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The effect of laser parameters (frequency and fluency) on the optical and structural characteristics of ZnO films deposited by PLD method

Scientific research paper

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ABSTRACT

The pulsed laser deposition is a practical synthesis route because of its unique advantages in growing various materials. Furthermore, the quality of thin films depends on different parameters in the deposition process. Meanwhile, ZnO has many applications in manufacturing optics, electronics, and optoelectronics instruments because of its exclusive properties. We have set up a PLD array to deposit the ZnO thin films on glass substrates. This study investigates the structural and optical characteristics of the films deposited at two different pulse repetition rates. Based on the optical-microscopic images and the scanning electron microscope (SEM) micrographs of films, increasing pulse repetition rate increases the uniformity of the particle size distribution and enhances film thickness. Also, the optical characterization performed by UV-Visible spectroscopy shows that the absorption and transmission rate, bandgap energy, and crystalline quality of the films can adjust by tuning the pulse repetition rate.

1 Introduction

Pulsed Laser Deposition (PLD) has emerged as a most popular synthesis technique because of its attractive principal features like simplicity implementation, high deposition rate, stoichiometric transfer material from target to the substrate, the possibility of deposition in a wide range of temperatures, and the possibility of depositing at different background pressures. PLD is a physical vapor deposition technique that can form various materials in various structures like thin films, multi-layers, nanostructures, and epitaxial films [1–3]. During the PLD process, carried out in a vacuum system, a high-energy beam of the pulsed laser focuses on the located target, resulting in evaporation/ablation on the target surface and removing a part of the material. Rejected materials produce a highly forwarded direct plume to the substrate, condense on it, and form the thin film [4].

ZnO has unique properties that make it a helpful semiconductor with its wide range of applications in optics, electronics, optoelectronics, and energy-saving industries. The direct wide bandgap (3.37 eV at room temperature) with a large exciton binding energy of 60 meV and high electron mobility and irradiation resistance makes it an ideal candidate for UV detection. The most common ZnO applications are luminescent materials, transparent conductive contacts, surface electro-acoustic wave devices, thin-film gas sensors, ultraviolet (UV) lasers, varistors, and solar cells [5–10]. Moreover, many different synthesis techniques prepare

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ZnO thin films like sputtering, reactive thermal evaporation, spray pyrolysis, sol-gel [14], and PLD [12].

The mentioned benefits above make PLD an exciting route for researchers. As many papers reported, the quality of the deposited ZnO films is directly impressed by deposition parameters like background pressure, substrate temperature [15], irradiation parameters, and post-annealing conditions[16–18]. Laser beam energy, pulse duration, pulse repetition rate are the effective irradiation parameters on the film's quality [19].

Energy density plays a key role in the ablation process, and subsequently by related properties of laser-induced plasma plume would influence the film properties [20]. The fluency should override the binding energy of target material constituents to remove an atom from the target surface by a laser pulse. Therefore, the ablation rate from the target is a function of laser fluency [21].

The pulse repetition rates (PRR) mainly impress the final film quality via two different effects. On one side, the pulse laser frequency has particularly affected the time interval for the ZnO plume towards the substrate. As a result, the adatoms do not have enough time intervals to locate the proper position in the lattice structure for the high pulse repetition rates [22]. On the other hand, at the high pulse repetition rate, the time between two laser pulses is not enough, so the temperature of the target surface cannot decrease to its initial amount. Thus, the next pulse operates at a higher temperature. This thermal effect causes an increased ablation efficiency due to a higher repetition rate [23]. According to the simulation results, more and smaller islands can be formed at higher pulse frequencies. The reduced island size can enhance the diffusion of adatoms from the top of the growing islands to lower levels on the substrate, resulting in a smoother film surface. On the contrary, lower pulse frequencies can diminish surface smoothness due to the reduced island density and the elevated average island size [24]. This contradiction leads to an optimum PRR value.

Most PLD processes use the Excimer lasers with higher energy and lower wavelength (KrF: 248 nm) and higher vacuum orders. The ZnO films grown by the shorter wavelength lasers show much higher quality because the higher wavelengths lead to subsurface heating of the target and producing undesirable defects [20]. Since excimer lasers often have higher energies with an almost flat top energy profile compared to the Gaussian energy profile of Nd: YAG lasers, the fluency varies intrinsically. This variation is therefore included in the deposition parameters [25].

We have previously designed and set up a PLD system to optimize it with a well-known Zinc Oxide material [26]. A Q-switch Nd YAG laser (1064 nm wavelength (1 Jcm-2) and 10-5 mbar) was employed as the irradiation source. These conditions thoroughly result in different film characteristics. The optical band gap and Urbach energy were calculated for the samples deposited by various fluencies as effective parameters. Moreover, we investigated the annealing effect [26], substrate heating mode [27, 28], and the growing seed layer effect on the film quality.

Although most of the laser parameters have been investigated in some publications [20, 22], the effects of PRR and fluency on the film's optical properties (band gap and Urbach energy) have been rarely investigated. Instead, the publications studied the effects of deposition parameters on the growth of different ZnO structures [29], doping ZnO films with other materials [30, 31], or the other optical characteristics of the films (photoluminescence) [22].

This paper also investigates ZnO film properties for two different PRRs to study the impact of laser repetition rate on the optical and structural characteristics of the films.

2 Method

2.1 Experimental setup

A PLD set-up consists of a vacuum system and a Q-switch Nd: YAG laser irradiation source (up to 216 mJ/pulse, 5 ns pulse duration, 1-10 Hz PRR at the 1064 nm wavelength). The vacuum system includes a deposition chamber, a high vacuum-mixing table, and pressure measurement tools. As shown in Fig. 1a, the irradiation chamber was fabricated of stainless steel, ~300 cm^3, with triplet windows and the target and substrate holder facing each other. The target holder is positioned at a 45° angle with the incident laser beam (Fig. 1b).

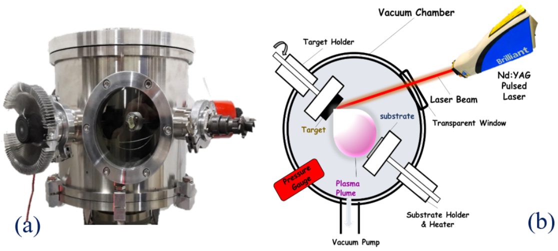

Figure 1. (a) The triplet- windows vacuum chamber. (b) The schematics of the PLD system mechanism

A ZnO tablet with 270 mm diameter and 3mm thickness is used as the target. It is prepared from the high purity ZnO powder (99.99%), pressed by 104 kPa hydrodynamic pressure at room temperature in a holder. The cubic glass slides (used as the substrates) were ultrasonically cleaned in soapsuds, acetone, and ethanol for 10 minutes per stage, dried in nitrogen flow, and then fixed on the substrate holder into the vacuum chamber distances 3.5 cm from the target.

2.2 Deposition Conditions

The chamber was evacuated up to the pressure of 5-10 mbar by a diffusion pump and a one-stage rotary backup pump. The background pressure was monitored by Pirani and penning gauges. The substrates were preheated to 350°C before starting the deposition process by an electric heater. Then the target was exposed by laser with 1 J/cm^2 fluency and the parameters summarized in Table 1. The final films post-annealed at 400° for 30 minutes after completing the deposition process.

Table 1- Laser irradiation parameters

Sample	P. R. R. (Hz)	Laser Fluence (J/cm^2)	Time exposure (min)
PRR 3.3	3.3	1	50:50
PRR 5	5.0	1	33:34

3 Results and discussion

Since the pulse frequency ranges between 1 to 10, we set 3.3 and 5 Hz as the studying cases located in the medium intervals. Therefore, PRR 3.3 and PRR 5 stand for the film deposited with 3.3 Hz and 5 Hz, respectively.

3.1 Structural and Morphological analysis

Figure 2 represents optical images of the film surfaces. It can be seen that the film deposited with the higher repetition rate (PRR 5) shows a highly condensed and uniform surface covering the whole substrate (Fig. 2b). In fact, by increasing the pulse repetition rate, the particles aggregate together and make films with higher density. The SEM images are another evidence for this claim.

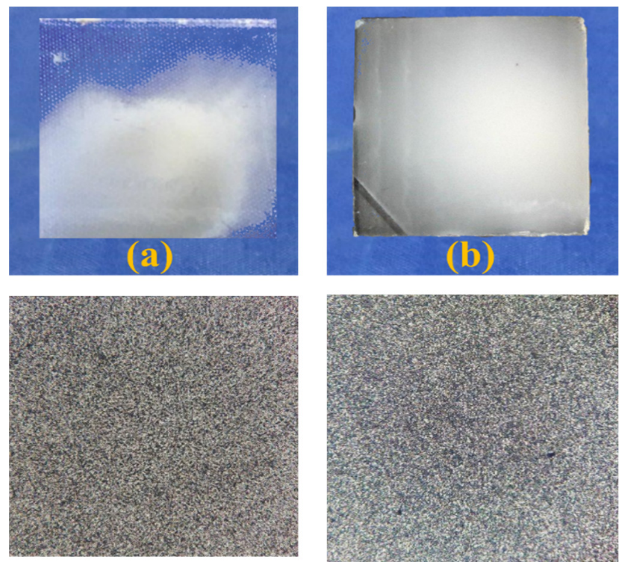

Figure 2. The photos and their optical microscopy images of:
(a) PRR 3.3 and (b) PRR 5.

In Fig. 3, The SEM micrographs of the film surfaces represent the porous structure of the layers. It indicates that an increase in pulse repetition rate causes an increase in the average particle sizes. The grain size is estimated to be 20-40 nm and 60-80 nm for PRR 3.3 and PRR 5, respectively.

Therefore, accumulated nanoparticles during a higher deposition rate result in the creation of greater particles. In addition, the thermal effects, as mentioned before, increase the ablation efficiency for PRR 5. Therefore, the same laser fluency can ablate the greater particles. Furthermore, the cross-sectional SEM images in Fig. 3 show the estimated film's thickness to be 1 µm and 1.18 µm for PRR 3.3 and PRR 5, respectively. This thickness growth (18%) occurred during the high pulse repetition when the subsequent deposition process occurs before the activated states are energetically released [29].

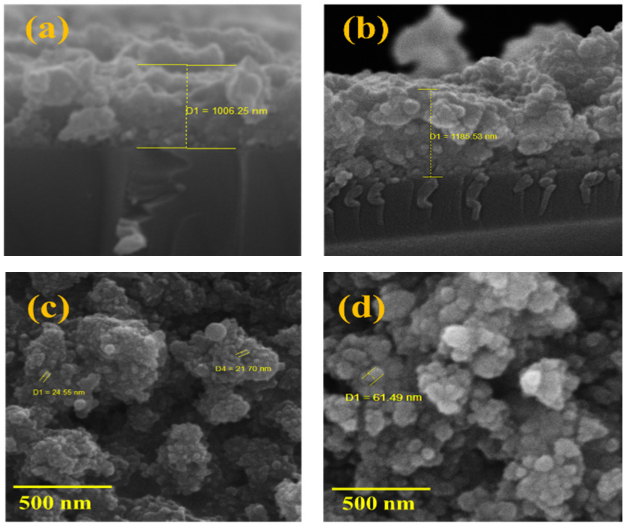

Figure 3. The morphological SEM micrographs of the film's surface (a) PRR 3.3 and (b) PRR 5. The cross-sectional SEM images of (c) PRR 3.3and (d) PRR 5.

3.2 Optical analysis

3.2.1 Effect of the Pulse Repetition Rate

Figure 4 shows the UV-Vis spectrum of the films. The inner picture relates to the films' absorbance. Both samples have an absorption peak near the UV region contributed to the ZnO bandgap. However, there is a blue shift in the absorption peak wavelength for PRR 3. It is at a value of 343 nm whereas 346 nm for the other one (about 0.03 eV). This partial shift results from the increasing size of the film's particle confirmed in SEM images (Fig. 3) [32].

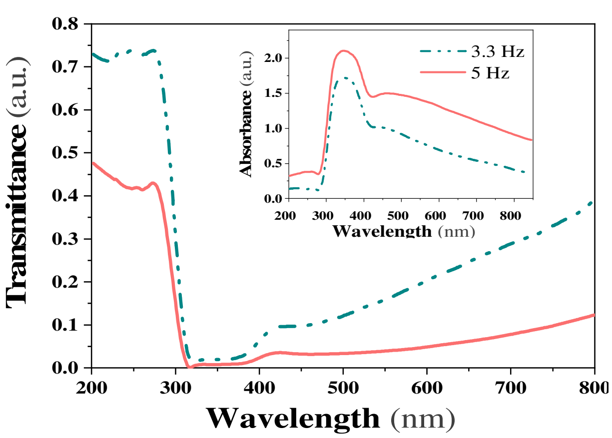

Figure 4. Absorbance and Transmittance spectra of films in ultraviolet and visible region

Compare the films' absorbance spectra at a glance, determine that the absorption of the films deposited with higher pulse laser frequency increased in the ultraviolet and visible region. This enhancement can be caused by increasing deposition rate, which leads to a rise in film's thickness, thereby enhancing the absorption of incident photons in the film and the scattering at the film surface that lower the optical transmittance [17].

Since the measured reflectance was negligible, the transmittance spectrum came from Eq (1), where A and T return to the absorbance and transmittance, respectively:

$$T = 10^{-A} . \tag{1}$$

As shown in Fig. 4, the optical transmittance of films sharply decreases in the near UV region due to bandgap absorption. According to the transmittance spectra, the film's absorbance reduces by 25% in the ultraviolet region and 10-30% in the visible region for PRR 3.3 compared to the other one. The lower transmittance value could be due to several factors such as film defects, particulates onto the surface, and light scattering at the rough surface, high thickness [33].

For the materials having direct transition like ZnO, the optical band gap energy is determined by the Tauc relation as follows (Eq. (2)):

$$\alpha h\nu = A(h\nu - E_g)^n \ , \tag{2}$$

$$T = e^{-\alpha t} , \tag{3}$$

Where α is the absorption coefficient, t attributes to film's thickness obtained from cross-sectional SEM images, hν equals to incident photon's energy, E_g is the energy gap, and n is a constant at a value of 0.5 for ZnO. The Tauc graph plotted in Fig. 5a, with $(\alpha h\nu)^2$ along the y-axis and hν along the x-axis, gives the optical bandgap with a sharp edge absorption using linear approximation. As shown in Fig. 5, the bandgap narrowed by 0.09 eV in the film with a higher pulse frequency. According to the references, a blue shift in the optical band gap occurs due to the relatively higher carrier concentration [34].

Presence of tail absorption profile in the visible region (Fig. 4, inner Pic), induced by optical absorption on intrinsic defects of the film's structure, so-called

"Urbach energy or Urbach tail width." The Urbach tail occurs due to a structural disorder. This energy characterizes as a consequence of all created defects in the film [33]. The Urbach energy can be estimated by the Urbach low as:

$$\ln\alpha = \ln\alpha_0 + \left(\frac{\nu}{E_u}\right), \tag{4}$$

where α_0 is a constant, and E_u Urbach energy is obtained from the slope of linear fit on the plot of lnα versus hν (Fig. 5b). The numerical value of the Urbach energy is 0.50 and 0.25 related to PRR 3.3 and PRR 5, respectively. As mentioned, this reduction in E_u value is due to a decrease in the number of defects in the film deposited with a higher pulse repetition rate. These results were well agreed with the similar works. They both indicated the formation of a higher quality film with the lower defect concentrations for the samples that depend on the pulse repetition rate. Thus, the results confirm each other; however, the approaches used for analyzing the samples are different [22].

3.2.2 Effect of the Laser Fluency

Laser fluency describes the optical energy delivered per unit of area (laser energy density). It comes from Eq. (5) for each laser pulse:

$$\text{Fluency} = \frac{\text{Laser Energy (J)}}{\text{Beam Area}\left(\text{cm}^2\right)}. \tag{5}$$

According to the above equation, fluency can be controlled by energy per pulse and the effective laser spot area. Therefore, we study four different fluencies (F1, F2, F6, and F14) by changing these two parameters. The parameters are summarized in Table 2.

Although the deposition rate varies linearly with the fluency, it has not affected the film texture, in 1064 nm wavelength, as also concluded by other publications [35].

Figure 6 shows the optical images of the samples. All samples were deposited in the same condition; however, F6 and F14 (with the higher fluency) indicated poor coverages. Such that some separated particles were settled on the substrate without a film formation. This is due to the high kinetic energy of the materials, which does not allow particles to locate on the substrate surface.

Table 2- Laser parameters

Sample	*F1*	*F2*	*F6*	*F14*
Energy per Pulse (mJ)	216	216	47	112
Laser Spot (mm)	5.2	4	1	1
Fluency (J/cm²)	1	2	6	14

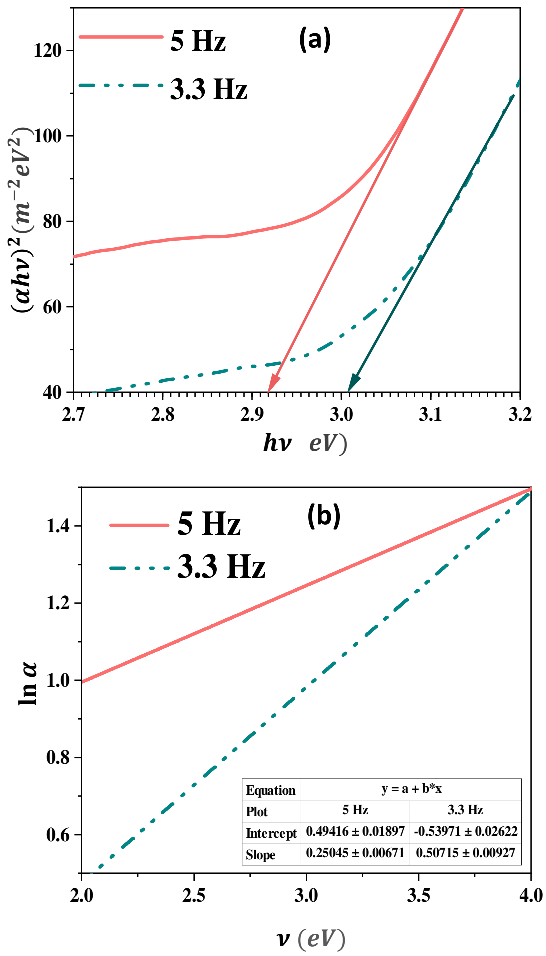

Figure 5. (a) Tauc graph ($(\alpha h\nu)^2$ versus hν) for ZnO samples; (b) Logarithmic plot of absorption coefficient versus photon energy.

The absorbance and transmittance spectra of the films in the ultraviolet and visible region are shown in Fig. 7. As we expected, F6 and F14, with their low surface coverage, have a little absorption and a small peak in the absorption edge at about 335 nm wavelength. According to information obtained from films' structure and UV-Vis spectra, the optical properties have been investigated for F1 and F2 (the films with the higher quality) using the Tauc plot and Urabch tail.

The Tauc plot in Fig. 8 obtains the films' optical bandgap. There is a slight blue shift in absorption edge for F1 and shows an enhancement in its band gap by 0.05 eV. Consequently, the average size of the particles in this sample is smaller than that of F2.

According to the absorbance tail in the visible region for both samples, defects in the films' structures are expected. Thus, Urbach energy is estimated based on Eq. (4) and plotted in Fig. 8. The Urbach energies are obtained about 0.8 and 0.6 for F1 and F2, respectively. As a result, it can be concluded that the concentration of defects decreased in the film deposited with higher fluency. These results are in good agreement with the published results regarding the defects prior to the present study [21, 25].

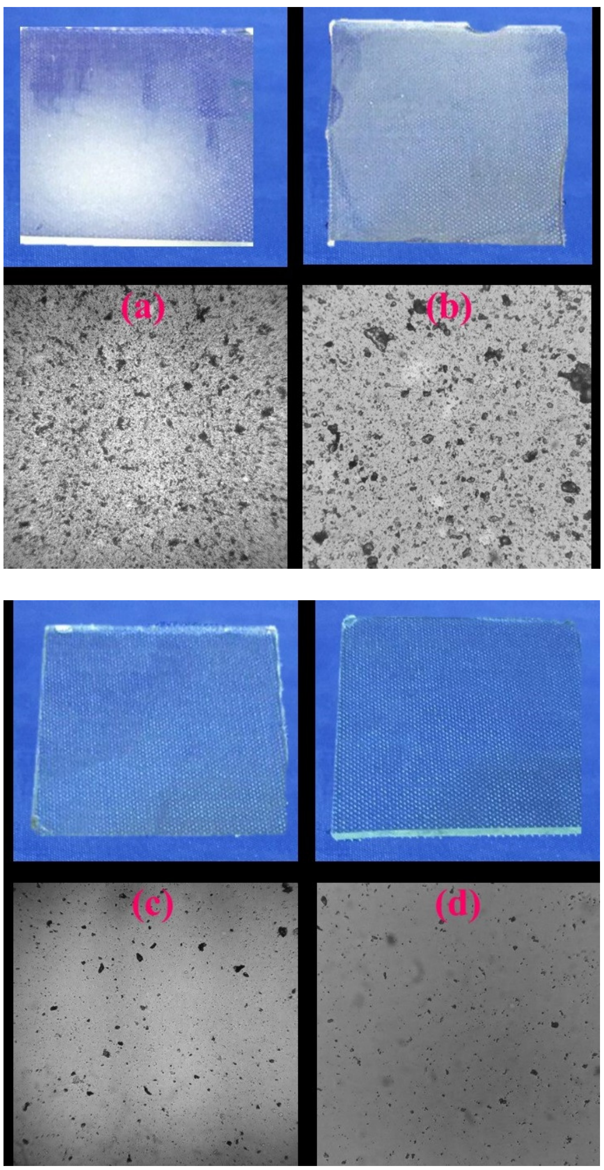

Figure 6. The photos and their optical microscopy images of: (a) F1, (b) F2, (c) F6, and (d) F14.

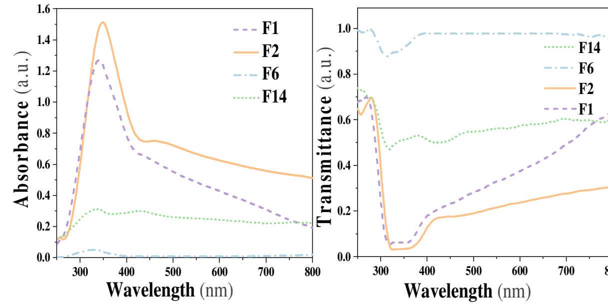

Figure 7. Absorbance and Transmittance spectra of films in ultraviolet and visible region

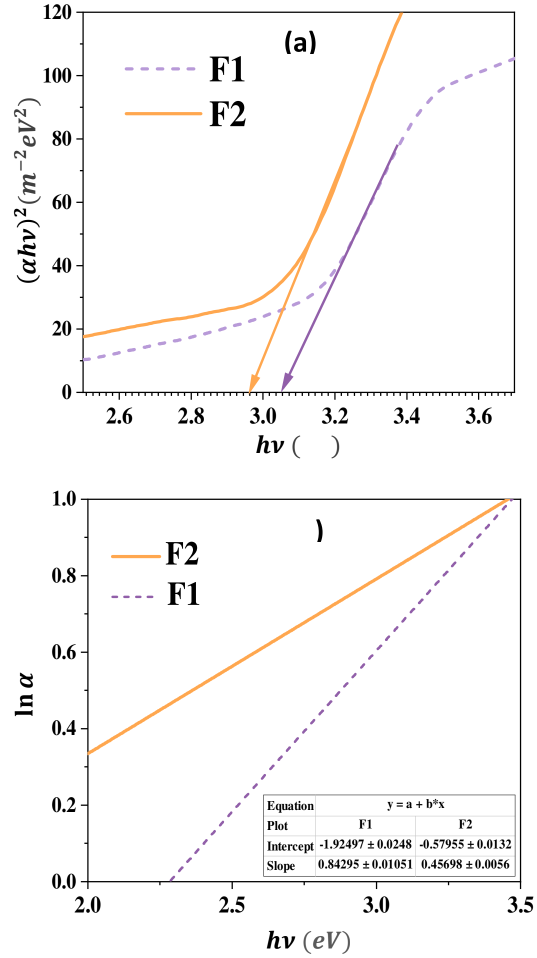

Figure 8. (a) Tauc graph for ZnO samples; (b) Logarithmic plot of absorption coefficient versus photon energy.

4 Conclusions

In summary, ZnO films are successfully prepared by pulsed laser deposition technique on the glass substrate. Structural and morphological results are affected by deposition rates based on SEM micrographs. The pulse repetition rate increases the deposition rate, the island density, and the film thickness. Furthermore, pulse repetition rate influences the optical properties of the ZnO films by affecting the number of defects in their structures. As the results indicated, the laser fluency can affect the bandgap energy of the films and their defect densities.

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