say that the WZO developed on the borosilicate better crystalline quality.

The effect of the nature of the glass substrate is visible on the SEM images; the increase in grain size, which corresponds to a coalescence of the small grains, is thus confirmed in the case of borosilicate substrate. It appears clearly on images SEM that the densification of the film is correlated with the results of XRD analyses.

3.2. RBS Analysis

Figure 3 shows the Rutherford backscattering spectroscopy (RBS) with 2 MeV He ions used to determine the composition and the thickness of W-doped ZnO films grown onto different glass substrates. The results are listed in Table 2, which revealed that the films deposited on

borosilicate are thicker and have better stoichiometry. By taking the ratio (Zn+W)/O, one can see that from the films deposited on borosilicate and Float glass we have the same value which is about 1.2 and the ratio of the film deposited on GGG shows a striking difference. From these results we can say that the composition of the layers depends on the substrate. The films of the WZO developed borosilicate substrate, which have a better stoichiometry have a small amount of tungsten. The variation in doping levels can occur during transport of the target elements to the substrate but also bonding probabilities on the substrate, which depends on the nature of the substrate surface [9].

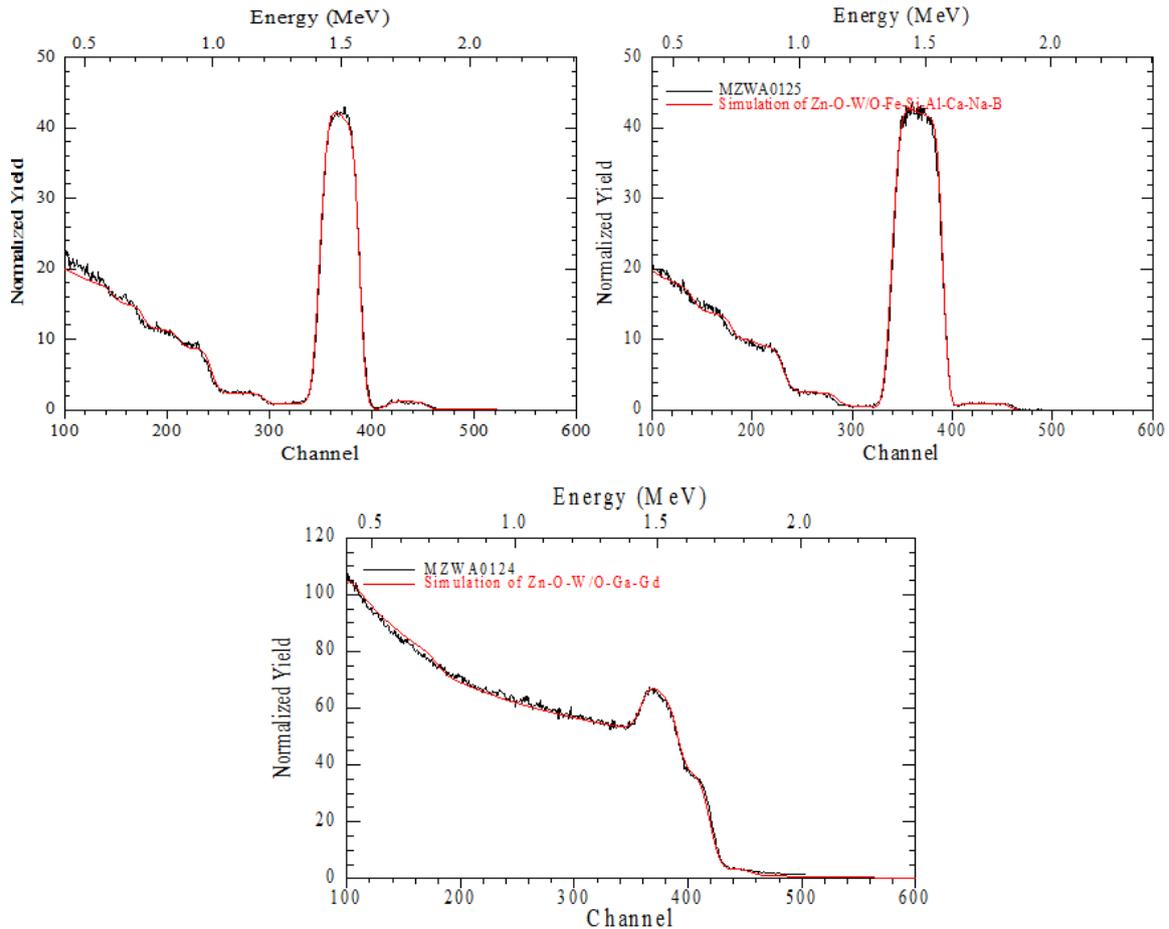


Figure 3. SEM images of a ZnO:W thin film deposited onto different glass Substrates

Table 2. Steochiometry and thickness of ZnO:W onto different glass substrates

Samples	Thickness (nm)	at.% Zn	at.% O	at.% W
ZnO :W/Float	279	55.332	44.412	0.256
ZnO :W/Boro	368	54.727	45.077	0.195
ZnO :W/GGG	281	30.316	69.294	0.39

3.3. Optical Properties

The transmission spectra of the film grown on different substrates are illustrated in Figure 4. The fundamental absorption started around 380 nm which is very close to the intrinsic band-gap of ZnO (3.3 eV) which is caused by the fundamental light absorption in the semiconductor. One can note that all the layers present a high transmittance in the visible region above 85% showing

that the film was highly transparent. This suggested that there were relatively less defect electronic states within the band gap usually associated with oxygen vacancy, interstitial zinc atom and their complexes, etc.

The flat aspect of the transmission of the film grown on GGG without interference fringes indicated the surface uniformity of the film.

The optical absorption coefficient (α) and the extinction coefficient (k) was evaluated from the transmittance (T) data using the relation:

$$T = e^{-\alpha d} \quad (3)$$

Where d is the film thickness and α is related to the coefficient (k) by:

$$k = \frac{\alpha \lambda}{4\pi} \quad (4)$$

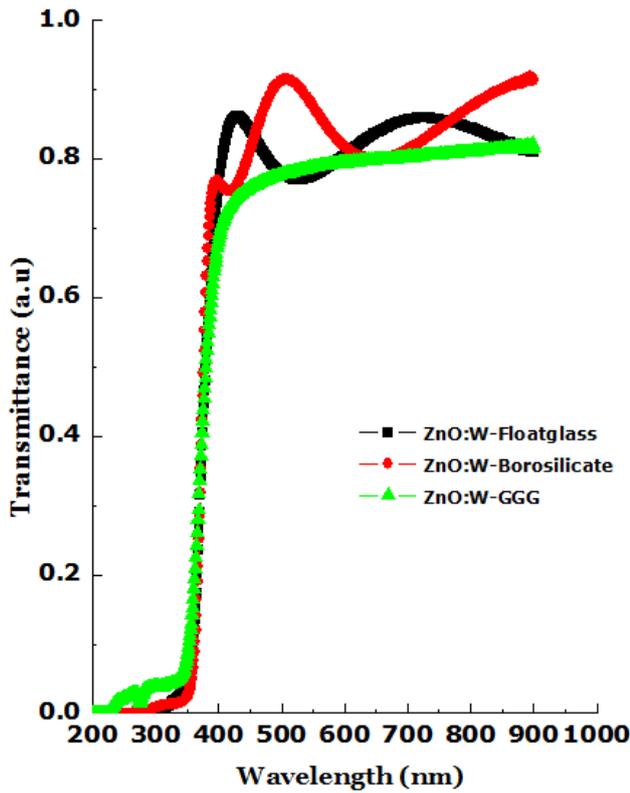


Figure 4. Transmission spectrums for the ZnO:W thin film grown on different glass substrates

The wavelength dependences of the absorption coefficient near the UV edge of the films for the three substrates are shown also in Figure 5.

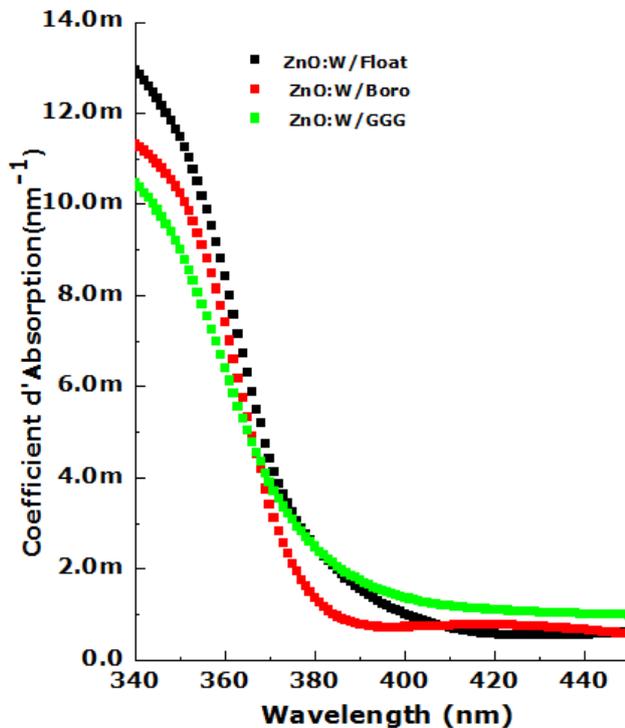


Figure 5. Wavelength dependence of the absorption coefficient of ZnO:W thin film grown on different glass substrates

The shift in the absorption edge can be accounted for in terms of the increase in carrier concentration and blocking of low energy transitions, which causes a Burstein Moss effect, which enhances the optical band gap.

Since ZnO is a semiconductor with a large band gap, the energy optical band gap (E_g) was estimated by assuming a direct transition between valence and conduction bands from the expression.

$$(\alpha \cdot h\nu)^2 = A(h\nu - E_g) \quad (5)$$

Where A is a constant.

The band gap of ZnO thin film was estimated by plotting $(\alpha \cdot h\nu)^2$ versus $(h\nu)$ and extrapolating the linear portion near the onset of absorption edge to the energy axis (at $\alpha=0$).

Figure 6 shows the plots of $(\alpha \cdot h\nu)^2$ versus $h\nu$ for W-doped ZnO films deposited onto different substrates.

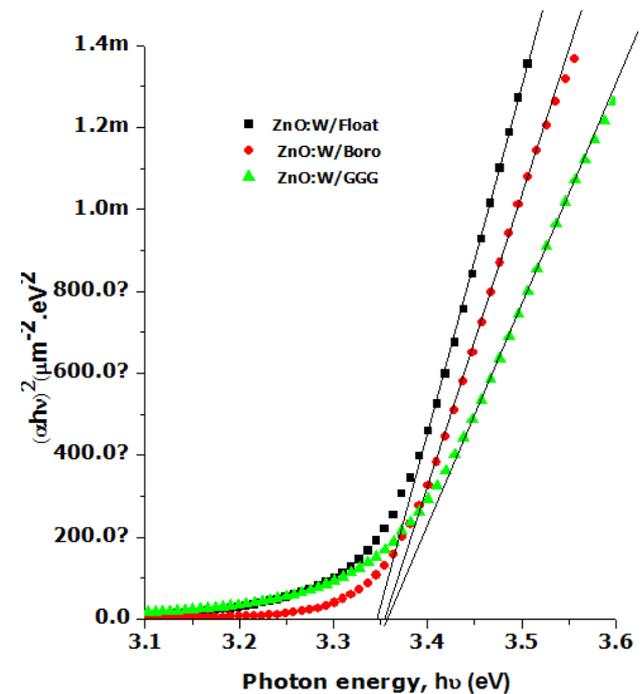


Figure 6. Plot of $(\alpha h\nu)^2$ as function of $h\nu$ for ZnO:W thin film grown on different glass substrates

The values of E_g for all the samples are reported in Table 3.

Table 3. optical band gap of ZnO:W onto different glass substrates

Samples	Band Gap Optic (eV)	Emperical parameter (meV)
ZnO :W/Float	3.345	158
ZnO :W/Boro	3.35	96
ZnO :W/GGG	3.36	200

The optical band gap shows a small variation by changing the substrates which gives 3.345, 3.35 and 3.36eV respectively for Float glass, Borosilicate and GGG.

The optical gap is defined as the minimum energy needed to excite an electron from the valence band to the conduction band. In pure undoped crystals the optical gap equals the energy separation between the band edges. On heavy doping, the donor electrons occupy states at the bottom of the conduction band, since Pauli principle prevents states from being doubly occupied, the optical band gap is given by the energy difference between the states with Fermi momentum in the conduction and valence band. This type of blocking of low energy transitions is known as Burstein–Moss effect.

The absorption coefficient in the near band edge in the energy region $h\nu < E_g$ empirically follows the exponential law, i.e. the Urbach tail is expressed by

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_0}\right) \quad (6)$$

Where α_0 is a constant and E_0 is an empirical parameter, usually weakly dependent on temperature and describing the width of the localized states in the bandgap but not their energy position. In [4] E_0 is considered as a parameter that includes the effects of all possible defects.

In the equation (6) by taking the semi logarithm of α and by plotting it versus $h\nu$ (ref Figure 7), where a linear relationship is observed. The slope of the linear fit is used to calculate E_0 , the quantities of E_0 for all the samples are listed in Table 4.

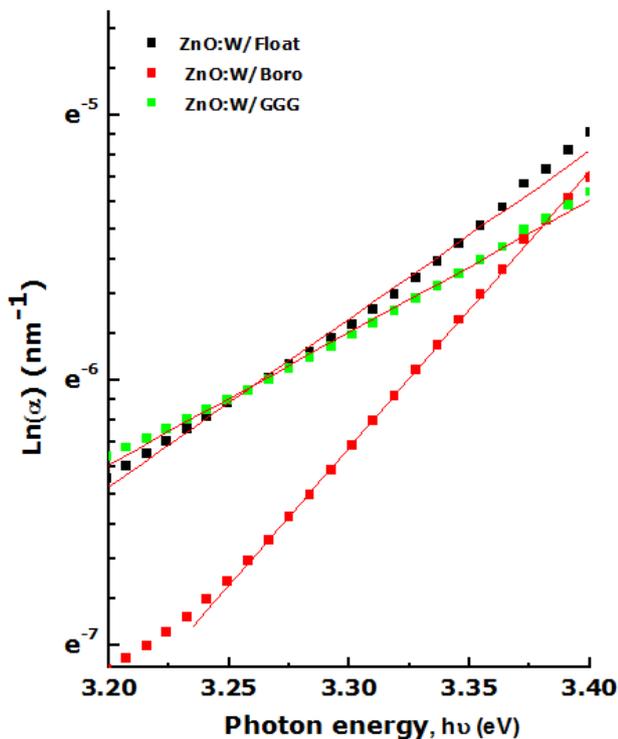


Figure 7. Plot of the semi logarithm of α versus $h\nu$ of ZnO:W thin film grown on different glass substrates

Table 4. Band gap calculate from PL spectrum of ZnO:W onto different glass substrates

Samples	Band Gap (eV)
ZnO :W /Float	3.27
ZnO :W/Boro	3.28

Giving E_0 from 200, 158 and 96 meV for GGG, Float and Boro respectively, the decrease of the empirical parameter E_0 when we use the Borosilicate indicates that there is better stoichiometry of ZnO films. The data of XRD measurements and the RBS results also testify to this. Thus, it is possible to assume that the stoichiometry between Zn and O can be improved.

For the ZnO films grown on the sapphire substrate by laser ablation [6], values of E_0 as low as 30 meV can be achieved by annealing in air, whereas as-deposited films show a value >60 meV. The value of E_0 from 80 to 100 meV is given in [1] for ZnO films prepared by CVD at different formation temperature.

Room temperature PL spectra from the ZnO thin films grown on borosilicate and GGG at 100mJ of laser power are show in Figure 8. The optical properties of the samples are found to be strongly dependent on the experimental parameters. For all the samples only the films deposited on borosilicate and GGG with a laser power of 100 mJ exhibit a typical luminescence behavior of ZnO with a narrow UV emission at 378 nm (3.28 eV) from the PL spectrum we calculate the band gap for these two samples and we can see that there is a deviation from the one calculate from the absorption coefficient. The results are listed in Table 4.

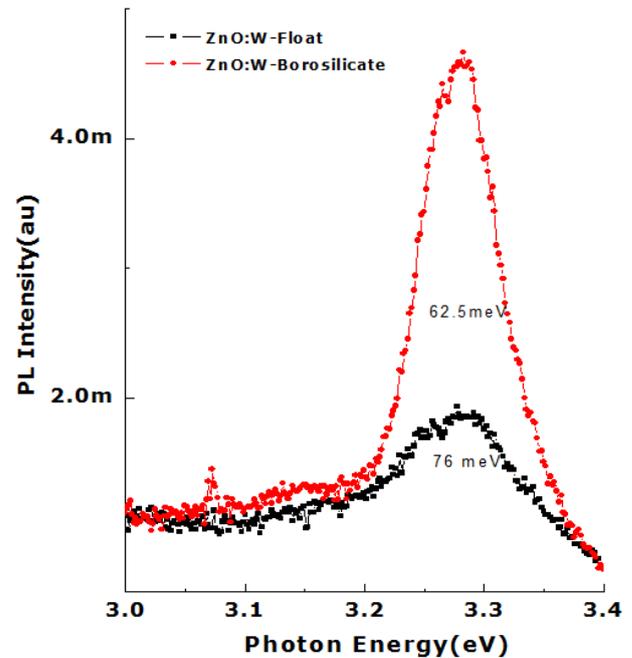


Figure 8. Room temperature photoluminescence spectrum of ZnO thin films grown on different glass substrates

The intensity of the films deposited on borosilicate is higher than the one on GGG and that confirm the results we obtained on the X-ray Diffraction.

Although the crystalline structure still maintains the high c -axis orientation of the ZnO film, evidently the film becomes more Zn rich and large amounts of oxygen vacancies (V_O) and zinc interstitial atoms (Zn_i) are created [8,9,10]. All these defects are related to an insufficient supply of oxygen during growth. The presence of the point defects, such as V_O , Zn_i , and V_{Zn} , caused by non-stoichiometry will perturb the periodic lattice potential, thus deteriorating the optical properties.

The strong emission is commonly attributed to the direct recombination of free exciton through exciton-exciton collision process. The broad green band emission from the ZnO is generally explained by the radial combination of a photo-generated hole with the electron in a singly ionized oxygen vacancy. The strong UV emission and the weak green band in the PL spectrum indicate that the film is of high optical quality, which are suitable for device.

4. Conclusion

We demonstrated to grow the ZnO:W thin film on three different glass substrates at the temperature of 300°C

using the PLD technique. The work reveal that the nature of the substrate play a key role in determining the ZnO:W film properties.

The results of near band-edge investigations of optical spectra and XRD measurements of deposited W-doped ZnO films have shown that optical absorption coefficients, bandgap energy E_g , empirical parameter E_0 , and the fwhm are strongly dependent on the growth conditions, during which the stoichiometry between Zn and O is improved when we use borosilicate as substrate.

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