Characterization of ZnO Film Grown on Different Substrates Using PLD

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أفنان كمال يوسف
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كانون الثاني 2010
1. Motivation

Nowadays, most of the principal optical devices – like light generators, detectors, transmitters, splitters, etc – have been demonstrated. Currently, research is focused on reducing the dimensions of these devices and implementing them as structural elements in integrated optical systems. Hence, new techniques need to be developed for fabrication of such systems with dimensions of the individual element down to the micrometer range [1].

Dielectric oxide materials demonstrate some properties that make them advantageous for certain applications. They are insulators with a wide band gap and therefore transparent in the wide wavelength range from ultraviolet to mid-infrared. Oxides reveal an excellent chemical and mechanical property and do not show deterioration.

In dielectric laser media, transitions between the energy levels of a dopant ion occur and, thus, the excitation states are typically localized.

ZnO has great advantages for light emitting diodes (LEDs) and laser diodes (LDs) over the currently used semiconductors. Recently, it has been introduced that ZnO as II–VI semiconductor is promising for various technological applications, especially for optoelectronic short wavelength light emitting devices due to its wide and direct band gap. The most important advantage is the high exciton binding energy (60 meV) giving rise to efficient exciton emission at room temperature [4]. As it is well known, exciton is a pair of electron and hole bound due to cumbolic interaction and plays an important role near the band edge for the resulting optical characteristics of the semiconductor.

A number of different techniques can be employed for the deposition of oxide materials, including electron beam evaporation (EBV), chemical vapor deposition (CVD), molecular beam epitaxial (MBE), ion-assisted deposition (IAD) and sol-gel methods [5].

Pulsed laser deposition (PLD) proved to be a favorable technique for the deposition of Zinc oxides at different technological conditions on different
substrates. That supposed to result in the different structural and microstructural properties, different surface morphology of the nanostructures to be obtained. Also the optical properties of ZnO are known to be sensitive for its structural quality \[^6\].

Recently stimulated emission and lasing action due to excitonic recombination at a very low threshold has been reported by optically pumping the highly c-axis oriented thin ZnO film grown on (0001) Sapphire substrate using Pulsed Laser Deposition technique \[^7\].

### 1.1 Fundamental of Pulsed Laser Deposition

Although laser evaporation technique was first used to make thin films even in the 1960s \[^8\], pulsed laser deposition (PLD) uses high-power laser pulses with an energy density of more than \(10^8 \text{Wcm}^{-2}\) to melt, evaporate, excite, and ionize material from a single target.

If the laser energy density is sufficient for ablation of the source target, the material evaporates, forming gas plasma with the characteristic shape of a plume. This plasma plume expands along the direction normal to the target surface. When it reaches a substrate, placed in front of the target, part of the evaporated material will form a thin film on this substrate.

The described PLD process can mainly be divided into four regimes \[^9\]:

1. The interaction of the laser beam with the target resulting in evaporation of the surface layers (evaporation regime).
2. The interaction of the laser beam with the evaporated materials causing the formation of isothermal expanding plasma (isothermal regime).
3. The anisotropic three-dimensional adiabatic expansion of the laser-induced plasma with a rapid transfer of thermal energy of the species in the plasma into kinetic energy.
4. Thin film growth.

Due to the correlation between these physical mechanisms involved in PLD process, only an approximated description of the phenomenon is
possible. This is the reason why a theoretical model does not exist to describe the whole PLD process. Instead, there exist several models, each of them analyzing in detail only one aspect of it, as the vaporization, the plasma formation and its expansion in vacuum or in presence of an ambient gas \cite{10}.

In particular, plasma expansion dynamic, that plays a crucial role in pulsed laser deposition, is not yet totally understood, even in the simpler case of propagation in vacuum. Furthermore, the expansion behavior is even more complex in the presence of an environmental gas, often used during PLD deposition of complex oxides.

In such case, additional physical processes affect the plume expansion behavior, such as plume deceleration and splitting, shock-wave formation, thermalization, etc. as a consequence of plasma–background gas interaction \cite{11}.

1.2 Brief overview of ZnO characteristics

The unique and fascinating properties of II-VI compound semiconductors have triggered tremendous motivation among the scientists to explore the possibilities of using them in industrial applications. Zinc oxide (ZnO) is a piezoelectric, dielectric, transparent, semiconducting oxide and optoelectronic applications in UV-Blue spectral range \cite{12}. In addition, due to its wide band direct band gap and its large photo response, ZnO is also very suitable for UV photo-detector application \cite{13}.

ZnO with a direct band gap of 3.37 eV at room temperature and a large excitation binding energy (60 meV), which is 2.4 times the effective thermal energy (K_pT=25meV) at room temperature, and biexcitation energy is 15meV. This is one of the key parameters that ZnO exhibits near-UV emission, transparency, conductivity, and resistance to high temperature electronic degradation \cite{15}.

ZnO crystallizes into a rugged Wurtzite structure which has two interpenetrating hexagonal sub-lattices of Oxygen and Zinc atoms
respectively, shifted along the c-axis by 5c/8. Another crystalline phase of ZnO which is cubic Zinc bland, although rarely observed, has also been reported by a few groups \cite{16}. The high cohesive energy of ZnO which is ~ 1.89eV makes it a highly stable and perhaps the most radiation hard material amongst the direct band gap semiconductor family, which ensure a long life and a high degradation threshold of ZnO based optoelectronic devices.

The high melting and boiling points of ZnO allow one to explore a variety of heat treatments required for alloying purposes and device formation. Being an oxide, ZnO also enjoys the extreme stability against the oxidation problem which can severely affect the device performance as in case of some of the III-V and II-V semiconductors such as GaAs, InAs and ZnS etc\cite{17}.

The grown thin films exhibited hexagonal grains of size ~ 50 nm well arranged in a honey comb fashion. The grain boundary between the grains served as cavity mirrors. The observed low threshold of pumping for efficient stimulated emission was attributed to the excitonic recombination.

Quantum confinement of excitons can further enhance the excitonic binding energy and may result in other interesting properties including extremely low threshold of lasing\cite{18}.

Table 1.1 shows a compilation of the basic physical parameter for ZnO. Still some uncertainty exists in these values. For example, in few reports it has been mentioned physical properties of wurtzite ZnO and therefore the hole mobility and effective mass.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice parameters at 300 K</td>
<td></td>
</tr>
<tr>
<td>(a_0, c_0)</td>
<td>0.32495 nm, 0.52069 nm</td>
</tr>
</tbody>
</table>
### 1.3 Historical background and Evolution

The efforts toward using Lasers in depositing thin films started soon after the invention of reliable high power lasers. Early observations of the ease with which the material could be vaporized by the intense interaction of high power laser pulses with material surface demonstrated that the intense laser radiation could be successfully used to deposit thin films of that material.

Despite an early successful demonstration of efficacy of the PLD, initial development was rather slow and even stagnant until 1980s. During this period, the deposition of semiconductor thin films was carried out using PLD only with limited success. The PLD of III-V semiconductors were mostly unsuccessful due to non-stoichiometric deposition probably owing to the high vapor pressure of constituents which resulted in the deficiency of group V elements in the grown structures

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<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.345</td>
</tr>
<tr>
<td>Density</td>
<td>5.606 g cm⁻³</td>
</tr>
<tr>
<td>Stable phase at 300 K</td>
<td>Wurtzite</td>
</tr>
<tr>
<td>Bond length</td>
<td>1.977μm</td>
</tr>
<tr>
<td>Melting point</td>
<td>1975 °C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>0.6 W.cm⁻¹°C⁻¹</td>
</tr>
<tr>
<td>Linear expansion coefficient (/C)</td>
<td>a: 6.5 × 10⁻⁶ , c:3.9 × 10⁻⁶</td>
</tr>
<tr>
<td>Static dielectric constant</td>
<td>8.656</td>
</tr>
<tr>
<td>Refractive index for Zinc blend</td>
<td>2.008</td>
</tr>
<tr>
<td>For Wurtzite structure</td>
<td>2.029</td>
</tr>
<tr>
<td>Energy gap</td>
<td>3.4 eV, direct</td>
</tr>
<tr>
<td>Intrinsic carrier concentration</td>
<td>&lt;10⁶ cm⁻³</td>
</tr>
<tr>
<td>Exciton binding energy</td>
<td>60 meV</td>
</tr>
<tr>
<td>Electron effective mass</td>
<td>0.24</td>
</tr>
<tr>
<td>Electron Hall mobility at 300 K for low n-type conductivity</td>
<td>200 cm² V⁻¹ s⁻¹</td>
</tr>
<tr>
<td>Minimum pressure at melting point</td>
<td>7.82atm</td>
</tr>
<tr>
<td>Ionicity</td>
<td>62%</td>
</tr>
<tr>
<td>Heat capacity Cp</td>
<td>9.6 cal/mol K</td>
</tr>
</tbody>
</table>
The year **1990**s brought rapid development of laser technology, which made PLD more competitive. By then PLD was extensively used to fabricate crystalline films of superconducting, ferroelectric, ferromagnetic oxides with epitaxial quality and their multilayer structures.

**In [1995] Craciun et al.**[^23] studied the transparent, electrically conductive and c-axis oriented ZnO thin films on silicon and Coming glass substrates employing either a KrF Excimer laser ($\lambda = 248$ nm) or a frequency-doubled Nd:YAG laser ($\lambda = 532$ nm). The quality of the ZnO layers grown by the shorter wavelength laser was always better than that of the layers grown by the longer wavelength.

**In [1997]**[^25] epitaxial thin films of ZnO were being grown by **Bagnall et al.** using plasma-assisted MBE at Room temperature optically pumped lasing. The lasing threshold was reported to be 240 kW/cm$^2$ for 300 nm films, pumped by a Q-switched Nd: YAG laser (10 Hz, 6 ns FWHM).

**Jin et al [2000]**[^28] deposited ZnO thin films on sapphire by using Nd: YAG pulsed laser ($\lambda=355$nm, 5 Hz) with the laser energy density of 2.5 J/cm$^2$ at a substrate temperature of 400°C. It was concluded that the UV luminescence intensity depends strongly on the stoichiometry in the ZnO film rather than the micro-structural quality of the crystal. In the same year, ZnO films were grown on (0001) sapphire substrate by **Bae et.al.**[^29]. The laser energy density was 2.5 J/cm$^2$. Pulsed Nd: YAG laser with a wavelength of 355 nm and a repetition rate of 5 Hz was used. Strong UV luminescence was obtained by increasing the substrate temperatures of ZnO films. This study suggests the possibility of using ZnO thin films in light emission device applications.

**In [2001]** ZnO films were deposited by **Jin et al.**[^31] on sapphire substrates by using an Nd: YAG pulsed laser ($\lambda=355$ nm, 5 Hz) with the laser...
energy density of 2.5 J/cm², at substrate temperatures of 400°C. The PL intensity of ultra-violet (UV) luminescence and the electrical resistivity generally increase as the oxygen pressure for the PLD of ZnO increases. The best quality with the minimum intensity ratio (defect related/UV) is obtained from the ZnO sample.

In [2002] a series of ZnO films with various thicknesses were prepared by Park et al. [34] on (0001) sapphire substrate by pulsed laser deposition (PLD) and Using a Nd: YAG pulsed laser with a wavelength of 355 nm. The laser repetition rate and energy density were maintained at 5 Hz and 2.5 J/cm², respectively. It is found that the crystalline quality, electrical and optical properties of the films strongly depend on the film thickness. It was believed that the films thicker than 400 nm were almost strain-free and exhibit the near-bulk ZnO properties.

Kaidashev et al. [2003] [35] studied the high electron mobility of A multistep pulsed-laser deposition (PLD). Process was presented for epitaxial, ZnO thin films on c-plane sapphire substrates. They obtained high electron motilities in a narrow carrier concentration range. The samples showed flat surface structure with grain size of about (0.5–1) μm, whereas the surfaces of low-mobility films consist of clearly resolved hexagonally faceted columnar grains of only (200-nm) size. In the same year Barik et al. [36] deposited ZnO QDs embedded in Al₂O₃ matrix at room temperature. Third harmonic of Q-Switched Nd:YAG laser (355 nm, 6 ns, and 10 Hz) with a fluence of ~4 J/cm² have successfully grown a multilayer of alumina capped ZnO QDs using PLD and observed conspicuous size dependent blue shift in the band gap of such a QD matrix.

In [2004] Shan et al. [37], prepared ZnO films on different substrate at different temperatures by using KrF Excimer laser (λ =248nm, τ=25ns) at about 1 J/cm² laser density. They found that all films showed (002)
orientation at the optimized conditions. Photoluminescence (PL) results indicate that the thin films fabricated at the optimized conditions show the intense near band PL emissions.

In this period of time Sans et. al. \cite{Sans} reported on the structural features and optical properties of wurtzite ZnO films epitaxial grown on sapphire, fluorite and mica substrates by means of pulsed laser deposition (PLD). Low cost mica substrates have been shown to be suitable to obtain ZnO thin films with optical and structural qualities suitable for optoelectronic applications.

Suchea et. al. \cite{Suchea} prepared Zinc oxide transparent thin films (ZnO) with different thickness by dc magnetron sputtering and pulsed laser deposition (PLD) techniques using metallic and ceramic targets onto silicon and Corning glass substrates using XeCl Excimer Laser 308 nm wavelength. This work indicated that the film surface characteristics were strongly influenced by the deposition technique and conditions applied, thus providing a tool for the enhancement of the film sensing capabilities.

Also Lorenz, et. al. \cite{Lorenz} studied the effect of N$_2$, N$_2$O and O$_2$ background gas on ZnO thin films grown by pulsed laser deposition (PLD) on $\alpha$-plane sapphire. Films with rough surface showed a broadening and splitting of the room-temperature CL peak into maxima at 3.21 and 3.26 eV, which could be due to either grain morphology or spatial variation of the electronic defect structure.

In \cite{Cho} Cho observed the effect of substrate temperature on the structure and the exciton lifetime of ZnO films. The surface roughness generally increases as the substrate temperature increases. The lifetime for the ZnO film deposited at 400$^\circ$C is found to be 168 ps. In the same year Zhao et.al. \cite{Zhao} studied ZnO thin films with c-axis (002) orientation growth on quartz glass substrate. High-quality ZnO films was obtained at such low temperature (100–250)$^\circ$C. The ZnO films obtained at different substrate temperatures have nano-crystalline structure with grain size in the range of about 30– 45 nm. The as-deposited films showed ultraviolet emission and
accompanied deep-level emission in PL spectra. However, the ZnO film deposited at substrate temperature 200°C exhibited strong UV emission with no deep-level emission due to its low intrinsic defects.

In 2007 Yamaguchi et al. fabricated ZnO films by PLD method with bias voltage to decrease defects in ZnO. The bias voltages of (-500 and +500)V were applied between the grid over substrate and the target to control the potential difference between the plume and the target. ZnO films were grown on Al$_2$O$_3$ substrates at substrate temperatures 20 and 700°C. However, applying bias voltage of -500V deteriorated the film surface condition and increased the density of defects. Also Novotny et al. in the same time found that the resistivity and carrier concentrations of ZnO thin films grown by pulsed laser deposition in the presence of active ionic or neutral nitrogen species, generated in an electron cyclotron resonance N$_2$ plasma source, were measured as a function of the source microwave power and substrate temperature. Most of the thin films were n-type, although in conditions leading to increased activation of the ionic nitrogen species, p-type behavior was observed.

In 2008 ZnO thin films were simultaneously deposited on sapphire (001) and Si (100) substrates at 5000°C by pulsed laser deposition. The ZnO film grown on sapphire had a smoother surface and smaller grain size, and exhibited a sharper X-ray diffraction peak with a smaller full width at half maximum compared to those on Si.

Simultaneously Sui et al. deposited ZnO films on c-plane (0001) sapphire substrate at 250 °C. It is observed that the band gap energy red shifts nonlinearly from 3.345 to 3.153 eV with increasing temperature. These properties are highly advantageous for the design and fabrication of ZnO-based fiber-optic temperature sensors, especially in the biological measurement.

Also Kang, et al. study the relationship between the ultraviolet emission and electron concentration of ZnO thin films were deposited on
(0001)Al$_2$O$_3$ substrates. And they found that the variation of electron concentration of pure ZnO is more related to that of UV emission intensity than that of visible emission intensity. It is because that free-electron-neutral-acceptor transition as origin of UV emission at room temperature is related to impurity concentration of pure ZnO.

In [2009] Wei and Zhang\textsuperscript{[63]} using ZnO powder and ceramic target to prepared ZnO/Si thin films obtained in O$_2$ ambient at pressure 1.3Pa and study the effect of temperate on the structural and optical properties of these films investigated systematically by XRD, SEM, FTIR, and PL spectra. A pulsed Nd:YAG laser with a wavelength of 1064 nm (repetition rate is 10 Hz and the pulsed duration is 10ns).

At this time Zhaoyang, and Lizhong\textsuperscript{[64]} studied the effect of oxygen pressure on the structural and optical properties of ZnO thin films deposited on Si (111) by using KrF Excimer laser was operated at wavelength of 248 nm and repetition rate 5Hz. The laser energy density was about 2.5 J/cm$^2$.

They found that the increasing of oxygen pressure from 1 Pa to 50 Pa contributed to the size of ZnO grains and then promote the UV emission of the films. In the same year Premkumar et. al.\textsuperscript{[65]} they deposited ZnO films on GaN and Sapphire substrate by PLD by using three different laser wavelengths Nd:YAG (1064nm, 532nm) and KrF(248nm). They found that the films grown at $\lambda$=532nm revealed the presence of ZnO nanorods and microrods. With diameter various from 250nm to 2$\mu$m and the length various between the 9 and 22$\mu$m.

Yu et al.\textsuperscript{[66]} studied the relationship between the photoluminescence and conductivity of undoped ZnO films grown on glass substrate with various oxygen pressures. The intensity of the deep-level-emission (DLE) and conductivity generally increased as the oxygen pressure decreased. The intensity of DLE peak was generally proportional to the conductivity. The
band gap energy values, determined from transmittance spectra, were around 3.30–3.34 eV, and decreased when the oxygen pressure increased.
1.5 Aim of the work

The aims of this work are Designing and constructing pulsed laser deposition (PLD) system and to reveal specific properties of ZnO nanocrystalline materials prepared by this technique.

Initially the series of samples have been prepared by PLD technique at different technological conditions on different substrates. That supposed to result in the different structural and microstructural properties, different surface morphology of the nanostructures to be obtained. Also the optical properties and nonlinearity of ZnO thin films are known to be sensitive for its structural quality.

The main objectives in this work are:

1. Characterization of structural, microstructural and photoluminescence properties of obtained material.
2. Correlation between the main technological parameters and material properties.
3. study the nonlinearity properties of ZnO by Z-scan technique in term of nonlinear refractive index $n_2$ and nonlinear coefficient $\beta_2$. 
2. Introduction

Pulsed laser deposition (PLD) is a thin-film deposition method, which uses short and intensive laser pulses to evaporate target material. The ablated particles escape from the target and condense on the substrate. The deposition process occurs in vacuum chamber to minimize the scattering of the particles. In some cases, however, reactive gases are used to vary the stoichiometry of the deposit. This chapter introduces the basics of the laser ablation. Topics like laser-target-interaction and formation of the plasma plume will be discussed, as well as process parameters and formation of the deposit.

2.1 Laser ablation mechanisms

In PLD a pulsed high-energetic laser beam is focused on a target resulting in ablation of material. At the early stage of the laser pulse a dense layer of vapor is formed in front of the target. Energy absorption during the remainder of the laser pulse causes, both, pressure and temperature of this vapor to increase, resulting in partial ionization. This layer expands from the target surface due to the high pressure and forms the so-called plasma plume.

During this expansion, internal thermal and ionization energies are converted into the kinetic energy (several hundred eV) of the ablated particles.

Attenuation of the kinetic energy due to multiple collisions occurs during expansion into low-pressure background gas. Usually, the laser ablation process is divided in two stages, separated in time:

1. Target evaporation and plasma formation
2. Plasma expansion.
2.1.1 Laser – Target interaction

Ideally the plasma plume produced should have the same stoichiometry as the target if we hope to grow a film of the correct composition.

If, for example, the target surface were heated slowly, say by absorbing the light from a CW laser source, and then this would allow a significant amount of the incident power to be conducted into the bulk of the target. The subsequent melting and evaporation of the surface would essentially be thermal i.e. the difference between the melting points and vapour pressures of the target constituents would cause them to evaporate at different rates so that the composition of the evaporated material would change with time and would not represent that of the target. This incongruent evaporation leads to films with very different stoichiometry from the target \[^{[8]}\].

To achieve congruent evaporation the energy from the laser must be dumped into the target surface rapidly, to prevent a significant transport of heat into the subsurface material, so that the melting and vapor points of the target constituents are achieved near simultaneously.

The high laser power density that this implies is most readily achieved with a pulsed or Q-switched source focused to a small spot on the target. If the energy density is below the ablation threshold for the material then no material will be removed at all, though some elements may segregate to the surface \[^{[68]}\].

In general the interaction between the laser radiation and the solid material takes place through the absorption of photons by electrons of the atomic system. The absorbed energy causes electrons to be in excited states with high energy and as a result the material heats up to very high temperatures in a very short time.

Then, the electron subsystem will transfer the energy to the lattice, by means of electron-phonon coupling \[^{[2, 8]}\].
When the focused laser pulse arrives at the target surface the photons are absorbed by the surface and its temperature begins to rise. The rate of this surface heating, and therefore the actual peak temperature reached, depends on many factors: most importantly the actual volume of material being heated. This will depend not only upon how tightly the laser is focused but also on the optical penetration depth of the material. If this depth is small then the laser energy is absorbed within a much smaller volume. This implies that we require a wavelength for which the target is essentially opaque and it is in general true that the absorption depth increases with wavelength. The rate of heating is also determined by the thermal conductivity of the target and the laser pulse energy and duration.

The actual sequence of events which occur when the laser pulse arrives at the target is illustrated in Figure (2.1), and presented below:

Firstly, a), the leading edge of the pulse causes the surface to melt. Then, b), the melt front proceeds further into the target as the molten material begins to evaporate. Then, c), dense plasma forms which are still opaque to the laser pulse causing its temperature to rise rapidly. Finally, d), this plasma expands rapidly, becoming more transparent as the plasma density decreases. The molten material which is left behind then begins to resolidify \(^1\).

As short pulse, high peak power, Q-switched lasers became available interest in PLD was rejuvenated. Laser-target interactions are notoriously difficult to model analytically due to there being at least three mechanisms operating in the process of absorption of radiation into the material.

**These mechanisms are commonly thought to be:**

- Phonon and electron excitation within the lattice.
- Free carrier excitation.
- Excitation of the resulting plasma and subsequent transfer of energy to the material.
A number of parameters like the absorption coefficient, reflectivity of the target material, the pulse duration $\tau$, wavelength $\lambda$, and laser fluence $f$ affect the interaction of the laser beam with the target.

The ablation process is difficult to model. This is particularly the case if a background ambient gas is present. However, have developed a one dimensional model which treats the laser generated plasma as an ideal gas at high temperature and pressure, which is then solved numerically. In this model the temperature, $T(x,t)$, at any point in the material during the laser pulse is determined using the following heat flow equation\cite{69}:

$$
\rho_i(T)C_{pi}(T) \frac{\partial T_i(x,t)}{\partial t} = \frac{\partial}{\partial x} \left( K_i(T) \frac{\partial T_i(x,t)}{\partial x} \right) + I_i(t) \{1 - R(T)\} e^{-\alpha(T)x} \quad i = 1,2 \quad \ldots \ldots \ (2 - 1)
$$

Where $x$ is the direction perpendicular to the plane of the target, $t$ is time, $\rho(T)$ and $C_p(T)$ are the density and thermal heat capacity per unit mass, $K$ is the thermal conductivity, and the subscript $i$ refers to the solid and liquid.
phase respectively. \( R(T) \) and \( \alpha(T) \) are the reflection and absorption coefficients of the target at the laser wavelength and \( I_o(t) \) is the laser intensity.

If the thermal conductivity is low over a nanosecond timescale then the first term on the right hand side of this equation can be ignored. Therefore the temperature of the target surface, \( x = 0 \), is given by \(^{70}\):

\[
\rho(T)C_p(T)(T - T_0) = (1 - R)I_o(T)\alpha(T)\tau \quad \ldots \ldots \ldots (2-2)
\]

Where \( T_0 \) is the initial temperature and \( \tau \) is the pulse duration.

Even this very simplified equation still retains the values \( \rho(T) \), \( C_p(T) \), and \( \alpha(T) \) which are functions of temperature and as such are not easily determined.

For material with a wide band gap such as ZnO, ablation by nanosecond pulse duration lasers occurs essentially by thermal processes according to Kelly \(^{71}\) and Miotello \(^{72}\). There are three regimes of thermal ablation, namely vaporization, heterogeneous boiling and explosive boiling, but only vaporization and explosive boiling are compatible with the time scale of nanosecond laser pulses. Since explosive boiling only occurs when the target reaches temperatures near the material's thermodynamic critical temperature \(^{73,74}\), the flow of material vaporized from the surface of a body at temperature \( T \) can be calculated by the Hertz-Knudsen equation, leading to an ablation rate \( \nu \) given by:

\[
\nu_r(T) = (1 - \beta) \sqrt{\frac{m}{2\pi k_B T \rho}} \frac{P_0}{\rho} \exp \left[ \frac{L_v}{k_B} \left( \frac{1}{T} - \frac{1}{T_b} \right) \right] \quad \ldots \ldots \ldots (2-3)
\]

Where \( T_b \) is the boiling temperature at pressure \( P_0 \), \( k_B \) the Boltzmann constant, \( b \) the back flux coefficient and \( L_v \) is the latent heat of vaporization of the material.
2.1.2 Laser – plasma interaction

In the description of the laser–plasma interaction, the laser pulse duration plays a crucial role. whereas in the case of nanosecond (ns) laser pulse, the forming plasma interacts with the laser beam “tail”, in the case of femtosecond (fs) laser pulse the previous mechanism doesn’t take place.

Because of the formation of a plasma in front of the target, the laser beam will be partially absorbed before it reaches the target i.e. so called (plasma shielding effect)\(^{(75)}\) and increases the plume ionization degree, complicating the plume expansion mechanism. Due to the plasma-laser interaction, the temperatures of the evaporated material increases therefore rapidly to extremely high values and the electrons are further accelerated. The excited particles will emit photons, leading to a bright plasma plume, which is characteristic for the laser ablation process.

The main absorption processes are the Inverse Bermsstrahlung (IB) and the direct single-photon processes \(^{(76,77)}\), IB involves absorption of photons by free electrons which are accelerated during collision with neutral or ionized atoms. The cross-section for IB via electron-neutral collisions is much smaller than that via electron ion collisions, but can be important for the initial plume of a weakly ionized gas. Initially, there may be very few "seed" electrons present, produced by thermal emission from the solid or multi-photon ionization processes.

The contribution from multi-photon processes increases with decreasing wavelength, but is particularly important for ultrafast lasers.

2.1.3 Plasma plume expansion

Since the onset of the material removal described in the previous sections takes place within a very short time after the pulse (1-100 ps), on the time scale of the plasma expansion (μs), the laser–target event can be regarded as a momentary release of energy.
The spatial structure of the vapor plasma at the early stage of its expansion is well known to be a cloud strongly forwarded in the direction normal to the ablated target. The reason of this characteristic plasma elliptic shape, called *plume*, is in the strong difference in pressure gradients in axial and radial directions: the plasma expands in the direction of maximum pressure gradient\(^{[78]}\).

Another important characteristic of the ablation plume pertinent to PLD is the angular distribution of the ejected species in the plume or simply the plume angular distribution\(^{[79]}\).

In case of vacuum the plume angular distribution is determined by the collisions of the plume particles among themselves in the initial stage. When plume is small however in the presence of the ambient gas the plume angular distribution is modified due to collision between the plume species and background gas atoms\(^{[80]}\). These collisions scatter the plume particles from their original trajectories and broaden the angular distribution.

It is generally expected that for a given background gas these additional collisions will lead to wider angular distribution of lighter plume species and similarly a scattering ambient with high mass will more effectively disperse the plume species compared to a low mass scattering ambient\(^{[2]}\).

Expansion the plume in vacuum is driven by the energy which is accumulated as thermal energy and energy which is stored as excitation and ionization in the initial layer. This energy is converted to kinetic energy of the atoms in the plume, and eventually all atoms will move with an asymptotic, constant velocity distribution. As soon as the laser pulse ends, there is little further transfer of energy and mass to the ablation plume, and the plume propagation can essentially be considered as an adiabatic expansion\(^{[81]}\).
Laser ablation with ultra short pulses (<1ps) has attracted a lot of attention, not only because of the access to ultrafast physical and chemical processes, but also because of the new prospects for applications in materials processing and thin film deposition films\cite{84}.

### 2.1.4 Plume- Substrate Interaction

In PLD, the deposition of the ablated material on the substrate surface can be regarded as instantaneous for every pulse, since the time scale of the atomistic processes involved in the film growth exceeds the deposition pulse duration. Each instantaneous deposition is followed by a relative long time interval, where no deposition takes place. Because of the instantaneous deposition at typical PLD conditions, the nucleation takes place after the deposition pulse and can be considered as post- nucleation. Such separated random deposition and subsequent growth is, furthermore, advantageous for the study of the effect of plume expansion dynamics on film growth kinetics developed in this work.

Parameters which control the instantaneous deposition rate are the laser energy density at the target, pulse shaping, the distance between target and the substrate and ambient gas properties\cite{78}.

### 2.2 Pulse shaping

Pulse shaping refers to a method, which allows the tailoring of the duration and intensity of the laser pulse. This method is used especially with short laser pulses\cite{87}.

The distribution of the deposited material on the substrate is connected with the angular distribution of the resulting plasma plume. For a point source of material the width of the film thickness distribution can be characterized by a dimensionless film width:

\[
\Delta = \frac{x_{1/2}}{L} \quad \cdots \cdots (2 - 4)
\]
Where $x_{1/2}$ is the coordinate of the point where the thickness of the film decreases to one half of its maximum, and $L$ is the separation of the substrate from the point source. This geometry is further explained in Figure (2.2).

The plasma divergence angle $\theta_{1/2}$ is the half-angle between the symmetric directions in the ablation plume where the material flux is half the value at its maximum.

![Figure (2.2): Definition of the dimensionless film width $\Delta=x_{1/2}/L$ and the angle of plasma divergence $\theta_{1/2}$.

In the case of PLD with Gaussian beams, only the central part of the beam leads to stoichiometric deposition whereas the beam edges may only heat the target or might not deposit all the elements stoichiometrically. For example a Gaussian-shaped pulse can be split into a pre-pulse with relatively low intensity and a second pulse of a longer duration and higher energy. When the deposition mechanisms of a target are known, the pulse shaping allows an accurate control of deposition, e.g. the generation of particulates can be strongly reduced.

The existing beam – shaping and homogenizing approaches can be divided into three classes as shown in figure (2.3):
2.3 Growth Kinetics during Pulsed Laser Deposition

The application of thin films in electronic devices requires smooth film surfaces and interfaces. Understanding of the different mechanisms affecting the growth mode is, therefore, necessary to control the surface morphology during thin-film growth.

Two independent processes, that is, nucleation and growth of islands, play an important role during vapor-phase epitaxial growth on an atomically flat surface. Here, nucleation causes the formation of surface steps and subsequent growth causes the lateral movement of these steps. Both processes are determined by kinetics since they take place far from thermodynamic equilibrium. These kinetic processes affect the final surface morphology and are, therefore, extensively studied.

2.3.1 Film Growth Modes

In the following a schematization of the possible ways of growth, determined by the thermodynamic approach of the balance between the free energies of film ($\gamma_F$) and substrate ($\gamma_S$) and the interface between film and substrate ($\gamma_I$) is given.

When the total free energy of the film surface and the interface equals the free energy of the substrate surface ($\gamma_F + \gamma_I < \gamma_S$), significant wetting is expected. This leads to layer-by-layer growth as described by Frank and Van der Merwe.
In the case of an increased total free energy wetting is energetically unfavorable and the deposit will take place minimizing the film substrate interface by means of islands growth; this is the case of Volmer-Weber mechanism \(^{[91]}\), where the energy due to the creation of interface is higher than the surface energy of the substrate and film \((\gamma_F + \gamma_I > \gamma_S)\).

At the intermediate case, a transition from the Frank and Van der Merwe to the Volmer-Weber growth mode can be observed. Here a crucial role is played by the mismatch between film and substrate, inducing a strain on the growing film. A layer-by-layer growth takes place in the first stage. Then, the thicker become the film, the higher is the elastic energy due to the strain. Such large strain energy can be lowered by forming islands in which strain is relaxed. This mechanism results in a continuous film of one or two monolayers onto which successively discrete islands are formed. This way of growth is the so-called Stranski-Krastanov \(^{[2,92]}\).

In the Figure (2.4), the previous regimes are depicted.

The previous approach doesn’t take into account the effect on the growth kinetic of the deposition parameters, such as the value of super saturation in the gas phase, the substrate vicinality and the crystallographic misfit between the film and substrate unit cells. For the effect of such parameters, different growth modes have been observed for the same film-substrate system, thus clearly indicating that growth techniques and parameters are crucial to determine the final film morphology.
Chapter Two Properties of Laser Deposition and ZnO Thin Films

Figure (2.4) Film growth modes- layer-by-layer: (a) Frank–Van der Merwe, (b) Volmer–Weber (c) Srtanski-Krastanov and (d) step flow [2].

A first difference should be done between homoepitaxy and heteroepitaxial. In the first case the film and substrate compounds are the same deposited and the substrate crystalline structure extends into the film during the growth. In case of heteroepitaxial, the materials of film and substrate are different, with different lattice parameters [91].

2.3.2 Growth Kinetics

For the sake of simplicity, in the following discussion will calculated on the growth kinetics in the homoepitaxy case, where complicating effects as lattice parameter misfit and Thermal coefficient expansions do not play a role.

Once adsorbed on the surface an atom, now called adatoms, may desorbs into the vapor or change adsorption site, in which case it can diffuse on the surface for several atomic length, before to be detached and incorporated in the crystal structure, as schematized in Figure (2.5).

The molecule-surface interaction is described by a potential that is a periodic function of the two coordinates parallel to the surface and a decreasing function of a third coordinate normal to it.
Assuming \( l_T \) is the terrace length, we define \( l_D \) as the average distance an atom can travel on a flat surface before being trapped. It is given by \[ (2 - 5) \]

\[ l_D = \sqrt{D_s T} \]

Where \( D_s \) is the surface diffusion coefficient of the adatoms, and \( \tau \) is the residence time before re-evaporation.

The surface diffusion coefficient \( D_s \) (typical values for metal oxides lie between \( 10^{-4} \) and \( 10^{-8} \) cm\(^2\) s\(^{-1}\)) is generally expressed as:

\[ D_s = a^2 v \exp \left( -\frac{E_A}{k_B T} \right) \]

Where \( E_A \) is the activation energy for diffusion, \( a \) is the characteristic jump distance and \( v \) is the sticking coefficient.

From equation (2-6) it became evident the importance of the deposition temperature in the PLD technique, since it controls, among others, the diffusivity of the adatoms. However, it is important to recall here that the adatoms mobility on the surface is determined not only by the deposition temperature but an important contributes in the nucleation process come from the redistribution of the kinetic energy of the incoming flux of impinging atoms.

The diffusion process is a crucial phenomenon that determines how the deposited materials rearrange itself on the surface and by a careful control of
these parameters it is possible to obtain 2D growth modes not only on singular, but also on vicinal substrates.

To understand this, two diffusion process have been considered, both determined by kinetic parameters \(^9^3^1\):

1. The interlayer mass transport: the diffusion of atoms on terrace.
2. The interlayer mass transport: the diffusion of atoms to a lower step.

In the case of fast interlayer mass transport, the mobility of the adatoms is high enough to enable atoms to reach the edges of the substrate steps, i.e. the diffusion length \(l_D\) is larger than \(l_T\), the average terrace width. In this case the nucleation on the terraces is prevented and the step-flow growth takes place.

Even on a vicinal substrate, a 2D growth will occur, until \(l_D > l_T\). Otherwise, if for some reason the distribution in \(l_T\) of the surface broadens, nucleation on the terraces will occur. When this happens, nuclei will form until a saturation density is reached. After that, the probability for atoms to attach to an existing nucleus exceeds the probability to form a new nucleus and so islands will start to grow.

In this case the interlayer mass transport plays a big role to determine the growth mode. In fact, to obtain a layer-by-layer growth mode in this situation, a steady interlayer mass transport should be present so that atoms deposited on top of a growing island must reach the island edge and then diffuse to a lower layer. In the ideal case, the nucleation's start after completion of a layer, but if there is no interlayer mass transport, nucleation will occur on top of islands before these have coalesced and this is the case of the so called second layer nucleation. The probability for second layer nucleation is related to the mean island radius at the time of stable clusters nucleation on top of the islands, \(R_C\). The value of \(R_C\) is, in turn, related to the parameter \(E_S\), that is the energy barrier for an atom to descend.
Across the step edge to a lower terrace, larger is the value of $E_S$, smaller will be the value of $R_C$, since the additional energy barrier lead to accumulation of the adatoms on top of the islands, with subsequently increase of second layer nucleation rate \cite{90}.

In the real system the growth mode is in between these growth modes described here. In some cases, even a transition from a layer-by-layer to a step flow growth on vicinal substrate can happen when the diffusion length of adatoms becomes comparable to the terrace width, i.e. when $l_D \approx l_T$. This can happen because either the substrate temperature, determining the surface diffusion length $l_D$ or the vicinal angle, determining the terrace width $l_T$, is changed.

### 2.4 Limitations and Advantages of PLD

1. Complex oxide compositions with high melting points can be easily deposited provided the target materials absorb the laser energy.

2. PLD allows the growth of films under a highly reactive gas ambient over a wide range of pressure.

3. The target composition is transferred instantaneously leading to a Stoichiometry deposition and as such the turnaround time is much faster for initial optimization of the growth conditions with this technique. This is a major advantage whenever there is a need for experimenting with different target compositions.

4. The PLD technique is found to be very effective and well suited for developing epitaxial films, and allows fabrication of multilayer's, hetero-structures and super lattices on lattice matched substrates.

5. In the PLD process during film growth suitable kinetic energy in the range 10–100 eV and photochemical excitation exist in comparison to
other deposition techniques, and is found to be beneficial for improving the quality of the deposited film.

6. The main practical limitation of PLD is its relatively low duty cycle, incorporation of particulates in the deposited films, although this is not unique to PLD, because particulate problem exists in the case of sputtering and MOCVD as well.

Up scaling for industrial production and deposition on large area substrates is still a major concern. The technique is ideally suitable for deposition on small substrates, and yields high quality films useful for research and allows fabrication of discrete devices.

Table 2.1: Performance features of Excimer and Nd: YAG lasers.

<table>
<thead>
<tr>
<th>Pulsed UV-Laser</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Excimer laser</td>
<td>- High power output</td>
<td>- Short operation life time.</td>
</tr>
<tr>
<td></td>
<td>- Good stability</td>
<td>- Complicated maintenance</td>
</tr>
<tr>
<td></td>
<td>- Flexibility for tuning</td>
<td>- Expansive and high purity gasses, constants refilling</td>
</tr>
<tr>
<td></td>
<td>- Laser output parameter</td>
<td>- Space consuming.</td>
</tr>
<tr>
<td>Nd:YAG laser</td>
<td>- Output energy sufficient for laser ablation</td>
<td>- Large energy drop for the 3rd harmonic mode</td>
</tr>
<tr>
<td></td>
<td>- Simple maintenance</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- Compact system</td>
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</tbody>
</table>
2.5 Pulsed Laser Deposition of Nano-Structure Semiconductor

Earlier a seemingly esoteric technique of Pulsed Laser Deposition (PLD) has emerged as a potential methodology for growing nanostructures of various materials including semiconductors \(^{[94]}\).

Since it is a cold-wall processing, which excites only the beam focused areas on the target enabling a clean ambient, it is highly suited for the growth of nanostructures with high chemical purity and controlled stoichiometry.

The other characteristics of PLD such as its ability to create high-energy source particles, permitting high quality film growth at low substrate temperatures \(^{[95]}\), simple and inexpensive experimental setup, possible operation in high ambient gas pressure, and sequential multi-target and multi-component materials' congruent evaporation make it particularly suited for the growth of oxide thin films and nanostructures.

In this section we shall present and discuss a few representative cases where PLD has been successfully applied for the growth of semiconductors thin films and nanostructures. These cases of various semiconductors also illustrate the current trend and the future promise that PLD holds.

2.6 Fundamental properties of ZnO

Recently, zinc oxide (ZnO) has attracted much attention within the scientific community as a ‘future material’. This is however, somewhat of a misnomer, as ZnO has been widely studied since 1935 \(^{[96]}\), with much of our current industry and day-to-day lives critically reliant upon this compound.

The renewed interest in this material has arisen out of the development of growth technologies for the fabrication of high quality single crystals and epitaxial layers, allowing for the realization of ZnO-based electronic and optoelectronic devices.
An overview of the basic properties of ZnO, including the crystal structure, energy band structure and thermal properties are presented, as well as an introduction to the basic electronic, optical properties and potential applications of ZnO.

### 2.6.1 Crystal structures

Most of the group-II-VI binary compound semiconductors crystallize in either cubic zinc-blend or hexagonal wurtzite structure where each anion is surrounded by four cations at the corners of a tetrahedron, and vice versa.

ZnO is a II-VI compound semiconductor whose ionicity resides at the borderline between covalent and ionic semiconductor.

The crystal structures shared by ZnO are wurtzite (B4), zinc blend (B3), and rock salt (B1), as schematically shown in Fig. (2.6). at ambient conditions, the thermodynamically stable phase is wurtzite.[97]

![Figure 2.6](image)

*Figure (2.6):* Stick and ball representation of ZnO crystal structures: (a) cubic rocksalt (B1), (b) cubic zinc blende (B3), and (c) hexagonal wurtzite (B4). The shaded gray and black spheres denote Zn and O atoms, respectively.

The wurtzite structure of ZnO can be considered to be composed of two interpenetrating hexagonal close packed (hcp) sub-lattices of cation (Zn) and anion (O) displaced by the length of cation-anion bond in the c-direction.

The lattice constant of the ZnO hexagonal unit cell are $a=3.250$ Å and $c=5.206$ Å.[104] Since ZnO is a two-element compound with different atoms,
so $c/a$ ratio for ZnO hcp unit is 1.60, which is a little smaller than the ideal value of 1.633 of hcp.

Each hexagonal close packed (hcp) consists of one type of atom displaced with respect to each other along the threefold $c$-axis by the amount of $u = 3/8 = 0.375$ (in an ideal wurtzite structure) in fractional coordinates (the $u$ parameter is defined as the length of the bond parallel to the $c$ axis, in units of $c$ or nearest neighbor distance $b$ divided $c$).

### 2.6.2 Lattice parameters

Lattice parameters are considered important, when one has to develop semiconductors devices. There are mainly four factors which determine the lattice parameters of the semiconductors\cite{11,100}.

(i) Free-electron concentration which affects the potential of the bottom of conduction band normally occupied by electrons.

(ii) Concentration of impurities and defects and the difference in ionic radii between these defects and impurities with respect to substituted matrix ions.

(iii) External strains (for example, those induced by substrate)

(iv) Temperature.

On the other hand, the strict periodicity of the lattice is disturbed by many imperfections or defects. These imperfections or defects have a considerable, controlling influence on mechanical, thermal, electrical and optical properties of semiconductors. They determine the plasticity, hardness, thermal and electrical conductivities.
2.6.3 Electronic Band Structure

A very important property of any given semiconductor is its band structure, because many important properties such as the band gap and effective electron and hole masses are derived from it.

ZnO is considered most suitable semiconductor among all his family members for ultraviolet lasing at room temperature, device application as well as possibilities to engineer the band gap, for this reason a clear understanding of the band structure is important to explain the electrical properties and many other phenomena because it determines the relationship between the energy and the momentum of the carrier.

The important method for the analysis of the energy region is based on photoelectric effect extended to X-ray region, namely, photoelectron spectroscopy (PES). As show in Figure (2-7)

![Figure (2.7): Band structures for ZnO: (a) B4 structure, (b) B1 structure, and (c) B2 structure](image)

2.6.4 Optical properties

The optical properties of a semiconductor are associated with both intrinsic and extrinsic effects. Intrinsic optical transitions take place between the electrons in the conduction band and holes in the valence band, including excitonic effects due to the Coulomb interaction. The main condition for exciton formation is that the group velocity of the electron and hole is equal.

Excitons are classified into free and bound excitons, in high quality samples with low impurity concentrations; the free exciton can also exhibit
excited states, in addition to their ground-state transitions. Extrinsic properties are related to dopant or defects, which usually create discrete electronic states in the band gap, and therefore influence both optical-absorption and emission processes \[^{[97]}\].

1. Transmission in ZnO thin films

As we mentioned above, that ZnO is a direct band semiconductor and a transparent conductive material. ZnO films are transparent in the wavelength range of \((0.3)\) and \((2.5)\) μm, and plasma edge lies between \((2)\) and \((4)\) μm depending on the carrier concentration. It is well known that a shift in the band gap edge appears with an increase in the carrier concentration, which can be controlled by deposition conditions such as doping level, substrate deposition temperatures, oxygen pressure, and film thickness \[^{[103]}\].

Optical properties in ZnO have been studied by a variety of experimental techniques such as optical absorption, transmission, reflection, photo-reflection, spectroscopic ellipsometry, photoluminescence, cathodoluminescence, calorimetric spectroscopy, etc.

The transmittance \((T)\) and reflectance \((R)\) data can be used to calculate absorption coefficients of the films at different wavelength. The absorption coefficient, \(\alpha\), is given by the relation \[^{[104]}\):

\[
\alpha = \frac{1}{t} \ln \left[ \frac{(1 - R)^2}{T} \right] \quad \cdots \cdots (2 - 8)
\]

Where \(t\) is the film thickness. Figure (2.8) show the optical transmission of ZnO thin film deposited on different substrate and different temperatures.

The absorption coefficient data can be used to determine the band gap, \(E_g\), using the following relation \[^{[2]}\):

\[
\alpha h\nu \approx A (h\nu - E_g)^{1/2} \quad \cdots \cdots (2 - 9)
\]
Where $A$ is the constant, $h\nu$ is the photon energy.

**Figure (2.8)** Show the optical transmission of ZnO deposited on a) Glass substrate\(^{[61]}\), b) Quartz substrate\(^{[51]}\), c) Sapphire substrate\(^{[63]}\) at different temperature.

**Figure (2.9):** Show the absorption coefficient of ZnO deposited by PLD on a) glass substrate\(^{[47]}\), b) quartz substrate\(^{[51]}\).
Photoluminescence of ZnO thin films

Photoluminescence (PL) is a powerful and a relatively simple method, extensively used as characterization technique of semiconductor physics for a number of reasons\(^{[105]}\).

Basically in PL measurements, a semiconductor sample is optically excited by an excitation source such as a laser which produces photons having energies larger than the band gap of the semiconductor. The incident photons are absorbed under creation of electron-hole pairs in the sample. After a short time the electrons eventually recombine with the holes, to emit photons, and light or luminescence will emerge from the sample. The energy of the emitted photons reflects the energy carrier in the sample.

The emitted luminescence is collected, and intensity is recorded as a function of the emitted photon energy, to produce a PL spectrum. In a PL measurement, the excitation energy is kept fixed, while the detection energy is scanned. The energy of emitted photon is characteristic for radiative recombination process.

At room temperature PL spectrum of ZnO is usually composed of a near UV-emission band (375 nm) and a green emission band (510 nm) although a yellow-orange band (610 nm) can also be observed in some situations. The near UV-band is closely related to the excitonic nature of the material and may be superposed with the free exciton emission, its phonon replica, bound exciton emission, as well as biexciton emission, as shown in figure (2.10).
Figure (2.10): PL of ZnO thin films deposited by PLD on
a) Glass substrate[61], b) Quartz substrate[51], c) Sapphire substrate[30].

Radiative recombination mechanisms observed in PL

Transitions between the coeducation band and valence band, exciton, donor and acceptor levels, are all shown in figure (2.11).

Upon excitation at energy above the bang gap, free electrons are created in the conduction band together with the free holes in the valance bond. These carriers will energetically relax down the band edge. Due to mutual coulomb interaction, electron-hole pair is formed[107].

This electron-hole usually called a free exciton (FE). Its energy is slightly smaller than the bang gap energy. This energy difference is the binding energy of the free exciton.

A neutral donor (acceptor) will give rise to an attractive potential, a free exciton might be captured at the acceptor (donor). Thus a bound exciton is formed (BE).

Figure (2.11): Schematic illustration of common recombination processes[108].
An electron bound to a donor can recombine directly with a free hole from a valence band. This kind of recombination is called free-to-bound (FB) transition.

Another possibility is that a hole bound to an acceptor recombines with an electron bound to a donor in donor-acceptor pair (DAP) transition. Both the donor and the acceptor are neutral before the recombination (i.e. the donor positively and the acceptor negatively charged). Thus there is a Coulomb interaction between the donor and acceptor after the transition and extra Coulomb energy is gained in the final state added to the radiative recombination energy. The transition energy $E_{(R)}$ depends on the distance $R$ between the donor and acceptor atoms\textsuperscript{[108]}.

The emission by the nanocrystalline structure will have the similar quantum size effect as quantum dots and can be described by the following equation\textsuperscript{[109]}:

$$E_{(gap,nanocrystal)} = E_{(gap, bulk)} + \frac{\pi^2 \hbar^2}{2R^2} \left( \frac{1}{m_e^*} + \frac{1}{m_h^*} \right) - 0.248 E_{Ry} \ldots \ldots \ (2-10)$$

The bulk band gap $E_{(gap, bulk)}$ is taken as 3.37 eV\textsuperscript{[14]} and the bulk exciton binding energy $E_{Ry}^*$ can be taken as 60 meV. The electron and hole effective masses are taken as $m_e^*=0.24m_0$ and $m_h^*=2.31m_0$, respectively. Additionally, $\hbar$ is Planck’s constant and $R$ is the radius of ZnO nanocrystals.

### 2.6.5 Electrical Properties

As a direct and wide band gap semiconductor with a large exciton binding energy (60meV), ZnO is representing a lot of attraction for optoelectronic and electronic devices. For example, a device made by material with a larger band gap may have a high breakdown voltage, lower noise generation, and can operate at higher temperatures with high power operation. The performance of electron transport in semiconductor is different at low and high electric field\textsuperscript{[11]}.
At sufficient low electric fields, the energy distribution of electrons in ZnO is unaffected much, because the electrons can’t get much energy from the applied electrical field, as compared with their thermal energy. So the electron mobility will be constant because the scattering rate, which determines the electron mobility, doesn’t change much.

When the electrical field is increased, the energy of the electrons from the applied electrical field is equivalent to the thermal energy of the electron. The electron distribution function changes significantly from its equilibrium value. These electrons become hot electrons, whose temperature is higher than the lattice temperature. So there is no energy loss to the lattice during a short and critical time. When the electron drift velocity is higher than its steady-state value, it is possible to make a higher frequency device \[^2\].

### 2.6.6 Non-Linear properties

- **Z-scan technique**

  The Z-scan technique is a single beam technique, which allows the determination of the real and imaginary part of the susceptibility \[^{110}\]. Figure (2.12) show a typical Z-scan experimental setup. This technique is simple, sensitive, single beam method that uses the principle of spatial beam distortion to measure both the sign and magnitude of refractive nonlinearities of optical materials. They use the Gaussian beam from a laser in tight focus geometry to measure the transmittance of nonlinear medium through a finite aperture in the far field as a function of the sample position Z.

  From the focal plan, in addition to this, the sample transmittance without an aperture is also measured to extract complementary information about the absorptive nonlinearities of the sample.

  This technique has several *advantages*, some of which are \[^{110}\]:

  - Simplicity: No complicated alignment except for keeping the beam centered on aperture.
• Simultaneous measurement of both sign and magnitude of nonlinearity.
• Data analysis is quick and simple except for some particular conditions.
• Possible to isolate the refractive and adsorptive parts of nonlinearity.
• High sensitivity, capable of resolving a phase distortion of A/300, provided the sample is of high optical quality.

Some of the disadvantages include:
• Stringent requirement of high quality Gaussian TEM$_{00}$ beam for absolute measurements.
• For non-Gaussian beams the analysis is completely different. Relative measurements against a standard samples allows relaxation on requirements of beam shape.
• Beam walk –off due to sample imperfections, tilt or distortions.
• Not suitable for measurement of off-diagonal elements of the susceptibility tensor except when a second non-degenerate frequency beam is employed.

*Figure (2.12) Z-scan experimental setup* [111]

The Z- scan technique has been used extensively to study different materials like semiconductors, nano-crystals, semiconductor – doped glasses, liquid crystals, organic materials, organic materials, biomaterials etc. to enhance its sensitivity and applicability new extensions have been added

*a. Closed – aperture Z-scan for sign and refractive nonlinearity*
Consider, for instance, a material with a negative nonlinear refraction and of thickness smaller than the diffraction length (Rayleigh range is where the size of the beam is a $\sqrt{2}$ larger than the waist size) and is given by:

$$Z_c = \frac{\pi \omega^2}{\lambda} \quad \cdots \cdots (2 - 11)$$

Where $\omega$, is beam radius at the waist $[^{113}]$.

This situation can be regarded as treating the sample as a thin lens of variable focal length due to the change in the refractive index at each position $[^{114}]$

$$n = n_0 + n_2 I \quad \cdots \cdots (2 - 12)$$

When the sample is far from the focus and closer to the lens, the irradiance is low and the transmittance characteristics are linear. Hence the transmittance through the aperture is fairly constant in this region. As the sample is moved closer to the focus, the irradiant increases inducing a negative lensing effect.

A negative lens before the focus tends to collimate the beam. This causes the beam narrowing lens after the focus tends to diverge the beam resulting in the decrease of transmittance.

As the sample is moved far away from the focus, the transmittance becomes linear in Z as the irradiance becomes low again. Thus the curve for Z versus transmittance has a peak followed by a valley for a negative refractive nonlinearity. The curve for a positive refractive nonlinearity will give rise to the opposite effect, i.e. a valley followed by a peak.

b. Open – aperture Z-scan for sign and refractive nonlinearity

In the above discussion a purely refractive nonlinearity was considered assuming that absorption nonlinearities are absent. The presence of multi-photon (two or more) absorption suppresses the peak and enhances the valley. While saturation of absorption produces the opposite effect. The
sensitivity of the experiment to refractive nonlinearities is entirely due to the aperture \[^{110}\].

The removal of the aperture will make the Z-scan sensitive to absorptive nonlinearities thus by doing the Z-scan with and without aperture both the refractive and absorptive nonlinearities of the sample can be studied. Z-scan studies of all the samples are performed using broadband source ns/ps pulses.

Z-scan technique developed by Sheik Bahae and his co-workers, the single beam z-scan technique with nanosecond laser pulses to measure nonlinear optical absorption and refraction properties of ZnO thin films and observed that the films have large nonlinear effects. The open-aperture curve exhibited a normalized transmittance valley, indicating the presence of nonlinear absorption in the film. The glass substrate had negligible nonlinear optical response at 532 nm, which was measured by the same method and hence the high nonlinear response observed here resulted from the ZnO films.

These plots are typical of samples exhibiting two photon absorption. Transmittance was a minimum at the focus and increased steadily on both sides of the focus. The nonlinear absorption coefficient \( \beta \) is obtained from the equation \[^{114}\]:

\[
\alpha(I) = \alpha_0 + \beta I \quad \cdots \cdots \quad (2 - 13)
\]

Where \( \alpha_0 \) is the linear absorption coefficient, \( I \) is the beam intensity.

Figure (2.14) show the open and closed aperture for ZnO thin films deposited on the glass substrate.
2.7 ZnO thin films processing by PLD

The processing parameters that play an important role during the deposition process of textured ZnO films include substrate temperature, background gas pressure, laser energy density, target to substrate distance, and the repetition rate. Oxygen incorporation into a growing film originates both from the oxide target and the background oxygen gas \(^{115}\).

2.7.1 Effect of substrate temperature

The substrate temperature in the PLD process is very crucial because it activates the surface mobility of the ejected species deposited onto the substrate surface and since the kinetic energy of ablated species in PLD is relatively higher than that observed in films deposited by other physical vapor techniques, a crystalline ZnO film with low surface roughness is easily obtained at low temperature \(^{24,116}\).

The c-axis orientation of ZnO film degrades at substrate temperature \((<200{\degree}C)\) due to reduced surface mobility and migration of species on the substrate surface, and the texture quality normally improves with increasing substrate temperatures \(^{47}\).

Re-evaporation of atoms from the surface of a deposited film at very high substrate temperature \((>600{\degree}C)\) has been observed resulting in the formation of an off stoichiometry thin film.
The nucleation process depends on the interfacial energies between the substrate surface and the condensing species, and is governed by the substrate temperature. The surface mobility of the condensing species defines the crystalline of the film.

Generally the species will diffuse through several atomic distances before sticking to a stable position within the newly formed film. A high substrate temperature favors rapid and defect free growth of crystallites due to full oxidation of Zn atoms and optimum surface diffusion of the species, whereas a low substrate temperature results in the growth of a disordered or a poorly crystallized structure.\textsuperscript{[117]}

Also observed that the optical transmittance (T) in the visible range (400–700 nm) increases slightly with increasing the substrate temperature from room temperature to ~300 °C, and this is related to the increase in grain size of the films with increasing substrate temperature\textsuperscript{[48]}, as see in figure (2.8).

### 2.7.2 Effect of Oxygen pressure

Attractive flexibility of the PLD technique is that it allows film growth over a wide pressure range beginning from ultra high vacuum to a high value of ~100 Pa. This particular feature has been extremely useful for the preparation of nanostructures of ZnO material, and for fabricating heterostructures using ZnO films with many other materials that require processing at varying oxygen pressure to form a metastable crystalline layered structure.

At low oxygen pressure (<0.5 mbar), the emitted atoms and ions from the target surface after laser interaction condense on the substrate surface to form a continuous film.

The mean free path of the ablated species depends upon the processing pressure and increases with decreasing pressure. The processing of film at very low oxygen pressures is generally known as laser molecular-beam
epitaxy (LMBE) where the mean free path of the plume species is much larger than the target to substrate distance \cite{15}. When films are processed under high pressures (>1 mbar) the ablated species undergo a large number of collisions with background gas molecules and the condensation of species in the gas phase results in the formation of nano-size particles.

The settlement of these nano-particles on the surface of the substrate promotes the formation of a film that is dense and smooth. The nucleation of nano-particles on the substrate is controlled either by the processing conditions, or by using a catalytic layer, and can lead to the fabrication of interesting nanostructures. Films deposited under very low pressure are often oxygen deficient, and thereby affect the micro structural and electrical properties \cite{118}, and therefore demand a careful optimization.

Moreover films deposited at low oxygen pressure ($10^{-5}$ to $10^{-4}$ Torr) are reported to be in a state of compressive strain exhibiting c-axis lattice parameter larger than the bulk value, and deposition at higher oxygen pressures ($10^{-2}$ Torr) leads to reduction in the strain with minimal surface roughness \cite{119}. The quality of the ZnO film at high pressure is found to improve with the pre-coating of an ultrathin nucleating layer grown at low pressure ($10^{-4}$ to $10^{-3}$ Torr)\cite{15}.

The optimized value of oxygen pressure for a desired property is found to be different in the reported literature and such variations can arise due to differences in the growth kinetics resulting from the varying nature of the target (oxide or metal; ceramic or single crystal), to substrate distance, and substrate temperature etc. Oxygen pressure influences both the deposition rate and the kinetic energy of ejected species.

The kinetic energy of the ablated species reduces with the increasing of pressure due to large number of collisions with background gas molecules and it is commonly observed that the size of ablated plume decreases with increasing of oxygen pressure. Therefore it is recommended to reduce the
distance between the target and substrate while working at higher pressures to maintain the optimum energy of the ablated species \(^2\).

With the increase of substrate temperature and oxygen pressure, the crystalline of the film is enhanced and allows the development of a smooth, dense and uniform microstructure with good adhesion to the substrate.

### 2.7.3 Control of the stoichiometry

The stoichiometry of ZnO films is an important parameter that plays a major role on their physical properties. This point is important since the conductivity of ZnO thin films is, among other parameters, a function of the oxygen vacancy concentration. In fact, oxygen vacancies create defect states in the band gap energy of ZnO that induce the green deep-level emission in photoluminescence.

These defect states are responsible for an absorption in the visible region and for optical losses in waveguide configurations. Therefore, for electrical and optical applications, oxygen deficiency in PLD-grown ZnO films has to be avoided.

The origin of a Zn-to-O ratio greater than unity in the ZnO films must be related to the optimized growth conditions by PLD.

On one hand, vacuum or very low oxygen pressures often used in PLD correspond to growth conditions involving an unbalanced incorporation of zinc and oxygen atoms in the films. On the other hand, ZnO being able to sublime when heated above 1200\(^0\)C, Zn atoms could recondense on the film surface after repeated laser irradiation while the oxygen is lost by vacuum pumping. Indeed non-stoichiometry film growth is assumed to be the norm when PLD is carried out under conditions leading to the formation of sufficiently dense plasma to cause material redeposition on the target \(^{120}\).

The enhanced desorption was confirmed by a relatively lower growth rate during UV-assisted PLD than conventional PLD. The application of this UV-assisted PLD technique resulted in the growth of epitaxial ZnO layers on
sapphire substrates that exhibited similar quality to the ZnO layers deposited at substrate temperatures at least 200°C higher \cite{2}.

2.8 Kind of Substrates for ZnO deposition

A variety of substrates have been used for growing ZnO films by the PLD process are discussed below and results obtained on amorphous glass, single crystal $\alpha$-$\text{Al}_2\text{O}_3$, Quartz and a number of oxide single crystal substrates are discussed.

- **Amorphous glass substrates**

  Generally on the amorphous substrates like glass the formation energy for the crystallization of ZnO is quite large in comparison to its growth on crystalline substrates that promote nucleation very quickly and hence growth of high quality ultrathin ZnO films on glass have been quite difficult.

- **Quartz substrate**

  Quartz, a form of $\text{SiO}_2$, is a very widespread mineral (12% in the Earth's crust). Pure quartz is fully transparent, whereas natural quartz can have some coloration due to impurities. From the crystallographic point of view quartz is a $\alpha$-form of silica. Depending on temperature and pressure, silica can exist in a large number of other modifications, which include $\beta$-quartz, tridymite, cristobalite, coesite, stishovite, and keatite. Thus, the $\alpha$-quartz and the $\beta$-quartz should be distinguished. In the framework of this thesis, where not explicitly noted, the $\alpha$-form of silica is meant under the name of quartz.

  The unit cell of the $\alpha$-quartz lattice contains three $\text{SiO}_2$ units. The lattice has trigonal symmetry and is acentric, which means that two modifications (right-hand and left-hand) of the $\alpha$-quartz crystalline lattice
exist. The fact, that quartz is optically active, is explained by this property of the lattice \[^{121}\].

➤ **Sapphire substrate (α-Al\(_2\)O\(_3\))**

Aluminum oxide occurs in several different modifications. The most stable one is α-Al\(_2\)O\(_3\) (sapphire). Sapphire has a corundum structure, the Brava is lattice of sapphire is hexagonal close-packed (hcp) structure with lattice constants of \(a=4.75 \text{ Å}\) and \(c=13 \text{ Å}\) \[^{123}\].

In the corundum structure of sapphire, Al atoms occupy two thirds of the octahedral interstitial voids of each successive hcp packed layer of oxygen atoms. Sapphire has large band gap of 9.7 eV, which enables the material to transmit light over a broad wavelength range from 150 nm to 5000 nm. Sapphire has a melting point of is 2040 °C, and it has extremely high chemical stability even at high temperatures.

With these unique properties, sapphire has various applications in the areas of optics, laser, semiconductors, optoelectronics, industry and military. Sapphire is also widely used as substrate material in thin film growth processes. The hexagonal structure of sapphire makes the material to be the top one choice of substrates for the other hcp materials such as GaN, AlN and ZnO, etc. The large band gap of sapphire makes optical characterization of the thin films developed on it to be carried out without disturbing.
The physical, thermal, electrical and mechanical properties of sapphire are listed in Table 2-2.

Table 2-2 Properties of sapphire

<table>
<thead>
<tr>
<th>PROPERTIES OF SAPPHIRE</th>
<th>PHYSICAL</th>
<th>THERMAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>Al₂O₃</td>
<td>Thermal conductivity 0.065 cal cm⁻¹ s⁻¹ °C⁻¹</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Hexagonal system (rhombohedra)</td>
<td></td>
</tr>
<tr>
<td>Unit cell dimension</td>
<td>a = 4.758 Å, c = 12.991 Å</td>
<td>Thermal expansion coefficient 8.40 x 10⁻⁶ °C⁻¹</td>
</tr>
<tr>
<td>Density</td>
<td>3.98 g cm⁻³</td>
<td></td>
</tr>
<tr>
<td>Hardness</td>
<td>9 mohs, 1525-2000 Knoop</td>
<td>Specific heat at 25 °C 0.10 cal g⁻¹</td>
</tr>
<tr>
<td>Melting point</td>
<td>2040 °C</td>
<td></td>
</tr>
<tr>
<td>Boiling point</td>
<td>2980 °C</td>
<td>Heat capacity at 25 °C 18.6 cal °C⁻¹ mol⁻¹</td>
</tr>
</tbody>
</table>
3. Introduction

In this chapter, the details of the various experimental procedures and the characterization techniques are described. Special aspects of experimental strategies are also pointed out and elaborated wherever necessary.

3.1 Deposition Equipment

The basic components of the PLD-system, the laser and the pulse shaping have been introduced. In addition the following sections consider the components inside the deposition chamber, namely, the target, the substrate and also the vacuum system.

3.1.1 Nd: YAG Laser Source

Nd:YAG laser (Huafei Tongda Technology—DIAMOND-288 pattern EPLS) shown in figure (3.1) was used for deposition of ZnO on different substrate.

The whole system is made of light route system, power supply system, computer controlling system, cooling system, etc. The light route system is installed into the hand piece, but power supply, controlling and cooling system are installed into the machine box of power supply.

Main technical parameters:

- Laser wavelength: (1064 /532) nm.
- Pulse energy: (100-1000) mJ.
- Pulse width: 10ns.
- Repetition frequency: (1, 2, 3,4,5,6) Hz
- Cooling method: inner circulation water cooling
3.2 Deposition chamber

The shape of the deposition chamber is cylindrical. Since the PLD system does not necessarily require ultra-high vacuum, the geometry of the chamber can be designed quite freely. The chamber has typically a large number of ports, e.g. for pumping system, gas inlets, pressure monitoring, target, substrate, laser beam and viewports. When designing a chamber, at least following aspects should be taken into account:

The arrangement of the components inside the chamber should not disturb the path of the laser beam.

- Access to the target and to the substrate should be straightforward, since these components will be changed frequently.
- The target-substrate distance should be adjustable.
- The deposition of the laser window should be eliminated as well as possible.
3.2.1 Target holder

The target holder keeps the ablation target fixed in the vertical orientation during the deposition process. In this study all the targets used in the deposition have been prepared from the corresponding powders. The targets used for PLD can be prepared by pressing the corresponding compounds in the powder form. Powders with smaller particle sizes yield better targets because it keeps them together when pressed.

Another important factor to be considered when choosing a powder is the purity of the powder. Choosing a powder with higher purity will lead to a target with lesser impurities.

The target is typically disk-shaped and it is necessary rotated during the deposition to achieve uniform erosion. Alternately the target assembly can house an (x, y) translation stage as well. A stepper motor can be used so that the target is stepped in both the x and y directions while the laser interaction spot is held stationary. such an arrangement offers a few advantages;

(i) That the target surface area can be used more effectively for a longer duration without groove formation.

(ii) The target assembly can be rotated (about the vertical axis) relative to the incoming laser beam.
3.2.2 Substrate heater

The most important features of a substrate holder are its movement relative to the target and plasma plume and ability to heat the substrate up to 400°C. Even with the simplest substrate holders, one should be able to adjust the distance between the target and the substrate. (This is usually performed by changing the position of the substrate, not the target).

The adjustment of the target-substrate-distance provides an opportunity to control the deposition rate, as well as the energy of the particles hitting the substrate.

In this system, the arrangement is placed parallel to the target surface at a suitable distance.

Figure. (3.2) The target and substrate holder
3.2.3 Vacuum system

Generally, the pumping and gas-flow systems required by a PLD-setup are simple and economical compared to other thin film deposition techniques. Most of the applications of PLD do not require high vacuum (HV) deposition conditions (< $10^{-5}$ Pa), so there are various alternatives for the pumping systems.

The deposition chamber is a 30 cm diameter made from quartz and fixed on a HSS-Stainless Steel flange containing a groove with O-ring for vacuum sealing and feed-through in the base for electrical connections (control the stepper motor and the substrate heater) and the chamber evacuated using rotary pump connecting directly to the chamber by stainless steel flexible tubes KF16 and KF25 are used to connect to the deposition chamber to get a vacuum up to $10^{-3}$ Torr and monitoring the pressure inside the chamber by using (Leybold - Heraeus) the pirani gauge.

![Figure. (3.3) The HSS- Stainless Steel flange](image)

Two cylinders of gas were connecting to the vacuum chamber (O$_2$ and N$_2$) through a variable needle valve and T-section connection, in this work, the effect of different background gas, different temperate (RT-500)$^\circ$C, different laser energy (400,600,800) mJ and different pressure on deposited ZnO on different substrate have been studied.
3. Target preparation

Zinc Oxide powder with high purity (99.999%) pressing it under 10 Ton to form a target with 2.5 cm diameter and 0.4 cm thickness. The target should be as dense and homogenous as possible to ensure a good quality of the deposit. The target after being ablated is shown in Fig. (3.5).
3.4 Preparation of Substrate Surface for Thin Film Deposition

Three different types of substrates were used for depositing thin films by laser ablation. They are glass plates, quartz plates and sapphire substrate.

✓ Glass and Quartz Substrate

We used the glass substrates (3×2 cm$^2$) and quartz substrate (2×1 cm$^2$) to deposit the metallic oxide. The substrates were first cleaned in distilled water in order to remove the impurities and residuals from the surface. Then cleaned in alcohol ultrasonically for 15 min subsequently dried prior to film deposition experiment.

✓ Sapphire Substrate

$\alpha$–plane ($\alpha$-Al$_2$O$_3$) single crystal sapphire substrate (MTI Corporation) is the popular for III-V nitrides, Both polished side (substrate surface is EPI polished via a spatial CMP procedure with RA< 5A) with square-shaped size 10mm x 10mm x 0.5 mm thick were etched in H$_2$SO$_4$:H$_3$PO$_4$=3:1 followed by ultrasonic cleaning in deionized water for 15 min, and finally dried. The main physical properties of the $\alpha$-Al$_2$O$_3$ substrate can describe in table (3.1).

Table (3.1): The some physical properties of $\alpha$-Al$_2$O$_3$ substrate

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Crystal Structure

- **Hexagonal**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice A</td>
<td>( a=4.758 \text{ Å} ), ( c=12.99 \text{ Å} )</td>
</tr>
<tr>
<td>Orientation Tolerance</td>
<td>+/- 0.5 (^\circ), ( \alpha ) plane orientation</td>
</tr>
<tr>
<td>Melting Point</td>
<td>2040 degree C</td>
</tr>
<tr>
<td>Density</td>
<td>3.97 gram/cm(^2)</td>
</tr>
<tr>
<td>Growth Technique</td>
<td>CZ</td>
</tr>
<tr>
<td>Crystal Purity</td>
<td>99.999%</td>
</tr>
<tr>
<td>Hardness</td>
<td>9 (mohs)</td>
</tr>
<tr>
<td>Thermal Expansion</td>
<td>( 7.5 \times 10^{-6} ) /(^\circ)C</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>46.06 @ 0 (^\circ)C</td>
</tr>
<tr>
<td></td>
<td>25.12 @ 100 (^\circ)C</td>
</tr>
<tr>
<td></td>
<td>12.56 @ 400 (^\circ)C</td>
</tr>
</tbody>
</table>

### 3.5 Procedure of Thin Film Deposition by PLD

The pulsed laser deposition experiment is carried out inside a vacuum chamber generally in \((10^{-3} \text{ Torr})\) vacuum conditions, at low pressure of a background gas for specific cases of oxides and nitrides. A schematic diagram of the set-up of laser deposition chamber, given in Fig.3.4, shows the arrangement of the target and substrate holders inside the chamber with respect to the laser beam. The focused Nd:YAG SHG Q-switching laser beam coming through a window is incident on the target surface making an angle of 45\(^\circ\) with it. The substrate is placed in front of the target with its surface parallel to that of the target. Sufficient gap is kept between the target and the substrate so that the substrate holder does not obstruct the incident laser beam. Modification of the deposition technique is done by many investigators from time to time with the aim of obtaining better quality films by this process. These include rotation of
the target, heating the substrate, positioning of the substrate with respect to the target etc.

![Diagram of pulsed laser deposition (PLD) system]

1. Nd:YAG Laser Head
2. O\textsubscript{2} cylinder gas
3. Stainless steel Flange
4. N\textsubscript{2} cylinder gas
5. Nd:YAG laser Power supply
6. Flexible tube KF16
7. Quartz Chamber
8. Substrate holder
9. Vacuum system
10. Variac devices

*Figure (3.6):* Pulsed laser deposition (PLD) system
3.6 Characterization Measurements

The characteristic measurements of this technique used to investigate the thickness, the structural features of the films were X-ray diffraction (XRD) and scanning electron microscopy (SEM). The optical features of the films were investigated by transmission through UV-Vis absorption spectroscopy, Photoluminescence and Z-scan technique to determine the non-linear refractive index.

3.6.1 Thickness Measurement

Film thickness measurement by optical interferometer method. This method was based on interference of light beam reflected from thin film surface and substrate bottom. He-Ne laser of wavelength (632.8nm) was used and the thickness is determined using the formula:

$$d = \frac{\Delta x}{x} \times \frac{\lambda}{2} \quad \cdots \cdots (3 - 1)$$

Where $x$ is fringe width, $\Delta x$ is the distance between two fringes and $\lambda$ is wavelength of laser light.

3.6.2 Structural and Morphological Measurements

A) X-Ray Diffraction Spectra

All ZnO layers were studied by X-ray diffraction (XRD) techniques. It is a noncontact and nondestructive technique used to identify the crystalline phases present in materials and to measure the structural properties of these phases.

X-ray diffraction measurement has been done and compared with the ASTM (American Society of Testing Materials) cards, using Philips PW 1840 X-ray diffract meter of $\lambda = 1.54 \, \text{Å}$ from Cu-K$\alpha$. 
The crystalline size is easily calculated as a function of peak width (specified as the full-width at half maximum peak intensity (FWHM)), peak position and wavelength.

The curve of diffracted intensity vs. 2θ will thus have the form of Figure (3.7a) in contrast to Figure (3.7b), which illustrates the hypothetical case of diffraction occurring only at the exact Bragg angle.

![Figure. (3.7): Effect of fine crystallite size on diffraction curves](image)

The width of the diffraction curve of Figure 3.7a increases as a thickness of the crystal decreases, because the angular range (2θ₁ - 2θ₂) increases as m decreases. The width B is usually measured, in radians, at an intensity equal to half the maximum intensity (FWHM). Therefore

\[
B = \frac{1}{2} (2\theta_1 - 2\theta_2) = \theta_1 - \theta_2 \quad \cdots \cdots (3 - 3)
\]

The path-difference equations for these two angles are similar, but related to the entire thickness of the crystal rather than to the distance between adjacent planes

\[
2\delta \sin \theta_1 = (m + 1)\lambda,
\]

\[
2\delta \sin \theta_2 = (m - 1)\lambda
\]

By subtraction,

\[
\delta (\sin \theta_1 - \sin \theta_2) = \lambda
\]
But $\theta_1$ and $\theta_2$ are both very nearly equal to $\theta_B$, so that

$$\theta_1 + \theta_2 = 2\theta_B (\text{aprox})$$

Therefore

$$\delta = \frac{0.89 \lambda}{B \cos \theta} \quad \cdots (3-2)$$

This is known as Scherrer’s formula \[103\]. It is used to estimate the size of very small crystals from measured width of their diffraction curves.

In this study we used the XRD to determine the crystal orientation of the ZnO target before ablation, the ZnO films on $\text{Al}_2\text{O}_3$ (0001) and the ZnO film on a glass and quartz substrate. To Determine the lattice parameters for the wurtzite structure the interplanar distance of $\{hkl\}$ plane is related to the lattice parameters $a$ and $c$ via the Miller indices $hkl$:

$$\left( \frac{1}{d_{hkl}} \right)^2 = \frac{3}{4} \left( \frac{h^2 + k^2 + hk}{a^2} \right) + \frac{l^2}{c^2} \quad \cdots (3-3)$$

For the lattice parameters determination of a c-plane oriented film includes a measurement of in order to determine the c lattice parameter, and for the determination of lattice from a second measurement of $d_{hkl}$ with either $h$ or $k$ different from zero.

The calculation of the film stress is based on the biaxial strain model. The strain is given by equation:

$$\varepsilon = \frac{c_{\text{film}} - c_{\text{bulk}}}{c_{\text{bulk}}} \quad \cdots (3.4)$$

Where $c_{\text{film}}$ and $c_{\text{bulk}}$ are the lattice parameter of the ZnO thin film, respectively)using interlayer spacing of the films the stress in the plane of ZnO film with a hexagonal crystal can be expressed as
\[ \sigma_{film} = \frac{2c_{13}^2 - c_{33}(c_{11} - c_{12})}{2c_{13}} \left( \frac{c_{film} - c_{bulk}}{c_{bulk}} \right) \quad \cdots \cdots (3 - 5) \]

The values of elastic constant from single crystalline ZnO are used, \( c_{11} = 208.8 \text{ GPa}, \ c_{33} = 213.8 \text{ GPa}, \ c_{12} = 104.2 \text{ GPa} \), substituting these values in the above equation gives:

\[ \sigma_{film} = -233 \left( \frac{c_{film} - c_{bulk}}{c_{film}} \right) \text{ [GPa]} \quad \cdots \cdots (3 - 6) \]

Where \( c_{bulk} = 5.2067 \text{ Å} \), which was obtained from ASTM card ZnO.

**B) Scanning electron microscopy (SEM)**

Scanning electron microscopy (SEM) is basically a type of electron microscope. SEM is used for various purposes;

- Topographic studies.
- Microstructure analysis.
- Elemental analysis if equipped with appropriate detector (energy/wavelength dispersive x-rays).
- Chemical composition.
- Elemental mapping.

Samples were mounted on aluminum stubs by double – sided sticky discs of conductive carbon, then gold coated by sputtering method at 1200 V, 20 mA, using vacuum coater (Polaron E6100, UK) as shown in figure (3.8) The SEM study carried out by (FEL Quanta 200, Netherlands) scanning electron microscope equipped with Energy dispersive X-ray (EDAX); determine the energy of the X-rays microanalysis a illustrated in fig. (3.9).
3.6.3 Optical measurement

A) Transmission measurement

A double-beam UV-IR 210A Spectrophotometer was used to measure the transmittance and absorption of ZnO film deposited at different conditions within the wavelength range (300-900nm). The background correction was taken for each scan.

The transmittance and reflectance data can be used to calculate absorption coefficients of the films at different wavelength. And the used to determine the band gap, $E_g$, using the relation (2-9)
B) Photoluminescence measurements

To gain more knowledge about the electronic structure, magnetic and electric fields can be applied in a controlled manner. Moreover external forces can be used in PL investigations, e.g. the strain by exposing the material to mechanical pressure. Since PL relies on radiative recombination, so it is very difficult for the investigation of non-radiative processes needs indirect methods, and the material having poor quality are hard to characterize through PL.

The experimental setup consists of an excitation source, cryostat, microscope objective, monochromatic, CCD-TV camera and additional components,

c) Z-scan measurement

Our Z-scans were all performed using a Q-switched Second harmonic generation Nd:YAG laser, with a wavelength of 532nm, repetition rate 6 Hz and pulse duration of 10ns. The laser had a Gaussian spatial profile, which is crucial to the Z-scan method.
Z-scan method is chosen because of its simplicity and sensitivity. While using only a single laser beam, the scan has the ability to find the sign, magnitude, and order of the nonlinear response of nonlinear optical materials. The main elements of the Z-scan method are shown in Fig. (3.10).
4. Introduction
In this chapter, we demonstrating the on how the deposition conditions parameters (substrate temperature, substrate materials, background pressure, laser wavelength and laser fluency, etc.). Affect the characteristics (such as crystal structure and surface morphology) of the grown films. However, the influence of the deposition conditions on luminescence properties of films has not yet been extensively studied because it’s a secondary effect and mainly because of the change in crystalline quality or crystal structure and the surface morphology of the films.

4.1 Effect of Deposition Conditions on the Characteristic of Thin films Grown Using PLD
4.1.1 Substrates Temperatures

The substrate temperature plays an important role in determining the structure of ZnO thin films which are fabricated on glass, quartz and sapphire substrates. Figure: (4.1) shows the XRD measurements results of the different ZnO films formed at substrate temperatures of RT, 100- 500°C. From curve (a) to curve (f), the ZnO films grown on glass substrate exhibit three or more obvious ZnO peaks in the diffraction pattern. The XRD peaks which are located at about $2\theta = 31.45^\circ$, $36.15^\circ$, $34.4^\circ$ and $47.3^\circ$ are attributed to ZnO planes (100), ZnO (101), ZnO (002), and (102), respectively.

As shown in Fig. (4.1) the deposits obtained at the low substrate temperature (RT), by nanosecond ablation of ZnO thin film compound mainly consist of polycrystalline phases with poorer crystalline quality as compared to others. With the increase of the substrate temperature other orientations related to ZnO also appeared. It indicates that the orientation of the crystal become random: the intensity of ZnO (100) diffraction peaks decreases, and the intensity
of the ZnO (002) diffraction peaks becomes more intense and sharper. The intensity of XRD peaks is related to many factors, which include crystallization quality, density, and thickness of thin films, and so on. The intensities of ZnO (002) peaks in XRD spectra are different due to the diverse crystallization quality and various substrate temperatures in spite of the same deposition condition [37].

Figure (4.2) shows the full width at half maximum (FWHM) of the ZnO thin films grown at the different substrate temperatures. The FWHM of the (002) peaks decreases with increases the substrate temperatures, the decrease of FWHM of (002) peak is related to the migration and diffusion rate of zinc and oxygen atoms.

At low temperature, the zinc and oxygen atoms have no energy to migrate to the normal lattice site. This leads to a broaden (002) peak and small grain size. But at high temperature, small grains have enough energy to combine together to from large grains, which leads to decrease of the FWHM of (002) peak [36]. From table (4.1) the substrate temperature is raised up to 400ºC, the FWHM decreases, but the crystalline quality become healthy as compared at low temperature. The FWHM of XRD depends on the crystalline quality of each grain and distribution of grain orientation.

The increasing of the substrate temperature is in favor for the diffusion of atoms absorbed on the substrate and accelerates the migration of atoms to the energy favorable positions, resulting in the enhancement of the crystalline and c-axis orientation of film. On the other hand, when substrate temperature is low, the adatoms are rapidly cooled and their diffusion or hopping distance becomes small. Thus, the surface becomes rough and its structure looks like polycrystalline [51].
Figure (4.1) XRD spectra of ZnO/glass at different temperature
a) RTºC  b) 100ºC,  c) 200ºC,  d) 300ºC,  e) 400ºC,  f) 500ºC.

*ZnO* ([100], [002], [101], [102], [004])
In both case, the lattice parameter is less than its value for ZnO powder (hexagonal ZnO, \(a = 3.250\) Å, \(c = 5.2067\) Å). This fact is attributed to surface effect which leads to the shrinkage in the \(c\)-lattice distortion and decrease the lattice parameter\(^5\).

**Figure (4.2)** The FWHM for ZnO (002) grown on glass at different substrate temperature

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>(2\theta) for (002) reflection</th>
<th>Interplanar spacing, (d) Å</th>
<th>Lattice constant Å</th>
<th>Strain (\varepsilon) ((\times 10^{-3}))</th>
<th>Stress (GPa)</th>
<th>FWHM°</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100</td>
<td>34.55</td>
<td>2.6030</td>
<td>5.206</td>
<td>-0.134</td>
<td>+0.0313</td>
<td>0.1392</td>
</tr>
<tr>
<td>200</td>
<td>34.45</td>
<td>2.6028</td>
<td>5.2056</td>
<td>-0.211</td>
<td>+0.0492</td>
<td>0.1314</td>
</tr>
<tr>
<td>300</td>
<td>34.5</td>
<td>2.6026</td>
<td>5.2052</td>
<td>-0.288</td>
<td>+0.0671</td>
<td>0.1234</td>
</tr>
<tr>
<td>400</td>
<td>34.55</td>
<td>2.5985</td>
<td>5.197</td>
<td>-1.862</td>
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<td>0.1456</td>
</tr>
<tr>
<td>500</td>
<td>34.4</td>
<td>2.5965</td>
<td>5.193</td>
<td>-2.631</td>
<td>+0.614</td>
<td>0.1236</td>
</tr>
</tbody>
</table>

Figure (4.3) shows XRD patterns of ZnO thin films grown on quartz substrate at laser fluence 1.6 J/cm\(^2\) in oxygen pressure 5×10\(^{-2}\) mbar at substrate temperature from RT to 500°C. For all the films only the ZnO (002) peak is observed, indicating that the films are crystalline with a hexagonal structure. It is found that the intensity of ZnO (002) orientation is weak for the films grown at RT and 100°C, but it increases with increasing substrate temperature to 400°C.
However, the intensity decreases when ZnO is deposited at 500°C. ZnO (002) peak shifts to higher angle with the temperature changing from 300°C to 500°C. It indicates the existence of residual stress due to different thermal expansion coefficients between ZnO film and substrate.

The full-width-at-half-maximum (FWHM) of the (002) diffraction peak are shown in figure (4.4).

Increases of substrate temperature results in the reduction of (002) FWHM for ZnO films deposited on quartz substrate, and the lowest line width of 0.1192° has been achieved at 300°C. Narrow FWHM of (002) peak means large grain size of film. High substrate temperature can offer more kinetic energy for mobility of particle on the surface to achieve better crystalline growth. This result agreement with that of J. N. Zeng et al.\cite{32}. They observed a similar variation in FWHM with substrate temperature when the ZnO films were prepared by PLD.
The film deposited at room temperature shows a minimum strain compressive (~ -0.55×10^{-3}), which increases monotonically to (~ -2.97×10^{-3}) at 400°C. The higher value of strain in the film deposited above 400°C and its decreases with decreasing of substrate temperature indicates that thermal stress
are contributed significantly to the observed strain. Further, the amorphous nature of quartz substrate rules out strain due to lattice mismatch. Hence the compressive strain in the films deposited

Above 400ºC is attributed to extrinsic stress and is considered intrinsic to the growth process. It has been reported in the case of ZnO films that O\textsuperscript{-} ions formed at the target have sufficient energies to bombard the growing film and cause implantation or displacement of surface atoms deeper into the film, resulting in compressive strain\textsuperscript{[140]}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure.png}
\caption{The FWHM for ZnO (002) grown on quartz at different substrate temperature}
\end{figure}

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
\textbf{Temp. °C} & \textbf{2θ for (002) reflection} & \textbf{Interplanar spacing, d Å} & \textbf{Lattice constant Å} & \textbf{Strain \(ε(×10^{-3})\)} & \textbf{Stress (GPa)} & \textbf{FWHM°} \\
\hline
RT & 34.1 & 2.6019 & 5.2038 & -0.55 & +0.129 & 0.1383 \\
100 & 34.6 & 2.6016 & 5.2032 & -0.67 & +0.156 & 0.1336 \\
200 & 33.95 & 2.6010 & 5.202 & -0.91 & +0.211 & 0.1318 \\
300 & 34.35 & 2.5977 & 5.1954 & -2.17 & +0.506 & 0.1192 \\
400 & 34.40 & 2.5956 & 5.1912 & -2.97 & +0.695 & 0.1659 \\
500 & 34.45 & 2.5890 & 5.178 & -5.5 & +1.291 & 0.1472 \\
\hline
\end{tabular}
\caption{The obtained result of the structural parameters from XRD for ZnO/Quartz thin films}
\end{table}
Figure (4.5) shows XRD patterns for the ZnO thin films grown on sapphire substrate temperatures. The peaks at about 34.4° and 41.6° correspond to the diffraction from the ZnO (002) and Al$_2$O$_3$ (006) planes, respectively. The ZnO (002) peaks are observed for all the samples. This indicates that ZnO films with a good c- axis preferred orientation can be obtained by PLD at substrate temperatures from RT to 500°C. In addition, there is one weak peak appearing at $2\theta=31.8^\circ$ as shown in fig. (4.5 b, d) which is corresponding to ZnO (100).

According to figure (4.5) the FWHM decreases with substrate temperature increasing. The FWHM of the XRD is influenced by many factors such as grain size, inhomogeneous stress distribution and crystal quality.

Figure (4.5e) shows intense sharp (002) peak with high intensity as compared to the other peaks. A homogenous strain in a film gives rise to a sharp peak in the intensity of the x-ray beam at the Bragg angle. However, if the mismatch strain distribution in the films were spatially inhomogeneous, local gradients in strain within the region sensed by the incident x-ray beam would cause x-ray peak broadening, resulting in a more diffused intensity plot.

The intensity of ZnO (002) peak at a substrate temperature of 400°C is most intense, which indicates an improvement in the ZnO film crystallinity, the full width at half maximum for the ZnO grown at 400°C is found to be 0.25° this result is agreement with C. Sui. et al [61]. Note that substrate temperature has no effect on the crystalline orientation, but does have an effect on the intensity of the peak signal.

The FWHM of $2\theta$ values reveals the crystalline of the film. The atomic kinetic energy is mainly determined by substrate temperature. Therefore, at a relatively high temperature, the atoms on the film surface can move quickly to look for the lowest energy sites and form the low energy structure [128]. As a
result, the structural quality of the ZnO film deposited at high substrate temperature is better than at low temperature. Meanwhile, in the films deposited at high substrate temperature, the number of grains with the c-axis orientation is large. So the XRD curve becomes smooth and the intensity of ZnO (002) peak becomes strong with the increasing of substrate temperature. The crystalline of the specimens becomes good. But when the substrate temperature is too high (for example 500°C), the adatoms are decomposed and re-evaporated from the surface. The ZnO film becomes thermodynamically unstable.

The enhancement of c-axis orientation with increasing substrate temperature above 100°C is attributed to increase in surface diffusion of the adsorbed species.

Fig. (4.5) also reveals shifts in the positions of (002) peaks with substrate temperature. The position of (002) peak shifts monotonically from 34.2º for the film deposited at room temperature to 34.49 for the film deposited at 400ºC, the later being quite close to the corresponding value of 34.467º for bulk. This is agreement with Q. P. Wang et al [141].

The lattice constant “c” was obtained from the position of the (002) peak for all the films, and was used to estimate the strain (ε) in the films along c-axis given by equation the variations of the strain with substrate temperature. The film deposited at 500°C temperature showed the maximum compressive strain (-3.59 ×10⁻³), which decreased monotonically to nearly zero at ~RT. Indicate that thermal stress does contribute significantly to the observed strain.
Figure (4.5) XRD spectra of ZnO/Sapphire at different substrate temperature

a) RT°C b) 100°C, c) 200°C, d) 300°C, e) 400°C, f) 500°C.
Figure (4.6) The FWHM for ZnO (002) grown on sapphire at different substrate temperature

Table (4.3) The obtained result of the structural properties from XRD for ZnO/Sapphire thin films

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>2θ for (002) reflection</th>
<th>Interplanar spacing, d Å</th>
<th>Lattice constant Å</th>
<th>Strain ε (×10⁻³)</th>
<th>Stress (GPa)</th>
<th>FWHM°</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>34.2</td>
<td>2.60280</td>
<td>5.2056</td>
<td>-0.21</td>
<td>+0.0492</td>
<td>0.1400</td>
</tr>
<tr>
<td>100</td>
<td>34.33</td>
<td>2.60220</td>
<td>5.2044</td>
<td>-0.44</td>
<td>+0.103</td>
<td>0.1394</td>
</tr>
<tr>
<td>200</td>
<td>34.40</td>
<td>2.60193</td>
<td>5.2038</td>
<td>-0.556</td>
<td>+0.129</td>
<td>0.1382</td>
</tr>
<tr>
<td>300</td>
<td>34.43</td>
<td>2.60152</td>
<td>5.2030</td>
<td>-0.71</td>
<td>+0.165</td>
<td>0.1301</td>
</tr>
<tr>
<td>400</td>
<td>34.49</td>
<td>2.5988</td>
<td>5.1976</td>
<td>-1.74</td>
<td>+0.407</td>
<td>0.2532</td>
</tr>
<tr>
<td>500</td>
<td>34.57</td>
<td>2.5940</td>
<td>5.188</td>
<td>-3.59</td>
<td>+0.839</td>
<td>0.1394</td>
</tr>
</tbody>
</table>

XRD results indicate that the c-axis of the grains become uniformly perpendicular to the substrate surface at the optimized temperature. It is suggested that the surface energy of (002) plane is lowest in the ZnO crystal. Grains with the lower surface energy will become larger as the film grows. Then the growth orientation develops into one crystallographic direction of the lowest surface energy. This means that the (002) texture of the film may be easily formed. Substrate temperature is crucial in that the low substrate temperature results in the low surface migration of adatoms, while the high substrate temperature causes the adatoms to re-evaporate from the film surface. The ZnO wurtzite structure makes the film grow in (002) performed orientation on all substrates at the optimized growth temperature.
4.1.2 Substrate Material

One of the difficulties in the growth of ZnO single crystal films lies in obtaining a suitable substrate material. In this section, we used three materials glass, quartz and sapphire as a substrate. Although there are lattice mismatched substrates, such as ZnO itself and ScMgAlO$_4$[142], currently the commercial availability and the crystalline quality of these substrates are not adequate particularly for large-scale application. To grow high crystalline quality ZnO films in large area is much important for material science as well as for device application.

The sapphire, having hexagonal close peck (hcp) crystal structure, high transparency in the desired UV-Visible spectral range, high melting point, rugged nature and low cost is currently the most popular choice for the growth of the ZnO despite the fact that the in-plane lattice mismatch is as high as ~18%. Therefore one of the challenges associated with the development and commercialization of ZnO based device is to achieve device – quality ZnO films’ growth on widely used. Low cost sapphire substrate in line with what has been done for its structurally and are spectrally close neighbor GaN [143], as well as waveguide laser operation of rare-earth and transition-metal ions in oxide crystalline materials such as Al$_2$O$_3$, Y$_3$Al$_5$O$_{12}$, YAlO$_3$, KY(WO$_4$)$_2$, and LiNbO$_3$ [138].

In this work, zinc oxide thin films have been prepared by pulsed laser deposition under fixed substrate temperature 400ºC, oxygen pressure 5×10$^{-2}$ mbar and laser fluence 1.6 J/cm.

Fig.(4.7) shows the X-ray diffraction (XRD) spectra of the as-grown ZnO films deposited on three types of substrates. The XRD measurements revealed that all of the obtained films were polycrystalline with the hexagonal structure,
and had a preferred orientation with c-axis perpendicular to the substrates. For the films on sapphire substrates only the (002) diffraction peak is observed and it locates at $2\theta=34.49^\circ$ and show relatively very high intensity than the film on other substrates.

The intensity of the (002) is more in ZnO/Sapphire than in ZnO/glass and ZnO/quartz. But for films on the other two types of substrates, besides the (002) peak, the (100) and (101) peaks still existed. This means that the film deposited on glass and quartz are polycrystalline with the hexagonal structure but on the sapphire substrate is single crystalline. This is agreement with work of G. Srinivasan and J. Kumar [144].

The full width at half maximum (FWHM) and the (002) peak are 0.2431°, 0.1889° and 0.2732°, for the ZnO film grown on glass, quartz and sapphire substrate respectively. The (002) located at $2\theta=34.55^\circ$, $2\theta=34.4^\circ$ and $2\theta=34.49^\circ$, for the ZnO films grown on glass, quartz and sapphire substrate respectively.

It is seen that the position of (002) peak is different for ZnO films deposited on different substrates. The different substrates will lead to different crystal lattice mismatch between the substrate and ZnO films. And the crystal lattice mismatch will cause different strain and stress in the films.

It can be seen that the ZnO films on sapphire substrates have better orientation, and the crystallinity of the film is best. This is in consistent with the results of XRD.
4.1.3 Film Thickness

The parameter that has to be taken into account for further properties and application in the field of spontaneous or stimulated emission is the thickness of ZnO films related to the grain size \[2\]. It is important factor to control the structural, optical and electrical properties of the ZnO films. ZnO films were deposited at oxygen pressure $5 \times 10^{-2}$ mbar, using a substrate temperature of 400°C.

This condition was referred to the optimized condition to emit UV light, elsewhere \[151\]. In the synthesizing process, all the conditions were maintained as the optimized condition, except the deposition time in the range of 30s to 50min in order to make a variation in the film thickness. The film thicknesses have

\[\text{Figure (4.7) The XRD spectra of ZnO films deposited on a). glass, b) quartz, c) sapphire}\]
been measured to be in the range 100-180 nm by optical interferometer method. ZnO and sapphire have the same hexagonal structure \(^{103}\). XRD pattern of ZnO thin film of various thicknesses are shown in fig. (4.8). Only (002) ZnO peak and (006) Al\(_2\)O\(_3\) peak were observed , all films grown in this work exhibit the same shape and the patterns assuming that all the films grown on sapphire substrates are with strongly c–axis orientation. The FWHM of 2\(\theta\) values linked to the grain size of the film.

The smaller FWHM means that the larger grain size, and the better crystal quality of the whole film. Increasing the film thickness enhanced the crystal quality of the film, indicated by the decreasing values of FWHM as shown in table (4.4). The XRD measurements indicate that the thicker films are more crystalline and have larger grains than the thinner films \(^{2}\).

![X-ray diffraction spectra of as-deposition ZnO thin films with different thickness.](image)

**Table (4.4)** The obtained result of the structural parameters from XRD for ZnO/sapphire thin films

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>2(\theta) for (002) reflection</th>
<th>Interplanar spacing, d Å</th>
<th>Lattice constant Å</th>
<th>Strain</th>
<th>Stress (GPa)</th>
<th>FWHM°</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>400</td>
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<tr>
<td>600</td>
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<td></td>
<td></td>
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<tr>
<td>800</td>
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<tr>
<td>1000</td>
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</tr>
</tbody>
</table>
Fig. (4.9) shows the XRD patterns of ZnO films grown on sapphire (α-Al₂O₃) substrate at a fixed temperature 400°C, 1.6 J/cm² laser fluence energy density and with and without oxygen pressures various from (5×10⁻² and 5×10⁻¹) mbar. All the films have only sharp (002) peak at diffraction angle 2θ=34.59° and strong reflection peak of sapphire (006) at diffraction angle 2θ=41.45°, which indicate that they are all highly c-axis orientation. Though the curve of the film at 5×10⁻² mbar has only (002) peak without other peaks, its intensity of the (002) peak is lower than and the value of the noise is higher than that of the others. In other words, the crystallinity of it becomes worse when the oxygen pressure reaches at 5×10⁻¹ mbar.

From fig (4.9) it can be see that the intensity of the ZnO film deposited at 5×10⁻¹ mbar extremely low than the others. Indicating that the ZnO film grown at that O₂ pressure has a very low crystalline quality.

The full width at half maximum (FWHM) of the (002) peaks of the ZnO films grown in O₂ pressure at 5×10⁻² mbar is low, but it is high at the O₂ pressure 5×10⁻¹ mbar. In general, the smaller the FWHM is, the higher the film crystallinity. From table (4.5), the value of the film at 5×10⁻¹ mbar is a little larger than the others, indicating its crystallinity is little worse.

In order to reveal a possible reason for the deterioration in crystalline quality for the ZnO film grown at high oxygen pressure 5×10⁻¹ mbar, we first considered the strain that may be accumulated in the film. The (002) lattice

<p>| | | | | | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>100</td>
<td>34.65</td>
<td>2.6025</td>
<td>5.2050</td>
<td>-0.326</td>
<td>+0.0760</td>
</tr>
<tr>
<td>150</td>
<td>34.7</td>
<td>2.5977</td>
<td>5.1954</td>
<td>-2.34</td>
<td>+0.546</td>
</tr>
<tr>
<td>180</td>
<td>34.73</td>
<td>2.5964</td>
<td>5.1928</td>
<td>-1.63</td>
<td>+0.622</td>
</tr>
</tbody>
</table>

### 4.1.4 Oxygen pressure

The oxygen pressure also plays an important role in the film crystallinity. Fig. (4.9) shows the XRD patterns of ZnO films grown on sapphire (α-Al₂O₃) substrate at a fixed temperature 400°C, 1.6 J/cm² laser fluence energy density and with and without oxygen pressures various from (5×10⁻² and 5×10⁻¹) mbar. All the films have only sharp (002) peak at diffraction angle 2θ=34.59° and strong reflection peak of sapphire (006) at diffraction angle 2θ=41.45°, which indicate that they are all highly c-axis orientation. Though the curve of the film at 5×10⁻² mbar has only (002) peak without other peaks, its intensity of the (002) peak is lower than and the value of the noise is higher than that of the others. In other words, the crystallinity of it becomes worse when the oxygen pressure reaches at 5×10⁻¹ mbar.

From fig (4.9) it can be see that the intensity of the ZnO film deposited at 5×10⁻¹ mbar extremely low than the others. Indicating that the ZnO film grown at that O₂ pressure has a very low crystalline quality.

The full width at half maximum (FWHM) of the (002) peaks of the ZnO films grown in O₂ pressure at 5×10⁻² mbar is low, but it is high at the O₂ pressure 5×10⁻¹ mbar. In general, the smaller the FWHM is, the higher the film crystallinity. From table (4.5), the value of the film at 5×10⁻¹ mbar is a little larger than the others, indicating its crystallinity is little worse.

In order to reveal a possible reason for the deterioration in crystalline quality for the ZnO film grown at high oxygen pressure 5×10⁻¹ mbar, we first considered the strain that may be accumulated in the film. The (002) lattice

<p>| | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>34.65</td>
<td>2.6025</td>
<td>5.2050</td>
<td>-0.326</td>
<td>+0.0760</td>
</tr>
<tr>
<td>150</td>
<td>34.7</td>
<td>2.5977</td>
<td>5.1954</td>
<td>-2.34</td>
<td>+0.546</td>
</tr>
<tr>
<td>180</td>
<td>34.73</td>
<td>2.5964</td>
<td>5.1928</td>
<td>-1.63</td>
<td>+0.622</td>
</tr>
</tbody>
</table>
spacing of the ZnO films was estimated from the XRD (002) peak position in order to calculate how much strain was present in the films. From table (4.5) the lattice spacing for the films deposited at $5 \times 10^{-1}$ mbar is larger than the others. In general, ZnO films are deficient in oxygen. This deficient may be alleviated by high ambient oxygen in the growth chamber during deposition. The higher the O$_2$ pressure in the growth chamber, the more oxygen is incorporated into the ZnO film lattice. When oxygen is excessively incorporated due to a high O$_2$ pressure, lattice expansion is likely to happen.

The crystalline quality can be also affected by the kinetic energy, as the oxygen pressure increases; the crystalline quality of the films becomes worse. The ablated species suffer more collision in the gas phase and thereby there velocity of the ablated species is decreased. At lower oxygen pressure, the ablated species have sufficient kinetic energy for diffusion and can thus diffuse to the right crystallographic sites. However at higher oxygen pressure, the ablated species have lesser kinetic energy which results in lesser diffusion resulting in poor crystalline quality of the films.

![Figure (4.9)](image.png)

Figure (4.9) XRD patterns of ZnO films grown on sapphire at various oxygen pressures.

<table>
<thead>
<tr>
<th>$O_2$ mbar</th>
<th>2θ for (002) reflection</th>
<th>Interplanar spacing, d Å</th>
<th>Lattice constant Å</th>
<th>Strain $\varepsilon$ ($\times 10^{-3}$)</th>
<th>Stress (GPa)</th>
<th>FWHM°</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5 \times 10^{-1}$</td>
<td>34.7</td>
<td>2.6009</td>
<td>5.2018</td>
<td>-0.94</td>
<td>+0.2194</td>
<td>0.1632</td>
</tr>
</tbody>
</table>
4.1.5 Irradiation conditions

Applications of material ablation by powerful lasers often require 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. Fig (4.10) shows the XRD spectrum of the ZnO films deposited on sapphire substrates employing the Q-switching Nd:YAG laser ($\lambda=1064$nm) and frequency-double Nd:YAG laser ($\lambda=532$nm) in oxygen background pressure $5\times10^{-2}$mbar. From the two wavelength we obtained the strong (002) peak attribute the hexagonal wurtzite structure of the ZnO formed on sapphire substrates. 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. The quality of the ZnO films grown by the shorter wavelength laser is better than that of the films grown by the longer wavelength.

The FWHM of ZnO films grown on sapphire substrate in oxygen ambient are $0.1339^\circ$ and $0.1964^\circ$ at $\lambda=1064$nm and $\lambda=532$nm, respectively.
Figure (4.10): XRD patterns of ZnO films grown on sapphire at various laser wavelength.

<table>
<thead>
<tr>
<th>Laser wavelength (nm)</th>
<th>2θ for (002) reflection</th>
<th>Inter planar spacing, d Å</th>
<th>Lattice constant Å</th>
<th>Strain (×10⁻³)</th>
<th>Stress (GPa)</th>
<th>FWHM°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1064</td>
<td>35</td>
<td>2.6019</td>
<td>5.2038</td>
<td>-0.556</td>
<td>+0.129</td>
<td>0.1372</td>
</tr>
<tr>
<td>532</td>
<td>34.6</td>
<td>2.595</td>
<td>5.190</td>
<td>-3.21</td>
<td>+0.747</td>
<td>0.1933</td>
</tr>
</tbody>
</table>

To remove (to 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 \( I_0(t) \) over the pulse duration \( t_p \). Therefore, the ablation rate is a function of fluence. A typical ablation threshold is of the order of 0.8-2.4 J/cm², depending on the target material and the laser wavelength \(^{[2]}\).

Figure (4.11) shows the X-ray diffraction patterns from the ZnO with different laser fluence. Thin films are grown with different laser fluence (0.8, 1.6 and 2.4) J/cm² at 400°C and at fixed oxygen pressure of 5×10⁻² mbar.

An XRD spectrum is shown in Fig. (4.11) reveals the influence of laser on the structure of the ZnO/α-Al₂O₃ films. As the laser fluence energy density
increases from (0.8 to 1.6) J/cm$^2$, the intensity of the ZnO (002) increases, then at 2.4 J/cm$^2$ is decreases. This indicates that at the lower fluence values (those corresponding to ~ 0.8 J/cm$^2$) the target surface melts, but the quantity of ablated material is too low to form a dense plasma.

At such low laser fluence the interaction process is more akin to the thermal evaporation that ablation. At high laser fluence 1.6J/cm$^2$ it is generally understood that the clusters with magic number are relatively more stable and are therefore likely to be deposited in the thin films or other quantum structures grown by PLD. To avoid having stable clusters in the deposit it is obvious that one should work at low laser fluence close to ablation threshold. At higher laser fluences the laser produced plasma contains a significant amount of highly energetic species. The high energy plum species after colliding with substrate may penetrate the substrate surface and get embedded in to it. These immobile atoms then act as additional nucleation centers and promote island type of growth. These islands along with naturally formed nucleation centers then grow in size and coalesce to form a continuous film.

For all the films no Zn or Al characteristics peaks and O peaks were observed and only ZnO (002) diffraction peak was observed. That is, orientation growth (002) plane of the ZnO/$\alpha$-Al$_2$O$_3$ thin film is dominant, the ZnO (002) diffraction peaks location are at $2\theta = 34.25$, 34.3, 34.5 and we can see the strongest reflection peak of sapphire (006) at diffraction angle $2\theta = 41.3^\circ$, 41.56$^\circ$ and 41.75$^\circ$ for different laser energy densities. It is observed that (002) diffraction angle is gradually shifted from 34.25 to 34.5 with increasing laser energy.
The XRD result indicates that (ZnO grown on sapphire substrate at 400°C temperature) posses a hexagonal wurtzite crystal structure, with preferably a perpendicular c-axis orientation to the surface the intensity of ZnO (002) at laser fluence 1.6J/cm² is very high as compare to the other planes.

Table (4.7) The structural parameters from XRD for ZnO/Sapphire thin films

<table>
<thead>
<tr>
<th>Laser fluence J/cm²</th>
<th>2θ for (002) reflection</th>
<th>Inter planar spacing, d Å</th>
<th>Lattice constant Å</th>
<th>Strain (×10⁻³)</th>
<th>Stress (GPa)</th>
<th>FWHM°</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.8</td>
<td>34.25</td>
<td>2.6022</td>
<td>5.2044</td>
<td>-0.442</td>
<td>+0.102</td>
<td>0.1332</td>
</tr>
<tr>
<td>1.6</td>
<td>34.3</td>
<td>2.6018</td>
<td>5.2036</td>
<td>-0.595</td>
<td>+0.138</td>
<td>0.1875</td>
</tr>
<tr>
<td>2.4</td>
<td>34.5</td>
<td>2.6012</td>
<td>5.2024</td>
<td>-0.825</td>
<td>+0.192</td>
<td>0.1392</td>
</tr>
</tbody>
</table>

Figure (4.12) shows the X-ray diffraction patterns from the ZnO with different repetition rate. Thin films are grown with different repetition rate (1, 6) Hz at 400°C, 1.6 J/cm² and at fixed oxygen pressure of 5×10⁻² mbar. The optimal laser conditions have been established for both the single – pulse ablation mode, and for high –repetition –rate ablation. We observed that the
short dwell time in the high –repetition –rate laser –target interaction leads to coupling between successive laser pulses and thereby incubation of the heating and evaporation processes. This results in a redaction of the laser ablation threshold.

Practical recipes are provided that lead to efficient ablation and control the phase state of the vapor as a self –consistent function of laser parameters, namely, the pulse duration, the energy per pulse, and the wavelength, all adjusted to the target parameters. We demonstrate implementation of these recipes for deposition of high –quality micron –thick optical films for optical waveguide application.

Pulsed laser deposition (PLD) when applied in its conventional form using low –repetition –rate laser emitting microsecond –range pulses,[147] generally leads to poor quality films contaminated by particles. It has been shown that this is a direct consequence of the use of the particular pulse parameters[2] that lead to a large volume of material being evaporated by each pulse. For example, the plume produced in this regime expands as a supersaturated vapor and therefore condensation occurs during the early stage of the expansion resulting in the formation of droplets from the vapor phase, which is then deposited onto the substrate. A solution to such droplet formation has been found with a deeper insight into the physics of the laser ablation process. It has been shown that the formation of droplets can be eliminated by changing the mode of operation of the laser. Similar average laser power is employed, but the energy is delivered in shorter pulses (10ns shorter, rather than 1.06μs), at energies around 6 orders of magnitude lower (microjoules rather than joules) but at much higher repetition rates (~6Hz rather than ~1Hz).
Figure (4.12) XRD patterns of ZnO films grown on sapphire at various repetition rate.

### Table (4.8) The structural parameters from XRD for ZnO/Sapphire thin films

<table>
<thead>
<tr>
<th>Laser repetition rate (Hz)</th>
<th>2θ for (002) reflection</th>
<th>Inter planar spacing, d Å</th>
<th>Lattice constant Å</th>
<th>Strain ε(×10⁻³)</th>
<th>Stress (GPa)</th>
<th>FWHM°</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>34.6</td>
<td>2.6028</td>
<td>5.2056</td>
<td>-0.211</td>
<td>+0.049</td>
<td>0.2132</td>
</tr>
<tr>
<td>6</td>
<td>34.75</td>
<td>2.6014</td>
<td>5.2028</td>
<td>-0.749</td>
<td>+0.174</td>
<td>0.2459</td>
</tr>
</tbody>
</table>
4.2 Surface Morphology

4.2.1 Effect of substrate Temperatures

ZnO were grown on sapphire at fixed oxygen pressure of $5 \times 10^{-2}$ mbar and 1.6 J/cm$^2$ laser fluence energy density. Figure (4.13) shows the SEM images of the ZnO thin films deposited at various substrate temperatures of (RT, 100, 200, 300, 400 and 500)$^\circ$C. The Non-dense ZnO films are obtained at RT. When the substrate temperature is 100$^\circ$C, 200$^\circ$C, and 300$^\circ$C the grain size is smaller (55.25, 57.3, 60, 24) respectively, and the films become relatively dense compared to films grown at RT$^\circ$C as shown in fig.4.13 (b-d). But in fig.(4.13e), the size of the particles is small, some holes appear and the surface of the thin film becomes coarse. The particles can crystallize easily and there are few defects in the films.

At higher substrate temperature increases to higher temperature, dense ZnO films are obtained, and their grain size obviously increase, especially the films at 500$^\circ$C which have coarse grains. The surfaces of ZnO thin films are more planer and compact as the mobility of adsorbent atoms increase at higher temperatures. There are some bright spots on the surface of ZnO thin films that are considered to be micro particles and drops, which are produced by ZnO target due to the large energy density of laser.

The appearance of these nanometric structures is in accordance with a known behavior: the depositing species need higher energies to allow the growth of nanostructured samples. In this case, this energy is provided to the adatoms by two ways. The first mechanism is the higher temperature of the substrate itself, thus supplying more energy to the depositing species. A second mechanism can be related to the observation that, for ablation of oxide materials in oxygen background atmosphere, the substrate heating also
influences the plume propagation, as reported by A. Sambri and et al.\textsuperscript{[12]} at higher temperatures the background gas resistance to plume propagation is reduced, leading to an increased velocity, and hence kinetic energy, of the species reaching the substrate during the film growth.\textsuperscript{[54]}.

The general rule (increasing the grain size and improvement of the crystal) does not work at high temperatures. We believed that it has two reasons.

1) Smaller film thickness.

2) Infact reflex (002) results from the nanostructure; they are oriented perpendicular to the surface. But they are of smaller size,

As explained before, high temperature provides enough energy for the adatoms to gain high surface mobility, which promotes the formation of the large columnar structure grains as confirmed by SEM image in Fig. (4.13f).
Figure (4.13) SEM image of the ZnO thin films deposited at various temperature of
a) RT°C, b) 100°C, c) 200°C, d) 300°C, e) 400°C, f) 500°C
4.2.2 Effect of Oxygen Pressure

The SEM images of the films deposited at fixed substrate temperature of 400 °C and at oxygen pressures of $5 \times 10^{-2}$ mbar and $5 \times 10^{-1}$ mbar are shown in figure (4.14). It is evident that quite different surface morphologies are evolved depending on O$_2$ pressure during film growth. As shown in Fig.(4.14a) the growth at high O$_2$ pressure of $5 \times 10^{-1}$ mbar consists of much larger grains and exhibits a rougher surface than the film grown at the low O$_2$ pressure of $5 \times 10^{-2}$ mbar$^{[2]}$.

The mechanism for the grain formation is described as follow. After initial free expansion from the target surface, the mean free path of the ablated particles is reduced in the presence of gas. More specifically, at higher ambient pressure, the more collisions and scatterings occur. Then the particles lose energy to the level adequate for forming ionic complexes or molecules. If these clusters reach the substrate surface, small grains, start to grow as they become the nucleus. On the other hand, most of the ablated particles can reach the substrate in the state near the single atoms if the ambient pressure is extremely low$^{[1]}$.

![Figure (4.14) SEM image of ZnO thin films deposited at various oxygen pressure](image)

a ) $5 \times 10^{-1}$ mbar, b) $5 \times 10^{-2}$ mbar

4.2.3 Effect of irradiation condition
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 \cite{2}. The unwanted micron sized particulates were found to be distribution over the film surface at longer wavelength and higher laser fluence. As the wavelength of laser was decreased from 1064 nm to 532 nm the particulate density and their average size on ZnO/Sapphire films surface significantly reduced and particulates are more uniform distribution in the films \cite{23}. Fig. (4.15) shows the SEM of the thin films deposited by using 1064nm and 532nm. It can be seen in these figures that the film surface is smooth and particulate free in case of deposition with 532nm wavelength, while the micron and submicron size spherical particulates are present at the surface of the ZnO thin film grown by using 1064nm wavelength \cite{2}.

![SEM images of ZnO thin films deposited at various laser wavelength a) 1064nm, b) 532nm](image)

The penetration depth of the laser is higher at 1064nm and could cause undesirable effects such as splashing of micron size particulates from the target. So the SEM image clearly shows the typical and large density of micron size particulates on the film surface. But the penetration depth of the laser is lower at 532 nm and it is more absorbed in the material than it is 1064 nm counterpart.
The particulates ejection from the target is lower at (λ=532nm), so the relatively smooth surface of ZnO was observed, as shown in fig (4.15), the shorter the wavelength smaller the penetration depth of the laser radiation into the material. This is in agreement with that of T. Premkumar et al. [65] which reported that the micro and sub-micro size particulates ejection from target is strongly depend on the penetration depth of the laser beam.

Fig.(4.16), the SEM image shows that the surface morphology of ZnO/Sapphire films deposited under 5×10^{-2} mbar of oxygen gas at substrate temperature 400°C.

The microstructure of the PLD ZnO films is found to change significantly with the deposition fluence laser energy. The films deposited at laser fluence 0.8J/cm² exhibit a porous fine grained microstructure see (Fig. 4.20a). As the fluence laser energy is raised to 1.6J/cm², the films exhibit isolated ZnO aggregation with size over (25.31) nm which differs strongly from the surface of films with deposition at fluence laser energy 1.6 J/cm² and 2.4 J/cm² (see fig. 4.6b, c). The samples show more aggregated particles with size in the range (25.31, 66.93) nm.
4.3 Optical Properties
4.3.1 Transmission

The optical properties of the films deposited by ns-PLD were measured by UV-Vis spectrophotometer. In order to measure the optical transmittance, the laser fluence energy density was set to be 1.6 J/cm² and the oxygen pressure was maintained at 5×10⁻² mbar with 150nm thick. The UV-Vis optical properties in the range from 300nm to 900nm at various temperatures from RT°C to 500°C are shown in fig (4.17). The average transmittance in the visible part of the spectra (400-700nm) is about 80-90%, for all the films analyzed. It is observed that the optical transmittance increases slightly with increasing the substrate temperature. These changes of the transmittances are associated to the increase
of the carrier concentration \cite{2}. By comparison, the absorption edge is observed at a slightly lower wavelength range for the 400°C temperature. The shift of absorption edge may be attributed to the difference in grain size \cite{51} and/or carrier concentration \cite{15}. From the results of XRD the ZnO/Sapphire film deposited at 400°C contained relatively small grain size; this was probably why the blue shift occurred. It suggested that the grain size indeed affects the optical properties significantly.

Fig. (4.18) shows the spectra of the ZnO films deposited on glass, quartz and sapphire substrates. The films deposited on the sapphire substrate shows high transmission compared to the films deposited either on the glass or on the quartz substrate. The shift in the absorption edge of the glass and quartz clearly reveals that ZnO films deposited on sapphire substrate is of better quality.

The optical transmittance of ZnO films were grown at the substrate temperature 400°C, also dependent on the film thickness as shown in figure (4.19).

In all case, the films were found to be highly transmittance in the visible wavelength region with an average transmittance 90%, with a fall-off for wavelength shorter than 380nm, characteristics of high quality ZnO films. This is in agreement with M. Sucheta et al \cite{103}. The position and the shape of the absorption edge observed for wavelength below 380nm were found to dependent on the film thickness.

Figure (4.20a) shows the optical transmittance of the ZnO films deposited on sapphire substrate at oxygen pressure (5×10^{-1} and 5×10^{-2}) mbar and at fixed substrate temperature 400°C with 1.6J/cm² laser fluence energy density. It is found that the optical transmission of the ZnO films at high oxygen pressure is low than for low oxygen pressure, this is indicate that the decreases in optical
transmission with increases oxygen pressure is due to the grain size cause, the lower oxygen pressures inducing smaller grain size \[2\].

Also the laser fluence affected on the transmission of the ZnO films, from the fig (4.20b) we found that the fall of transmittance is very sharp near the absorption edge. The ZnO films deposited at 1.6J/cm\(^2\) given high optical transmission than the other laser fluence energy density. The sharp absorption edge at the wavelength of about ~ 380nm is observed in all the spectra, this is corresponds to ZnO excitonic transition indicating high crystalline and optical characteristics of the ZnO films grown on sapphire substrate.

The oscillatory curve of transmittance implies that the drown ZnO films have a flat surface and uniform thickness \[103\].

*Figure (4.17): UV-VIS transmittance spectra of the ZnO/Sapphire films at different substrate temperature.*
Figure (4.18): UV-Visible spectrum of ZnO films deposited on glass, quartz and sapphire.

Figure (4.19): UV-Vis transmission spectra of ZnO thin films and the Sapphire substrate with various thicknesses grown at 400°C.

Figure (4.20): UV-VIS transmittance spectra of the ZnO/Sapphire films

a) at various oxygen pressure  b) at various laser fluence
4.3.2 Optical Energy Gap

In general, the substrate deposition temperature also affects other properties of the film such as direct band gap. The optical band gap \( (E_g) \) was derived assuming a direct transition between the edge of the valence and conduction band.

The plot of \( (\alpha h\nu)^2 \) as a function of the energy of incident radiation has been shown in fig (4.21). The energy band gap is obtained from intercept of the extrapolated linear part of the curve with the energy axis, the direct band gap of the ZnO films increases from 3.1 eV - 3.5 eV as the substrate deposition temperature increases from room temperature to 400ºC, and then decreases to 3.3 eV. This shift of the bandgap can be explained by the Burstien -Moss effect \(^2\) in which the absorption edge shifts toward higher energy with an increase of carrier concentration \(^6\). This reveals that at high substrate temperature will create more defects such as oxygen vacancies, and those increased defects will result in the increase of \( E_g \). Furthermore, more oxygen vacancies may cause a carrier concentration increases, thus the energy gap slightly increases although \( E_g \) must decrease as result of the increase of grain size \(^2\).

Fig.(4.22). The optical band gap energies determined from the obtained spectra are 3.26, 3.4 and 3.5eV for ZnO thin films deposited on glass, quartz and sapphire substrates respectively.

In figure (4.23). The optical band gap value can be extrapolated from the linear region. Using this procedure, the optical energy gap of the as-deposited ZnO films was determined and found to be in the range 3.05 to 3.4 eV, values similar to the ones reported in the literature for films grown by PLD and other techniques \(^{146}\). The actual value of the optical energy gap was observed to
depend on the thickness of the film. As can be seen, the energy gap decreases slightly with increasing thickness. Therefore, further investigations are needed to clarify the influence of the growth parameters on the optical energy gap of ZnO thin films. In any case, there are several mechanisms that can cause the observed energy gap shifts, such as:

(i) Improvement or degradation of crystallinity.
(ii) Modifications in the height of the barrier due to change of the crystallite dimension,
(iii) Quantum size effects
(iv) Variations in the density of impurities and compressive or tensile strains.

The oxygen pressure also affects the direct bandgap of the ZnO thin films. The direct bandgap of the ZnO films decreases from 3.5 eV - 2.9 eV as the oxygen pressure increases from 5×10^{−2} mbar to 5×10^{−1} mbar as shown in fig (4.24). This decrease in the direct bandgap with an increase in oxygen pressure is due to a decrease in carrier concentration. This is also explained by the Burstien–Moss effect [1] which is related to the carrier concentration of the film.
Figure (4.21): the $(a\nu)^2$ vs. photon energy for ZnO films deposited at different temperature.

Figure (4.22) Variation of $(a\nu)^2$ with photon energy ($h\nu$) of ZnO films as a function of films substrate.
Figure 4.23 Variation of \( (\alpha h)^2 \) with photon energy \( (h\nu) \) of ZnO films as a function of films thickness.

Figure 4.24 \( (\alpha h)^2 \) vs. photon energy for ZnO films deposited at different \( O_2 \) pressure.
4.3.3 Refractive index

The refractive index \( n \) was determined from the reflectance data using the relation \(^{103}\)

\[
 n = \frac{1}{T} + \left( \frac{1}{T} - 1 \right)^{1/2} \quad \ldots \ldots (4 - 1)
\]

Where \( R \) is the reflection of the films. Fig (4.26) shows the variation in refractive index of ZnO film with wavelength. The ZnO films deposited on sapphire substrate at various substrate temperatures from RT°C to 500°C. The increase in the substrate temperature results in the all overall decrease in the refractive index in the visible/near infrared region. This decrease is due to the overall decrease in reflectance with the film substrate temperature. The values of
the refractive index for the films of different substrate temperatures vary in the range from 1.5 to 2.07, which are less than those reported by W. Teng et al \cite{104}.

![Figure 4.26 Variations in refractive index of the films with wavelength](image)

**4.3.4 Photoluminescence**

**4.3.4.1 Effect of Substrate Temperature**

Room temperature PL in ZnO attributed to the recombination and emission of free excitons through an exciton –exciton collision process, where one of the exciton radioactively recombines to generate photon \cite{21}. The UV emission also called as the near band edge emission (NBE) originated due to the recombination of the free excitons through an exciton –exciton collision process while visible emission is known as deep level emission (DLE).

Fig (4.27) show the room temperature Photoluminescence spectra obtained from the ZnO thin films deposited on sapphire (α-Al₂O₃) at different substrate temperature, at fixed oxygen pressure 5×10⁻²mbar and 1.6 J/cm² laser fluence energy density. All spectra of ZnO films in fig (4.27) show a typical luminescence behavior with two emission peaks, UV PL characteristics of ZnO films showed strong relation to the substrate temperature. The intensity of two
peaks increases markedly with the increases of substrate temperature in the range of RT-400ºC and decreases when the substrate temperature reaches over 400ºC. Due to the large exciton bending energy of ZnO, about 60meV, excitons could be observed at room temperature. It has also been reported that thermal energy at room temperature can break the bound excitons into free excitons because of small binding energy of bound excitons, few millielectrons volts [51].

Inset in fig (4.27) shows the intensities of the DLEs. The DLE centers of the ZnO films deposited at RT, 200 and 500ºC are 505nm (2.45eV), 545nm (2.27eV), and 518nm (2.39eV), respectively.

It is interesting to note that the ZnO film deposited at substrate temperature of 400ºC observed only strong ultraviolet emission at 345.06nm (3.596eV). However, the single ultraviolet emission in the present experiment is obtained from a nanocrystalline ZnO film deposited by a simple PLD method. It implied that the DLE has no relation with the crystalline defects like grain boundaries or dislocations. We calculate the energy gap for Nanocrystals by using the equation (2-10). The theoretical \( E_{\text{gap, nanocrystals}} \) = 3.65eV.

It is understood that the DLE is probably relative to the variation of the intrinsic defects in ZnO films, such as Zinc vacancy \( V_{\text{Zn}} \), oxygen vacancy \( V_{\text{O}} \), interstitial zinc \( \text{Zn} \), interstitial oxygen \( \text{O} \), and antisite oxygen \( \text{O}_{\text{Zn}} \). Different intrinsic defects correspond to various excited energies in DLE [72]. As our experiment proceeded at a fixed oxygen pressure of \( 5 \times 10^{-2} \text{mbar} \), there should be a competition between the substrate temperature (which decided the reactive velocity) and oxygen pressure. When the deposited temperature is lower (for example RT–200ºC), the oxidation reactive velocity maintains a lower level and the continual supply of O atoms are sufficient to combine to ZnO with Zn ions, and there are still residual O ions which may exist as \( O_i \) defects in ZnO films. When the temperature increases further to 400ºC, in the same oxygen
pressure of $5 \times 10^{-2}$ mbar the supply of O atoms is inadequate in comparison with the reactive velocity, leads to the formation $V_{Zn}$ and $O_{Zn}$ defects. As a result, deep level emission is expected (see the inset chart of Fig. 4.27). When the substrate temperature holds at about 400ºC, there is a balance between the substrate temperature and oxygen pressure, i.e. the reactive velocity assorts with the supply of oxygen under this oxygen pressure, leads to the formation of ZnO film with the lowest concentration of intrinsic defects. As a result, highest UV emission with no deep-level emission was observed. Therefore, it is deduced that single UV emission should be obtained from the ZnO film with near perfect stoichiometry.

![Figure (4.27) PL spectra obtained from films deposited on sapphire substrate with the deposited temperature of: a) RTºC, b) 200ºC, c) 400ºC, and d) 500ºC.](image)

4.3.4.2 Effect of laser fluence
Photoluminescence of the crystalline ZnO film deposited on $\alpha$-Al$_2$O$_3$ substrate was also characterized. Note that PL results of the thin films fabricated at room temperature. Fig.(4.28) Shows the PL spectra of the films. Near band emission are found in all thin films, however, the intensity of UV emission peak is strongly dependent on the laser energy density. It can be seen that the intensity of UV emission peaks increases with the increases of the laser energy density in the range of $(0.8, 1.6$ and $2.4) \text{ J/cm}^2$. The strongest UV emission (around 378 nm) with a narrow Full Width at Half Maximum (FWHM) of 16.12 nm is observed from the films deposited at $(1.6) \text{ J/cm}^2$. And from Fig.(4.28) shows the intensities of the ZnO films deposited at $0.8 \text{ J/cm}^2$ and $2.4 \text{ J/cm}^2$ are $(384)\text{nm}$ and $(388)\text{nm}$ respectively.

![Figure (4.28) PL spectra obtained from films deposited on sapphire substrate with the Laser fluence of: a) $0.8 \text{ J/cm}^2$, b)$1.6 \text{ J/cm}^2$, c)$2.4\text{J/cm}^2$.](image)

**4.3.5 Non-linear refractive index**
In the present investigation, we have employed the single beam Z-scan technique with nanosecond laser to measure the nonlinear optical absorption and refraction properties of ZnO thin films and observed that the films have large nonlinear effects. A Q-switching Nd:YAG laser (532nm, 10ns, 6Hz) was used as the light source. The sample was moved in the direction of light incident near the focal spot of the lens with the focal length being 200mm. The radius of the beam waist $\omega_0$ was calculated to be 35.4$\mu$m. The Rayleigh length $z_0$ was estimated to be 7.8mm. A typical result of the z-scan measurement which corresponds to the far-field normalized transmittance as a function of the distance from the lens focus of a typical ZnO/sapphire film without and with a collecting aperture is shown in figure (4.29) and (4.30) respectively.

The closed-aperture Z-scan at 532nm in the transmission direction at different energies. The transmission was also started with a linear behavior at the far field of the sample position (-Z) with respect to the focal plane at $Z=0$mm. The curve exhibited a peak-to-valley shape, the transmission returns to the linear behavior at the far field of the sample position (+Z).

The behavior of Z-scan curves was very agreement with that obtained by Sheik-Bahae et al.\textsuperscript{[115]}, and N. Venkatram\textsuperscript{[147]}. As results, the closed aperture Z-scan measures the change in the transmittance of a beam, as the sample passes through the focal plane. The change in on-axis intensity is caused by self-focusing or self-defocusing by the sample as it travels through the beam waist. This modified refractive index distribution then acts like focusing lens. Hence, when the sample approaches to the focal plane, it will focus the converging beam more tightly. In the far field, this increases beam divergence and is measured as a decrease in energy through the aperture. At the focal plane, the divergence of the beam is unaffected by the sample and the detector measures no net change in transmittance. As it leaves the focal plane, the sample will
focus the diverging beam. In the far field this decreases beam divergence and is measured as an increase in power through the aperture.

A valley followed by peak is the hallmark of a positive $n_2$. The peak to valley profile displayed in the figures, demonstrates the sample exhibited a self-focusing effect, i.e., it has a positive nonlinearity at 532nm. Closed aperture measurements contain contributions from both the intensity – dependent changes in the transmission and in refractive index $^{[114]}$.

The nonlinear refractive index is directly proportional to the input energy, i.e. the larger phase shift gives the larger nonlinear refractive index.

In all the closed-aperture curves, the peak to valley difference $\Delta T$ is vary between (0.09) to (0.37) at the highest energies. The closed – aperture Z –scan defines variable transmittance values, which used to determine the nonlinear phase shift and the nonlinear refractive index. This can be shown in table (4.9).

![Figure (4.29)](image)

**Figure (4.29)** closed –aperture Z-scan at 532nm for different incident laser energy.

*The open –aperture* curve exhibited a normalized transmittance valley, indicating the presence of nonlinear absorption in the film. The sapphire substrate had nonlinear optical response at 532nm, which was measured by the same method and hence the high nonlinear response observed here resulted from the ZnO/sapphire films.
These plots are typical of samples exhibiting two–photon absorption. Transmittance was a minimum at the focus and increased steadily on both sides of the focus. In the open–aperture z–scan, the nonlinear behavior of the transmission curves is very agreement with the result reported by N. Vankatram\textsuperscript{147}. The transmittance is sensitive to the nonlinear absorption as a function of input energy pulses. The change in the intensity is caused by two–photon absorption as it travels through the beam waist. In the focal plane where the intensity is greatest, the largest nonlinear absorption is observed. At the far field of the Gaussian beam, where \( \| Z \| \gg \| Z_0 \| \), the beam intensity is too weak to elicit nonlinear effects. The higher order of the two-photon absorption present in the measurement depends on the energy levels of the sample. A symmetric valley is contributed to the positive nonlinear absorption coefficient \( \beta \), indicating the two–photon absorption. The nonlinear absorption coefficient is inversely proportional to the input energy. The open–aperture Z-scan defined variable transmittance values, which used to determined absorption coefficient. This can be shown in table (4.9).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.30}
\caption{open–aperture Z-scan at 532nm for different incident laser energy.}
\end{figure}
The table shows different values of $\beta$, which depends on the change in input energy. As a comparison to the input energy, the value of $\beta$ is decreased as the energy increased.

Table (4.9) Nonlinear refractive index and absorption coefficient versus input energy.

<table>
<thead>
<tr>
<th>Incident energy (mJ)</th>
<th>Closed –aperture</th>
<th>Open –aperture</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{valley}}$</td>
<td>$n_2$ (cm$^2$/GW)</td>
</tr>
<tr>
<td>100</td>
<td>0.2294</td>
<td>0.162</td>
</tr>
<tr>
<td>140</td>
<td>0.2559</td>
<td>0.165</td>
</tr>
<tr>
<td>180</td>
<td>0.2866</td>
<td>0.167</td>
</tr>
</tbody>
</table>
5. Conclusions

- ZnO thin films were prepared by PLD on sapphire with substrate temperatures from (RT to 500)°C. All films are crystalline and (002) orientated. Films grown at 400°C are relatively dense and the grain size is smaller and uniform, as the substrate temperature increases to 500°C the grain size slightly increases. From the SEM images, we found that the nondense ZnO films are obtained at RT. But when the substrate temperature is 400°C, the grain size is smaller and the films become relatively dense.

- The structural and optical properties of the ZnO films are found to be dependent on the film thickness. The crystal structure of the ZnO films is hexagonal wurtzite and the films are highly oriented. As the film thickness increases, the crystallinity is improved and the crystallite size becomes larger. The average transmittance for all the films is over 90% in the wavelength range (300-900) nm and the transmittance in UV region decreases with the increase of film thickness. The optical band gap is dependent on the film thickness, for the thinner films the optical energy band gap is higher.

- The effect of ambient O
  2 pressure on the properties of grown on sapphire substrate. In an O
  2 pressure 5×10⁻² mbar, fully c-axis oriented ZnO thin films with a relatively smooth surface and a good crystallinity and orientation were grown. But at O
  2 5×10⁻¹ mbar, a roundelay oriented ZnO film was grown processing a very low crystalline and a rough surface.

- The Photoluminescence (PL) results indicates that the thin films fabricated at the optimized conditions show the strongest UV peak was found at (345nm) (3.596eV) from ZnO films grown at (1.6J/cm² and 400°C). This result is
consistent with that the XRD investigation. And broad band invisible region at RT, 200 and 500°C are 505nm (2.45eV), 545nm (2.27eV), and 518nm (2.39eV), respectively.
5.1 Future Work

Based on the conducted experimental work the following ideas and technological challenges appeared.

✓ For the epitaxial grown the ZnO, used other crystalline orientations of Al₂O₃, according to some specificities of ZnO. For example epitaxial ZnO films grown on R-cut sapphire substrate were found to possess a strong optical anisotropy at near bandgap photon energies.

✓ Using a mixing of background gases N₂ + O₂ with high vacuum to enhancement the quality of the films.
## Appendix Table (1.1): Review of ZnO deposited on different condition.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Laser &amp; fluence if/cm²</th>
<th>Pulse duration (ns)</th>
<th>Repetition rate (Hz)</th>
<th>Gas pressure (mTorr)</th>
<th>Sub.-Targ. Distance (cm)</th>
<th>Temp. °C</th>
<th>Band gap (eV)</th>
<th>Main observations</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>V. Craciun 1994</td>
<td>Glass, Silicon</td>
<td>KrF (248nm) 0.5-5</td>
<td>-</td>
<td>-</td>
<td>O₂ 5×10⁴-2×10²</td>
<td>4</td>
<td>350</td>
<td>3.26</td>
<td>C-axis orientation films (002) with FWHM value less than 0.15⁰, electrical resistivity 5×10-2Ω cm, surface morphology was featureless and fractured surface exhibited columnar structure, optical transmission higher than 85% in Visible region, refractive index around 1.98</td>
</tr>
<tr>
<td>V. Craciun 1995</td>
<td>Glass, Silicon</td>
<td>KrF (248nm) Nd:YAG (532nm) 0.4-4</td>
<td>-</td>
<td>-</td>
<td>O₂ 5×10⁴-3×10³</td>
<td>4</td>
<td>100-500</td>
<td>3.27</td>
<td>C-axis orientation films (002) with FWHM value less than 0.16⁰, surface morphology was flat and fractured surface exhibited a dense, columnar structure. Optical transmission higher than 85% in Visible region, refractive index around 1.9</td>
</tr>
<tr>
<td>V. Srikant 1997</td>
<td>c-sapphire</td>
<td>ArF (193nm) 6</td>
<td>-</td>
<td>-</td>
<td>O₂ 10</td>
<td>5</td>
<td>500-800</td>
<td>3.36-3.413</td>
<td>The crystal structure of films follows the epitaxial relationship of (001) of Al₂O₃. Both RT and cryogenic temp. PL showed a remarkable band-gap transition, and clear excitonic structure could be seen at cryogenic temp. the optical refractive index was measured in range of 375-900nm by varying angle spectroscopic.</td>
</tr>
<tr>
<td>X.W. Sun 1999</td>
<td>a-Al₂O₃</td>
<td>Nd:YAG (355nm) 2.5</td>
<td>-</td>
<td>5</td>
<td>O₂ 50,200,300, 500</td>
<td>5</td>
<td>400</td>
<td>2.25-3.3</td>
<td>In XRD and scanning electron microscopy as the oxygen pressure for the thin film deposition increases the crystalline of the samples degrades, all samples show a typical luminescence behavior with the two emissions of narrow UV and a broad green-yellow band.</td>
</tr>
<tr>
<td>B. J. Jin 2000</td>
<td>a-Al₂O₃</td>
<td>Nd:YAG (355nm) 2.5</td>
<td>-</td>
<td>5</td>
<td>O₂ 1×10⁴-1.20,200 and 400</td>
<td>5</td>
<td>200-600</td>
<td>-</td>
<td>C-axis-oriented, strong UV luminescence was obtained by increasing temperature. Broad band green-yellow luminescence, Good crystalline quality has been obtained for ZnO films deposited at substrate temperatures higher than 300°C and at an oxygen pressure higher than 200 mTorr</td>
</tr>
<tr>
<td>S. H. Bae 2001</td>
<td>a-Al₂O₃ (001)</td>
<td>Nd:YAG (355nm) 2.5</td>
<td>6</td>
<td>5</td>
<td>O₂ 350</td>
<td>5</td>
<td>200-700</td>
<td>-</td>
<td>The ZnO film grown at 400°C substrate temperature showed the highest UV PL Intensity, while the most intense blue-green PL was obtained from the samples grown at a higher temperature of 600°C</td>
</tr>
<tr>
<td>B. J. Jin 2001</td>
<td>a-Al₂O₃ (001)</td>
<td>Nd:YAG (355nm) 2.5</td>
<td>-</td>
<td>5</td>
<td>O₂ 50,200,300,400</td>
<td>5</td>
<td>400</td>
<td>2.25-3.3</td>
<td>The intensity of UV luminescence is generally proportional to the electrical resistivity and stoichiometric, but not much related to the microstructures</td>
</tr>
<tr>
<td>J. N. Zeng 2002</td>
<td>Silicon, Quartz</td>
<td>KrF (248nm) 0.3 - 2.85</td>
<td>23</td>
<td>-</td>
<td>O₂ 6.5</td>
<td>5</td>
<td>RT-700</td>
<td>-</td>
<td>Highly c-axis orientation, optical and electrical properties show different behaviors in vacuum and oxygen ambient with increasing laser fluence. Combined with high laser fluence, oxygen ambient plays an important role in removing defects due to excess zinc or oxygen vacancy.</td>
</tr>
<tr>
<td>Y. Nakata 2002</td>
<td>Quartz, Sapphire (0006)</td>
<td>KrF (248nm) 3.0</td>
<td>-</td>
<td>2</td>
<td>He or O₂ 0.5 and 20</td>
<td>1-3</td>
<td>Room temp.</td>
<td>3.2</td>
<td>Transmittance measurement showed that the crystalline films have a clear cut off at about 350nm. Ultraviolet photoluminescence at about 390nm was observed under 308nm excitation.</td>
</tr>
<tr>
<td>M.C park 2002</td>
<td>Sapphire (0001)</td>
<td>Nd:YAG (355nm) 2.5</td>
<td>-</td>
<td>5</td>
<td>O₂ 350 mbar</td>
<td>5</td>
<td>400</td>
<td>3.23-3.267</td>
<td>SEM and XRD analysis were utilized to investigate the effects of misfit strain on the surface morphology and the crystallinity. The crystalline qualities, electrical and optical properties of the films depended on the film thickness and were improved with increasing the film thickness. the films thinner than 400 nm are under the severe misfit strain.</td>
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Table (1.1)  

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<th>Substrate</th>
<th>Laser &amp; fluence J/cm²</th>
<th>Pulse duration (ns)</th>
<th>Repetition rate (Hz)</th>
<th>Gas pressure</th>
<th>Sub. Targ. Distance (cm)</th>
<th>Temp. °C</th>
<th>Band gap (eV)</th>
<th>Main observations</th>
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<td>S. Barik 2003</td>
<td>Sapphire (0001)</td>
<td>Q-switched Nd:YAG (355nm)</td>
<td>4</td>
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<td>10</td>
<td>O₂</td>
<td>4</td>
<td>Room Temp.</td>
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<td>F.K. Shan 2004</td>
<td>Glass GaAs Si(111)</td>
<td>KrF (248nm)</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>O₂</td>
<td>200 mbar</td>
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<td>RT-600</td>
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<td>J. A. Sans 2004</td>
<td>Fluorite Sapphire Mica</td>
<td>Nd:YAG (354.7nm)</td>
<td>~10</td>
<td>8</td>
<td>10</td>
<td>O₂</td>
<td>2×10⁴ mbar</td>
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<td>600 for Fluorite Up to 800 sapphire</td>
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<td>S. S. Kim 2004</td>
<td>Silicon (001)</td>
<td>KrF (248nm)</td>
<td>3</td>
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<td>10</td>
<td>O₂</td>
<td>5×10⁻³ -5×10⁻⁴ mbar</td>
<td>4</td>
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<td>W. Zhao 2005</td>
<td>Silicon (111)</td>
<td>KrF (248nm)</td>
<td>2.5</td>
<td>-</td>
<td>5</td>
<td>O₂</td>
<td>20 Pa</td>
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<td>250-700</td>
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<td>S. Christou 2005</td>
<td>Si Glass</td>
<td>XeCl (308nm)</td>
<td>-</td>
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<td>O₂</td>
<td>-</td>
<td>350</td>
<td>3.21</td>
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<tr>
<td>J. H. Jo 2005</td>
<td>Al₂O₃ (001)</td>
<td>KrF (248nm)</td>
<td>20</td>
<td>5</td>
<td>5</td>
<td>O₂</td>
<td>5-150 mTorr</td>
<td>4</td>
<td>500</td>
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<tr>
<td>M. Suchea 2005</td>
<td>α-Al₂O₃</td>
<td>KrF (248nm)</td>
<td>2.5</td>
<td>-</td>
<td>-</td>
<td>O₂, N₂, N₂O</td>
<td>1 mbar</td>
<td>10</td>
<td>600 for (N₂O, O₂)</td>
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<tr>
<td>M. Lorenz 2005</td>
<td>Silicon Glass</td>
<td>XeCl (308nm)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Ar</td>
<td>8×10⁻³ mbar</td>
<td>-</td>
<td>Room Temp.</td>
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<tr>
<td>Y. W. Sun 2005</td>
<td>Silicon</td>
<td>KrF (248nm)</td>
<td>3</td>
<td>15</td>
<td>20</td>
<td>O₂</td>
<td>100mbar</td>
<td>3</td>
<td>Room Temp.</td>
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<tr>
<td>A. Meaney 2005</td>
<td>r-Al₂O₃ c-Al₂O₃</td>
<td>Nd:YAG (266nm)</td>
<td>1.4</td>
<td>2</td>
<td>-</td>
<td>O₂</td>
<td>10⁻³ mbar</td>
<td>520</td>
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Table (1.1): Continue

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<th>Substrate</th>
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<th>Background Gas pressure</th>
<th>Sub.-Targ. Distance (cm)</th>
<th>Temp. °C</th>
<th>Band gap (eV)</th>
<th>Main observations</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>K. Ramam 2006 Glass Nd:YAG (355nm) 5</td>
<td>6</td>
<td>10</td>
<td>O₂ 1×10⁵</td>
<td>6</td>
<td>RT,200,300</td>
<td>3.39,3.37,3.395</td>
<td>The optical transmission window of such obtained films, i.e., T%(max)&gt;95% is broader than those of other transparent conducting oxides, the conductivity level (of the order of 103 W-1 cm-1), the films were act as highly antireflective coatings.</td>
<td>[47]</td>
<td></td>
</tr>
<tr>
<td>S. Cho 2006 Sapphire KrF (248nm) 2 100-400-700</td>
<td>-</td>
<td>5</td>
<td>350</td>
<td>6</td>
<td>400-700</td>
<td>In XRD the peaks at about 34.4° and 41.6° correspond to the diffraction from the ZnO (002) and Al₂O₃ (0006) planes, respectively. The (FWHM) for the ZnO grown at 700 °C is found to be 0.22°. PL spectrum shows a strong emission peak at 3.356 eV (369.5nm) with a FWHM of 32 meV and two weak emissions, one at 3.305 eV (375.2 nm) and the other at 3.227 eV (384.2 nm).</td>
<td>[48]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>B. I. Kim 2006 Sapphire (0001) KrF (248nm) 2.1</td>
<td>5</td>
<td>O₂</td>
<td>500</td>
<td>The FWHM decreases rapidly but the grain size increases almost at the same speed until 24 h of oxygen treatment, and after that they begin to saturate. The 3.23 eV peak of PL spectra in ZnO thin films have been decreased by the high-pressure oxygen treatment.</td>
<td>[49]</td>
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</tr>
<tr>
<td>M. Liu 2006 Silicon Nd:YAG (1064nm) 5</td>
<td>10</td>
<td>10</td>
<td>O₂ 0.13 Pa</td>
<td>4</td>
<td>100-500</td>
<td>The thickness of the film increases with the increase of substrate temperature, but decreases with the increase of the substrate temperature over 400°C. The XRD peak at around 2θ = 348° is attributed to (0 0 2) plane of ZnO thin films. The average grain size of the particles increases with the increase of substrate temperature. In PL two emission peaks, a UV peak is at 369 nm and a blue peak is at 457 nm.</td>
<td>[50]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>L. Zhao 2006 Quartz Nd:YAG (1064nm) 7</td>
<td>100</td>
<td>10</td>
<td>O₂ 11 Pa</td>
<td>2.3</td>
<td>100-250</td>
<td>3.26-3.28</td>
<td>The ZnO films obtained at different substrate temperatures have nanocrystalline structure with grain size in the range of about 30–45 nm. The as-deposited films show ultraviolet emission and accompanied deep-level emission in PL spectra.</td>
<td>[51]</td>
<td></td>
</tr>
<tr>
<td>H. Jianing 2006 Si (111) Nd:YAG (1064nm) 47</td>
<td>10</td>
<td>10</td>
<td>O₂ 0.13 Pa</td>
<td>4</td>
<td>300-700</td>
<td>Revealing that substrate temperature plays an important role in improving the crystalline quality of ZnO film the narrowest FWHM at the substrate temp. 600°C. The strong emission peak caused by the defects. The SEM images show that the surfaces of ZnO films were more planar and compact as the substrate temperature increased.</td>
<td>[52]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>M. Liu 2006 Si (111) Nd:YAG (1064nm) 200nJ/pulse</td>
<td>10</td>
<td>10</td>
<td>O₂ 10⁻⁴ Pa</td>
<td></td>
<td></td>
<td></td>
<td>The results show that the focus position has an important effect on the deposition rate, surface morphology, crystal quality and optical properties of the ZnO thin films deposited at 59.5 cm have the highest deposition rate, the narrowest FWHM of XRD peak at (002), the strongest UV and blue PL spectra.</td>
<td>[53]</td>
<td></td>
</tr>
<tr>
<td>Y.V. Villaneueva 2006 Glass Nd:YAG (355nm) 300mJ</td>
<td>5</td>
<td>10</td>
<td>O₂ 50-100</td>
<td>6</td>
<td>250</td>
<td>XRD scans of the samples indicated that ZnO [002] crystals were predominantly grown on heated glass (at temperatures of 250 °C under ambient oxygen pressures of 50 Torr and 100 mTorr. X-ray reflectivity measurement gave thickness and roughness values of 45.8 nm and 3.5 nm, respectively, while atomic force microscopy measured 60 nm and 3.8 nm, respectively. PL spectra indicated an emission peak at 339 nm wavelength.</td>
<td>[54]</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H. Yamag. 2007 Al₂O₃ (1121) Nd:YAG (266nm) 5</td>
<td>10</td>
<td>10</td>
<td>-</td>
<td>3.6</td>
<td>20 - 700</td>
<td>-</td>
<td>The bias effects were more obvious for the films grown at 700°C than that grown at 20°C. When the films were prepared at 700°C with bias voltage of ~500 V, the ZnO films had flat surface with hexagonal patterns which indicated the crystal was highly oriented to c-axis. Further, PL intensity from the deep level due to the defects such as V₃O and/or Zn decreased drastically.</td>
<td>[55]</td>
<td></td>
</tr>
</tbody>
</table>
Table (1.1): Continue

<table>
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<tr>
<th>Substrate</th>
<th>Laser &amp; fluence /cm²</th>
<th>Pulse duration (ns)</th>
<th>Repetition rate (Hz)</th>
<th>Gas pressure</th>
<th>Sub.-Target. Distance (cm)</th>
<th>Temp. °C</th>
<th>Band gap (eV)</th>
<th>Main observations</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>J. Zhao 2007</td>
<td>Silicon</td>
<td>KrF (248nm) 2.5</td>
<td>-</td>
<td>5</td>
<td>O₂</td>
<td>-</td>
<td>500-650</td>
<td>Thin film deposited in oxygen ambient shows ring RHEED pattern. There is a compressive in-plane stress existing in the ZnO epilaxial film, but a tensile one in the polycrystalline film. The ZnO polycrystalline film shows more intense ultraviolet emission (UVE) with a small (FWHM) of 89 meV. It is suggested that the atomically flat epilayers may be powerfully used as transitive strata to grow high-quality ZnO films suitable for the fabrication of optoelectronic devices.</td>
<td>[56]</td>
</tr>
<tr>
<td>M. Novotny 2007</td>
<td>r-Al₂O₃</td>
<td>Nd:YAG (266nm) 1.4</td>
<td>6</td>
<td>4</td>
<td>N₂:O₂ 15:85</td>
<td>5.5</td>
<td>300-630</td>
<td>Most of the thin films were n-type, although in conditions leading to increased activation of the ionized nitrogen species, p-type behavior was observed. These experimental observations were found to be in qualitative agreement with recent theoretical calculations of the activation energies of N acceptors and compensating donor defects in ZnO.</td>
<td>[57]</td>
</tr>
<tr>
<td>S. Chakra. 2007</td>
<td>α-c + r Al₂O₃</td>
<td>Nd:YAG (266nm) 1.4</td>
<td>6</td>
<td>10</td>
<td>-</td>
<td>5.5</td>
<td>300</td>
<td>The films were all p-type over a wide temperature range (200-450 K) with hole concentration of ~5 x 10¹⁸ cm⁻³ and mobility of ~7 cm²/Vs at 300 K. Photoluminescence studies indicate an overall decrease in the optical quality upon nitrogen incorporation, although an observed peak may indicate the presence of acceptor-neutral (AXN) bound excitons.</td>
<td>[58]</td>
</tr>
<tr>
<td>B. L. Zhu 2008</td>
<td>Glass</td>
<td>KrF (248nm) 348mJ/Pulse</td>
<td>25</td>
<td>5</td>
<td>O₂ 12 Pa</td>
<td>7</td>
<td>RT- 500</td>
<td>The films at 200°C have maximum Eₘ and Eₜ values, which may be due to its smallest grain size. The UV emission is only observed in the films at 200°C. This may be related to its high stoichiometry.</td>
<td>[59]</td>
</tr>
<tr>
<td>L. Han 2008</td>
<td>Sapphire</td>
<td>KrF (248nm) 300mJ/pulse</td>
<td>20</td>
<td>5</td>
<td>O₂ 4.5x10⁻³</td>
<td>5</td>
<td>500</td>
<td>-</td>
<td>The ZnO film on sapphire had a better crystalline quality, as compared to that on Si, although they both showed a strong c-axis orientation. TEM analyses revealed the nature of polycrystalline ZnO initiated from an amorphous buffer layer on Si substrate, while single-crystalline ZnO epilayer grew from a polycrystalline buffer layer on sapphire substrate.</td>
</tr>
<tr>
<td>C. Sui 2008</td>
<td>c - Al₂O₃ (0001)</td>
<td>Nd:YAG (355nm) 2.5</td>
<td>-</td>
<td>-</td>
<td>O₂ (6.7-46.7) Pa</td>
<td>-</td>
<td>250</td>
<td>-</td>
<td>The FWHM for 1θ curve of (0002) peak is 0.25°, corresponding to that of films grown using other deposition method. The band gap energy red shifts monotonically with temperature increase from 3.345 to 3.113 ev. Moreover, the sharp absorption edge of ZnO films after annealing at 300 °C still overlaps that of the as deposited sample, indicating an excellent thermal stability.</td>
</tr>
<tr>
<td>H. S. Kang 2008</td>
<td>α-Al₂O₃ (0001)</td>
<td>Nd:YAG (355nm) 2.5</td>
<td>-</td>
<td>-</td>
<td>O₂ (6.7-46.7) Pa</td>
<td>-</td>
<td>400</td>
<td>-</td>
<td>The relationship between the UV luminescence and the electron concentration of ZnO was systematically investigated. Origin of the dominant UV emission in ZnO thin film was identified as a free electron-neutral-acceptor transition (eA⁰) through temperature dependence of PL measurement.</td>
</tr>
<tr>
<td>X. Q. Wei 2009</td>
<td>Si (111)</td>
<td>Nd:YAG(1064nm) 200mJ/pulse</td>
<td>10</td>
<td>10</td>
<td>O₂ 1.3 Pa</td>
<td>4</td>
<td>400-800</td>
<td>The growth temp. of ZnO films fabricated using the powder target is higher than that of ceramic target. Because the contamination of ZnO powder and the low efficiency of the laser energy transforms into ZnO plasma.</td>
<td>[63]</td>
</tr>
<tr>
<td>W. Zhaoyang 2009</td>
<td>Si (111)</td>
<td>KrF (248nm) 2.5</td>
<td>5</td>
<td>5</td>
<td>O₂ (1-50) Pa</td>
<td>5</td>
<td>650</td>
<td>-</td>
<td>Films grown at 29 Pa and 50 Pa have excellent UV emission and high quality crystallinity. The values of lattice spacing of d002 decreases with the increase of O₂ pressure the increase of the O₂ pressure from 1 Pa to 50 Pa contributes to the size of ZnO grains, and then promote the UV emission of the films.</td>
</tr>
<tr>
<td>T.Premk. 2009</td>
<td>Sapphire</td>
<td>Nd:YAG (1064nm-532nm) 8</td>
<td>10</td>
<td>1x10⁻⁶ mbar</td>
<td>4</td>
<td>600</td>
<td>-</td>
<td>SEM images clearly evidenced the growth of ZnO nanorods and microrods on GaN and Al₂O₃ substrate at wavelength 532nm</td>
<td>[65]</td>
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<tr>
<td>Yu 2009</td>
<td>Glass</td>
<td>Nd:YAG 532nm 18.5</td>
<td>7</td>
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<td>O₂ 40-150mTorr</td>
<td>2.5</td>
<td>150</td>
<td>The intensity of the deep-level-emission (DLE) and conductivity generally increased as the oxygen pressure decreased</td>
<td>[66]</td>
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<td>Symbol</td>
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**Abbreviations**

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[111] Z-Scan Measurements From Wikipedia, the free encyclopedia.


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