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Original article

Effect of laser energy density on ZnO / α- Al2O3 of films grown by pulsed laser deposition

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Abstract

In this work, Pulsed Laser Deposition (PLD) was employed for preparation of the thin films of Zinc Oxide on Sapphire α- Al_2O_3 (0001). The effect of laser energy density on the structure and optical characterizations of the ZnO films have been studied by X-Ray diffraction (XRD), and Scanning Electron Microscopy (SEM). The results showed that crystalline and (002)-oriented ZnO films were obtained at laser fluence 0.8, 1.6, and 2.4 J/cm^2 and the optimized growth ZnO films were at substrate temperature of 400 ^{o}C.

Optical transmission for all films was around 85-90% within the visible region of the spectrum.

Key words: Pulsed-laser deposition; Zinc oxide thin films; Nanostructures; Nd: YAG Q-Switching (SHG).

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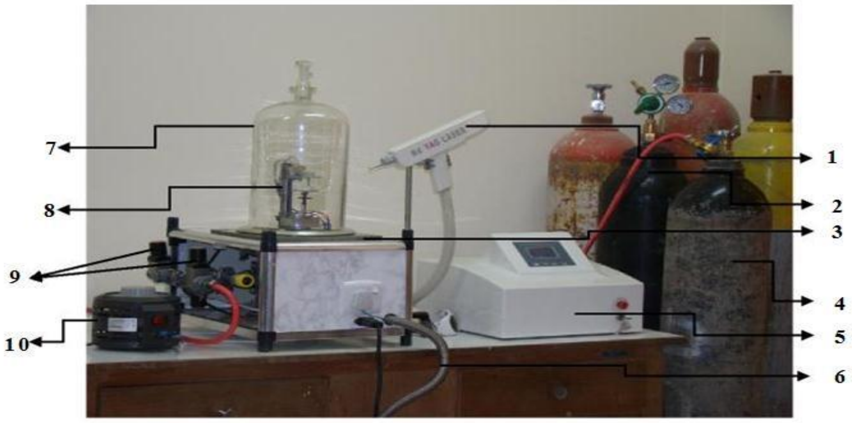
Introduction

Thin films of ZnO have wurtzite structure with a wide band gap of (3.37 eV), low resistivity and high transparency in the visible and near infrared region of the electromagnetic spectrum, (1,2,3&4). This wide band gap semiconductor has been the subject of a significant number of studies for a fascinating range of applications, which include transparent electrodes in display (TCO),(5), surface electro acoustic wave devices ,(6) ,ultraviolet laser, (7,8&9). Different deposition techniques have been employed to deposit thin films of ZnO including electrochemical deposition (ECD) technique (10&11), magnetron sputtering ,(12) , Metal organic chemical vapor deposition ,(13) and pulsed laser deposition (PLD) , (14& 15). ZnO films grown by present work have many advantages over other methods due to less ion bombardment, controlled activation of growth with near stoichiometric ratio films that exhibits distinctive and typical ZnO crystalline structure and photoluminescence (PL) properties (16). Furthermore, the deposition of high quality films at relatively low temperature substrate without the use of heated filaments, but instead a laser is used as an external energy source results in an extremely clean films with minimum contaminants , (17&18). For the growth of ZnO thin films, Sapphire (α-Al_2O_3) has been commonly used as substrates. Epitaxial grown of ZnO thin films on α-Al_2O_3 substrate have been characterized by domain-matching epitaxy. ZnO thin films on sapphire were fabricated for light-emitting diodes in which emission from both sides is preferred , (19). Solid-state lasers attracted increasing attention induced by the invention of thin disk laser set-up. This concept improves the performance of high-power laser by decreasing the dimensions of the active medium in order to reduce thermal stress. The typical thickness of the active media is, currently, in the range of several hundreds of micrometers, and it is desirable to utilize even thinner layers. Thus, films of active material with the thickness in the range of tens or hundreds of micrometers can find their application as active media in solid-state thin disk lasers. The application of pulse laser deposition technique can be especially favorable in this case, since the active medium, Bragg mirrors and antireflection coatings can be fabricated as a multilayer structure in a single process. In the present work, the Pulse Laser Deposition (PLD) is used to prepare ZnO thin films on α-Al_2O_3 substrates at 400 ^oC temperature. Moreover, the influence of laser power of 0.8, 1.6 and 2.4 J/cm^2 during the process of deposition.

Experimental part

Pulse Laser Deposition (PLD) system

Firstly, the sapphire substrates were imprinted in (H_2SO_4:H_3PO_4) in the ratio (3:1) and then ultrasonically cleaned by in deionized water, followed by drying and fixed on substrate holder of the Pulse Laser Deposition (PLD) system used in this work as shown in Fig.1.



1. Nd:YAG Laser Head.
2. O2 cylinder gas
3. Stainless steel Flange.
4. N2 cylinder gas.
5. Power supply Nd:YAG laser

6. Flexible tube KF16
7. Quartz Chamber.
8. Substrate holder
9. Vacuum system
10. Variac devices

Figure; 1. Pulsed laser deposition (PLD) system.

In order to obtain a homogenous film thickness, the substrates were kept rotating during the deposition process. All films were grown at an optimal substrate temperature of 400 °C with an oxygen background pressure of 2×10^{-2} mbar. A ZnO sintered target, of high purity (99.99 %) supplied by Fluka, was attached in a home designed vacuum chamber supplied by a double frequency Q- switched Nd:YAG pulsed laser operated at 532 nm. The target was ablated with pulse duration of about 10 ns, and with energy density of 0.8, 1.6 and 2.4 J/cm^2 directed on the target to produce plasma plume. XRD measurements were performed using diffractometer with Cu K-α1 radiation (λ = 1.5405A°) to investigate the films structure. The film morphology was investigated by scanning electron microscopy (SEM) using FEL Quanta 200 (Netherlands). With optimized deposit time the film thickness of (150 nm) was measured using He-Ne laser with wavelength λ = 632.8 nm.

Results and Discussion

Effect of irradiation conditions on the films structure

Application of material ablation by powerful lasers often requires precise control over the properties of the ablation plume; namely wavelength, laser fluence and pulse repetition rate. The laser wavelength also affects the properties of ZnO films since the light absorption in the target is much stronger at shorter wavelength. Figure; 2 shows the XRD spectrum of ZnO films deposited on sapphire substrates employing the Q-switching Nd:YAG laser (λ = 1064 nm) and frequency-double Nd:YAG laser (λ =532nm) in oxygen background pressure of 5×10^{-2} mbar. The obtained (XRD) patterns show strong (002) peak, which is attribute to the hexagonal wurtzite structure of the ZnO formed on sapphire substrates.

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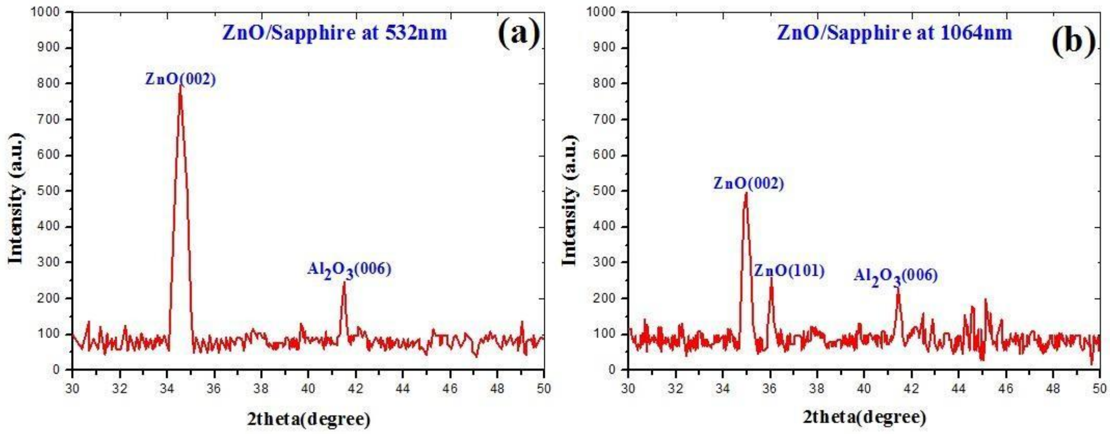
The crystalline structures of the deposited films were found to depend not only on the substrate temperature and oxygen pressure, but also on the wavelength of the used laser. The quality of the ZnO films grown by the shorter wavelength laser was better than that of the films grown by the longer wavelength.

The FWHM of ZnO films grown on sapphire substrate in oxygen ambient are 0.1339^o and 0.1964^o at the wavelengths 1064 nm and 532 nm, respectively.



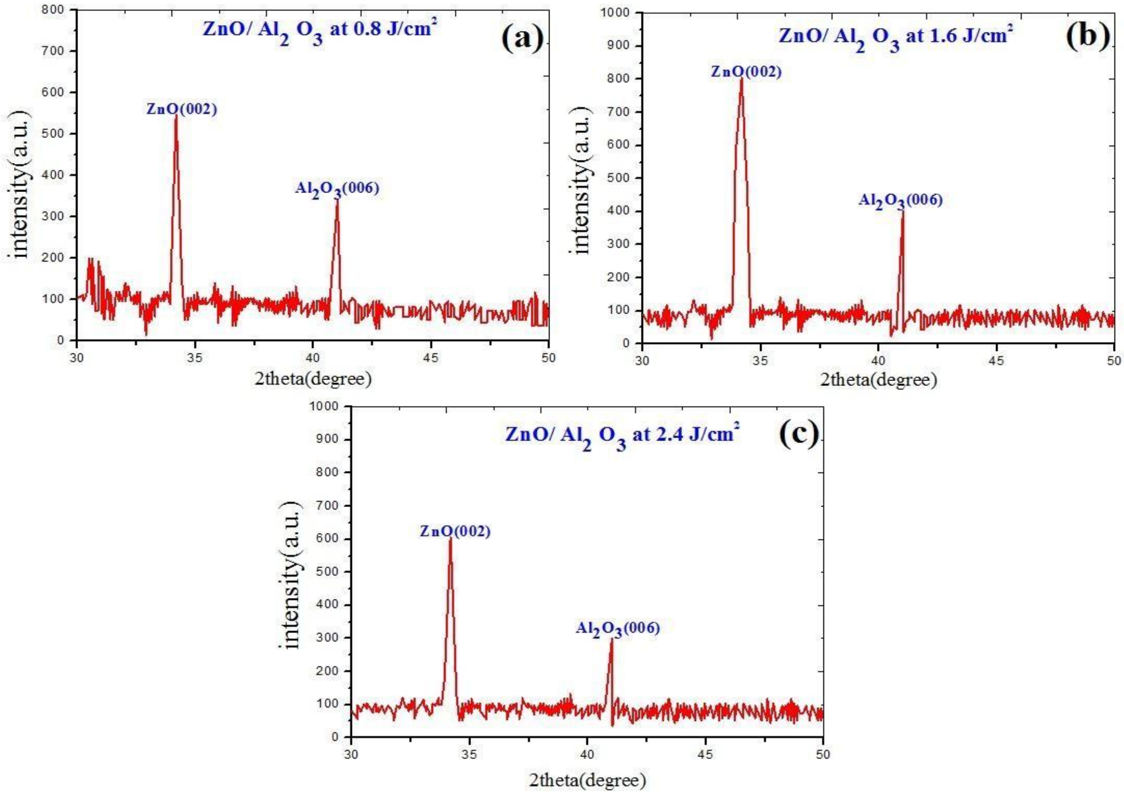
Figure; 2. XRD patterns of ZnO films grown on sapphire at various laser wavelengths.

Table; 1.The obtained result of the structural parameters from XRD for ZnO/Sapphire thin films.

Laser wavelength nm	2θ for (002) reflection	Inter planar spacing, d Å	Lattice constant Å	Strain (×10^{-3})	Stress (GPa)	FWHM°	Mean Grain size (nm)
1064	35	2.6019	5.2038	-0.556	+0.129	0.1372	60.87
532	34.6	2.595	5.190	-3.21	+0.747	0.1933	42.20

To remove (ablate) an atom from a solid surface by a laser pulse, the energy delivered to a single atom should exceed the binding energy of that atom. The energy absorbed in the target material per unit surface area depends on the laser fluence (F), which is the time integral of the laser intensity I_o (t) over the pulse duration t_p. Therefore, the ablation rate is a function of the laser fluence. A typical ablation threshold is of the order of 0.8 - 2.4 J/cm^2, depending on the target material and the laser wavelength.

Figure 3 illustrate XRD patterns reveals the influence of laser on the structure of the ZnO/α-Al_2O_3 films .Thin films grown with different laser fluence (0.8, 1.6 and 2.4) J/cm^2 at 400 ^{o}C with fixed oxygen pressure of 5×10^{-2} mbar. For all films no Zn or Al and O characteristics peaks were observed; only ZnO (002) diffraction peaks were observed. The orientation growth (002) plane of the ZnO/α-Al_2O_3 thin film was dominant, whereby, the ZnO (002) diffraction peaks location were observed at 2θ = 34.25^o, 34.30^o and 34.50^o. The strongest reflection peak of sapphire (006) at diffraction angle 2θ = 41.30°, 41.56° and 41.75° for different laser energy densities. By increasing the laser energy, it was observed that (002) diffraction angle has gradually shifted from34.25° to 34.50°. The XRD results inferred that the films grown on sapphire substrate retain a crystal structure of hexagonal wurtzite with a perpendicular c-axis orientation to the surface. The intensity of ZnO (002) at laser fluence 1.6 J/cm^2 was very high in comparison to the other planes and the full width at half maximum (FWHM) is more broadening.



Figure; 3. Shows the X-ray diffraction spectra of the ZnO/αAl_2O_3thin films at different laser fluence

The crystal sizes of ZnO thin films were determined using Scherrer's equation,(15).

$$D = 0.9\lambda/\beta\cos\theta \qquad (1)$$

Where λ = 1.54A° and β (FWHM) were determined from the broadening of the ZnO diffraction line. The values of the main grain size from XRD pattern of thin films are given in Table; 2 , since the grain size is inversely proportional to the FWHM, the grain size steeply decreases from the largest value of 62 nm to the smallest of 44.46 nm as the laser energy fluence was increased from 0.8 to 1.6 J/cm^2. It gradually increases to 59.92 nm with a further increase in the laser energy fluence to 2.4 J/cm^2. At higher laser fluences the laser produced plasma containing a significant amount of highly energetic species. The high energy plum species after colliding with the substrate may penetrate the substrate surface and get embedded into it. These immobile atoms then act as additional nucleation centers and in turn promote island type of growth. These islands along with naturally formed nucleation centers then grow in size and coalesce to form a continuous film ,(17).

Table (2) X-ray diffraction data summary of ZnO thin films with different laser fluence grown by pulsed laser deposition

Laser fluenc J/cm^2	2 for (002) reflection	FWHM	Mean Grain size (nm)
0.8	34.25	0.1332	62.60
1.6	34.3	0.1875	44.46
2.4	34.5	0.1392	59.92

1. Effect of irradiation conditions on film's morphology

The surface morphology of the PLD grown thin films has been found to be dependent on process parameters such as laser wavelength and laser fluence. Both at longer wavelength and higher laser fluence, the unwanted micron sized particulates were found to be distributed over the film's surface. As the wavelength of laser is decreased from 1064 nm to 532 nm the particulate density and their average size on the ZnO/Sapphire films surface significantly reduced and particulates are more uniformly distributed in the films. Figure 4 shows SEM images of the thin films deposited by using laser wavelengths of 1064 nm and 532 nm. It can be seen in these images that the film surface is smooth and particulate free in the case of deposition at laser wavelength of 532 nm, while micron and submicron size spherical particulates were present on the surface of the ZnO film grown by using 1064 nm laser wavelength.

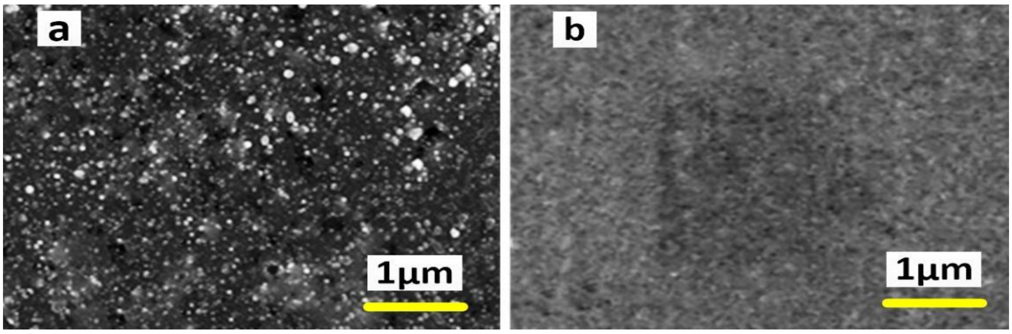
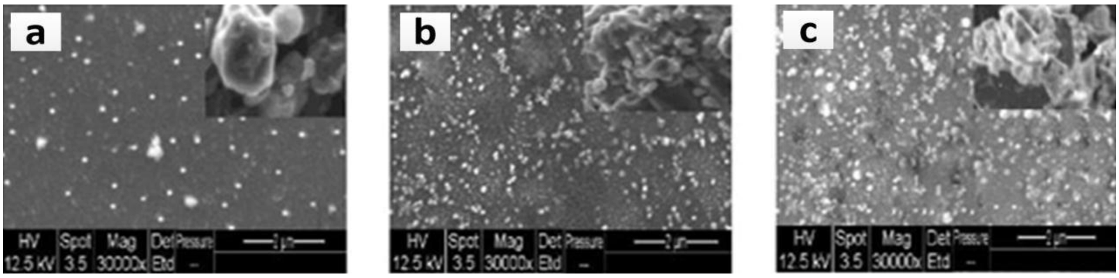


Figure 4. SEM images of the ZnO thin films deposited at various laser wavelength (a) 1064nm, and (b) 532nm.

The penetration depth of the laser is higher at λ = 1064 nm and could cause undesirable effects such as splashing of micron size particulates from the target. On the other hand the penetration depth of the laser is lower at λ = 532 nm and it is more absorbed in the material than in the case of the λ = 1064 nm counterpart; The particulates ejection from the target is lower at λ = 532 nm and therefore a relatively smooth surface of ZnO was observed, as shown in figure 4(b). This is in agreement with results reported by T. Premkumar and *et al.*, (20) , which state that the micro and sub-micro size particulates ejection from target is strongly dependent on the penetration depth of the laser beam.

The surface morphology of the PLD grown thin films has been found to be dependent on process parameters such as laser fluence. At higher laser fluence, the unwanted micron sized particulates were found to be distributed over the film surface , (20) . Figure; 5 shows SEM images of surface morphology of $ZnO/\alpha\text{-}Al_2O_3$ films deposited under 5×10^{-2} mbar of oxygen at substrate temperature of 400 ^oC. The microstructure of the PLD ZnO films was found to change significantly with the deposition fluence laser energy. The films deposited at laser fluence of 0.8 J/cm^2 exhibit a porous fine-grained microstructure as shown in Figure (5a), as the fluence laser energy is raised to 1.6 J/cm^2, the films exhibit isolated ZnO aggregation with size over 21.31 nm (figure 5 (b)),which differs strongly from the surface of films deposited at fluence laser energy of 2.4 J/cm^2 as shown in figure 5 (c), where the sample showed more aggregated particles with size of 40.67 nm.



Figure; 5. SEM images of $ZnO/\alpha\text{-}Al_2O_3$ thin films grown at 400 ^oC substrate temperature and laser fluence a) 0.8 J/cm^2, b) 1.6 J/cm^2 and c) 2.4 J/cm^2

2. Optical properties

Figure; 6 shows the optical transmittance (T) in the wavelength range of 200-900 nm; the average transmittance over visible part of the spectra (400 - 700nm) is about 88% for all the PLD deposited films. Additionally, the fall of transmittance is very sharp near the absorption edge. The optical transmittance in the visible range is found to be slightly dependent on the substrate temperature, which is due to the increase in the grain size of the films with the increase in the laser fluence energy density .The plot of $\alpha h\nu$ versus the incident radiation energy is presented in Figure; 7 . The energy band gap is deduced from interpolation of the linear part of the curve with the energy axis. The optical energy band gap of the films increased from 3.21 eV to 3.41 eV as the laser fluence increased from 0.8 J/cm^2 to 1.6 J/cm^2 and then decreased to 3.1 eV at laser fluence of 2.4 J/cm^2

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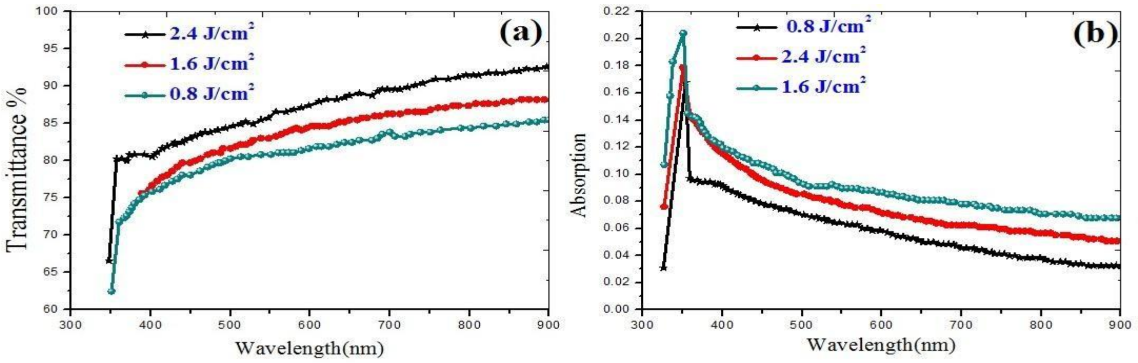

Figure 6. (a) Optical transmittance and (b) Absorption spectra of the ZnO/α-Al2O3 thin films are grown at 400 oC substrate temperature, with different energy.

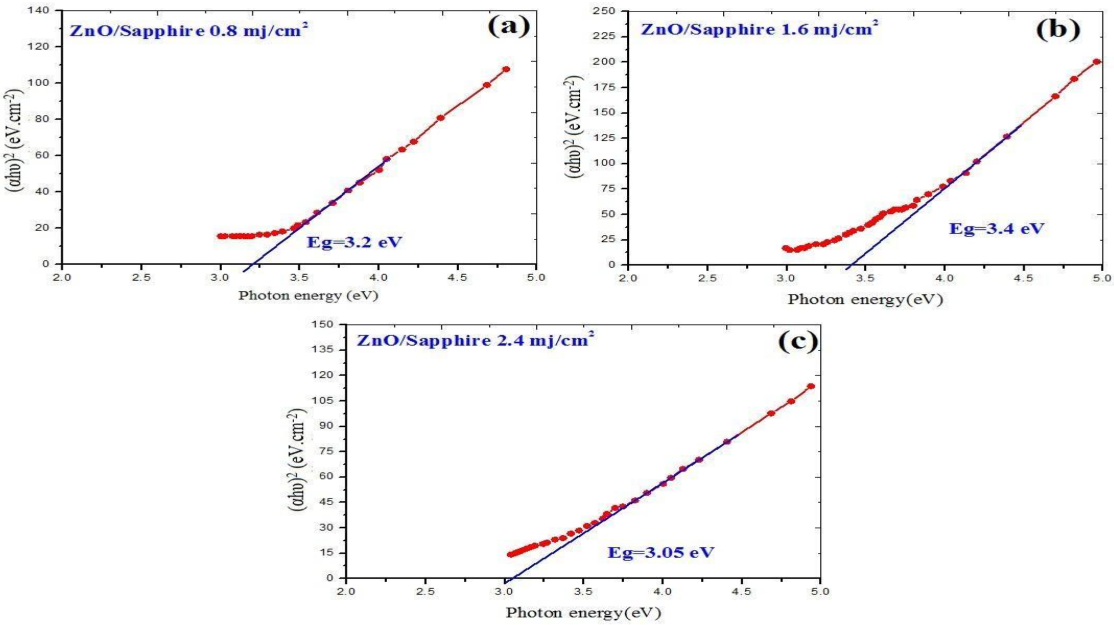

Figure 7. (αhν) with hν to determine the E_g of ZnO/α-Al_2O_3thin films are grown at 400 ^{o}C substrate temperature at (a) 0.8 J/cm^2, (b) 1.6 J/cm^2, (c) 2.4 J/cm^{2}crystalline structure of the films is hexagonal wurtzite with (002) crystalline orientation.

Conclusions

ZnO films were deposited on α-Al_2O_3 substrate by Pulsed Laser Deposition. The structural and optical properties are established to be reliant on the laser fluence. The
The average transmittance for all prepared samples is over 85% in the visible wavelength range of the spectrum. The optical energy band gap E_g is dependent on the laser fluence with the highest E_g observed for the 1.6 J/cm^2 energy density depositedsample. From SEM the average grain size is roughly estimated to be 21.31 -40.67 nm. The strongest UV emission around 378 nm with a narrow full width at half maximum (FWHM) of 19.12 nm is observed for the films deposited at 1.6 J/cm^2.

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