Laser-ablated plasma for deposition of ZnO thin films on various substrates

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Received 16 February 2001; accepted 7 May 2001

Abstract

We report optical and structural properties of ZnO films deposited by pulsed laser deposition technique on (100) n-type silicon and quartz substrates at various pressures of background gas. ZnO plasma was created using KrF laser (248 nm) at various pressures of the ambient gas, oxygen. Laser induced plasma at varying fluence on the target was investigated using optical emission spectroscopy and 2-D images of the expanding plumes. X-ray diffraction, atomic force microscopy, and spectro-photometry were used to characterize as grown films. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: ZnO; Pulsed laser deposition; Laser-ablated plasma; Thin film; Spectroscopy

1. Introduction

After its success in the growth of high quality superconducting thin films [1–3] in late eighties, pulsed laser deposition (PLD) has emerged as a versatile technique for deposition of various materials including ferroelectrics, ferrites, amorphous diamond and other ultra hard phases, polymers, compound semiconductors, and nano-crystalline materials [4]. Among the several characteristics that distinguish PLD from other film growth techniques is congruent (stoichiometric) deposition and hence has been used to grow superconducting superlattices and superconducting device structures [5–7]. Recently, combinatorial methods, an approach in which a large number (library) of materials are synthesized, processed and screened for specific properties, have been applied to the discovery and optimization of several functional materials [8,9]. However, the problem of particulates and the uniformity of grown thin films have limited the use of PLD, especially for semiconductors and other electronic thin film materials.

II–VI semiconductors are attractive for potential in acoustic, electronic, and optical applications such as surface acoustic wave, acousto-optic, piezo-optic, piezo-electric and photoelectric devices in particular, voltage photo-phosphorescent devices [10]. However, all the conventional II–VI semiconductor materials degrade during device operation due to generation of defects in them. ZnO, a direct band gap II–VI semiconductor, is a novel photonic material with crystal structure similar to that of GaN. Unique properties of ZnO are a direct bandgap of 3.37 eV at room temperature (RT), large bond strength with large exciton binding energy (\(E_x = 60\) meV) and a high melting temperature of 2248 K. The strength of Zn-to-O bond is larger than that of Ga-to-N. These properties make ZnO a good candidate material for optical devices such as blue LED’s besides widely used GaN. Furthermore, since ZnO films are highly \(c\)-axis oriented, self-textured ZnO films can be synthesized on any semiconductor substrate \[11–14\] such as Si and GaAs. ZnO being stable at high temperature can withstand high temperature annealing and treatment processes associated with doping and forming ohmic contacts. It is expected that degradation of the material caused by generation of defects during operation of device will not pose a serious problem. Transparent conducting ZnO films have been extensively studied in recent years because of their low cost, relatively low deposition temperature and stability in hydrogen plasma compared to ITO and SiO\(_2\) films. These advantages are of considerable interest for solar energy conversion applications \[15\]. Various techniques being used to grow ZnO films are metal-organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE),...
sol-gel deposition, electron-plasma sputtering, reactive evaporation, spray pyrolysis and PLD [16,17]. It is now accepted that laser produced plasmas play an essential role in determining the ultimate characteristics of the deposited films. A general feature of ablation plasma (also known as ‘plume’) is their high ion and electron temperature, and their high degree of ionization. Depending on laser power and pulse duration, the laser ablated plume consists of atoms/ions in the excited states or clusters. In this paper, we report on the structural and optical properties of ZnO thin films deposited by PLD technique. We have studied the influence of the deposition parameters, such as oxygen pressure and substrate temperature on the deposited film. In order to prepare the high quality ZnO thin film, the detailed spectroscopic investigation of the plume produced during film deposition was undertaken. An attempt is made to correlate the properties of the deposited film with plasma characteristics.

2. Experimental details

Experimental lay out for depositing thin films and investigating laser ablated plumes is shown in Fig. 1. The ZnO thin films were grown in a stainless steel vacuum chamber which can be evacuated by a turbo-molecular pump to a base pressure of $5.0 \times 10^{-6}$ Torr. KrF excimer laser (Lambda Physik, COMPex205, $\lambda = 248$ nm, pulse duration of 25 ns, repetition rate of 10 Hz) giving maximum energy of 650 mJ/pulse was used to ablate a stoichiometric ZnO (purity 99.9%) target. Laser fluence on the target was in the range 1–4 J/cm². The films were grown at ambient pressures of oxygen (purity 99.9%) of 2, 5, and 10 mTorr on Si (100) and quartz substrates placed at distance of 5 cm from the target. Films of thickness 400 nm were grown at room temperature (RT) and at 550°C. Structural properties of as-grown film were investigated using X-ray diffraction (XRD) and atomic force microscope (AFM). Optical properties such as UV-visible transparency and optical band gap of as-grown film were measured by using UV-visible spectro-photometry (UVV).

The emission spectra of the plasma plumes produced during the ZnO thin film deposition were recorded using monochromator (Acton Research, SpectraPro-308i) equipped with an ICCD (Intensified Charge Coupled Device, Princeton Inc., ICCD-576G) and a detector controller (Princeton Inc., ST-138S) connected to a digital oscilloscope. The gate width of 20 ns was kept fixed for recording spectra at time delays, (with respect to ablating pulse), varying from 50 to 500 ns using a pulse delay generator (Princeton Inc., PG-200). Plasma emission was recorded at distances of 1–10 mm from the target surface at laser fluence of 1–4 J/cm².

![Experimental layout for pulsed laser deposition.](image-url)
3. Results and discussion

3.1. Plasma dynamics

Emission spectra of the laser ablated zinc oxide were recorded at various spatial positions of the plume at different laser fluence in the presence of oxygen gas at pressure of 2.5, and 10 mTorr at varying delay times with respect to the ablating pulse. Fig. 2 shows emission spectra recorded at 5 mm away and parallel to the target surface with laser fluence of 2 J/cm² in oxygen at a pressure of 5 mTorr. The spectra were recorded at time delays varying from 50 to 300 ns in steps of 50 ns. Table 1 shows various observed emission lines. The lines were identified using the information available in the literature [18]. At low laser fluence and at short delay times, three peaks corresponding to green emission around 510 nm, red emission around 650 nm, and UV emission around 390 nm were observed. However, at fluence used for thin film deposition, atomic and ionic lines of Zn predominate the spectra. The intensity of the emission lines decreases with the increase in distance from the target surface.

The ambient gases used in PLD either thermalize the plasma species through multiple collisions or compensate the loss of an elemental component of the target through incongruent ablation. Several theoretical investigations have been reported to understand the formation and evolution properties of laser ablated plasmas [19–23]. The plasma expanding in a background gas has been studied using fluid dynamic models and has been shown that the so-called Knudsen layer modifies the distribution of the species to a drifted (shifted) Maxwellian distribution [19,20]. The collisions between the expanding plasma species and the gas molecules are shown to result in a shock wave [24–28]. The front propagates with gradually decreasing velocity. For ablation in a gas like oxygen, simple oxide molecules are also formed in the expanding ablation plume resulting in oxide film on the substrate [26–28]. To understand the dynamics of the laser ablated plumes, 2-D images of the expanding plumes in different environments were recorded at various delay times. The evolution of the plume is simulated using hydrodynamical model [21]. It is assumed that the initial expansion is unaffected by the presence of ambient gas. However, at later times, collisions between the ambient gas and plume

| Wavelength (nm) | Zn I   | Zn II  |
|----------------|--------|--------|
|                | 301.835| 317.218|
|                | 303.578| 368.347|
|                | 307.206| 379.629|
|                | 307.900| 398.923|
|                | 301.835| 405.771|
|                | 303.578| 419.044|
|                | 307.206| 423.332|
|                | 307.900| 434.944|
|                | 301.835| 464.915|
|                | 303.578| 466.165|
|                | 307.206| 467.625|

Fig. 2. Emission spectra of Zn in 5 mTorr of oxygen, laser fluence of 2 J/cm² at various delay times.
species dominate which attenuates and slows down the plume. Fig. 3 shows 2-D ICCD images ($\lambda = 300 \sim 800$ nm) of the plume in oxygen at a pressure of 5 mTorr at various delay times. Fig. 4 shows the variation of plume front edge with time in vacuum, 5 and 10 mTorr of oxygen. The plume size ($R$) is related to the ambient gas pressure and to the laser energy ($E$) by $R \sim (E/P)^{1/3}$, where $r$ is the ratio of specific heats of the elements in the plume and $P$ the oxygen ambient gas pressure [24]. The increased collisions due to increase in ambient pressure decreases the propagation range of the plume. The velocity of $1.68 \times 10^4$ and $1.53 \times 10^4$ m/s at 300 ns of the expanding front at pressures of 5 and 10 mTorr, respectively, is estimated.

3.2. Characteristics of pulsed laser deposited films

The crucial parameters in PLD are the deposition temperature, pulse repetition rate, and the pressure of the background gas during deposition. We deposited ZnO films in ambient pressure of 2, 5 and 10 mTorr of oxygen on Si (100) and quartz at RT and at 550°C. XRD of the films, using CuK$\alpha$ grown at pressures less than 10 mTorr at RT showed the films to be highly oriented along (002) plane, implying c-axis of the film uniformly perpendicular to the surface. At pressures of 10 mTorr, (004) plane is also observed. The width of diffraction peaks and hence size of

![Fig. 3. 2-D images of ZnO ablated plume at various delay times in 5 mTorr of oxygen.](image)

![Fig. 4. Variation of plume front with delay time at different pressures various ambien.](image)

![Fig. 5. XRD pattern of ZnO films deposited on quartz at RT at various pressures.](image)
the nanocrystallites is highly influenced by the temperature of the substrate. Fig. 5 shows XRD of ZnO films grown at various pressures of oxygen at RT. The sharpened and enhanced diffraction peaks (FWHM) with increasing pressure implies that the particle size increases at lower ambient pressures. In order to confirm the effect of temperature and substrate, films were deposited on Si also. Fig. 6 shows XRD of films grown on quartz and Si at 550°C in 5 mTorr of ambient pressure. Films are textured along (002) plane. The comparison of Figs. 5 and 6 conclusively confirms that substrate temperature and ambient gas pressure are the factors that control the width of the diffraction peaks and hence the size of the nanocrystallites.

Surface morphologies of the films were studied using AFM. Measurements were done in air. Film samples were scanned over areas of $1 \times 1$ μm$^2$ at several different locations on the film surface. Fig. 7 shows AFM picture of as-grown films at pressures of 2, 5, and 10 mTorr of oxygen at RT. Surface morphology varied among films grown at various different ambient pressures. The films grown at high oxygen pressure were smoother and the grain size became smaller than that grown at low pressure. The dependence of quality of films on ambient pressure can be understood by considering (Zn, O) plume size, and reactive oxygen density. In general, ZnO films are oxygen deficient. This deficiency is to be compensated from reactive oxygen created from ambient oxygen. The plasma density depends on ambient pressure (plasma oxygen collision) and decreases rapidly away from the target.

Fig. 6. XRD pattern of ZnO films deposited at 5 mTorr of oxygen pressure at 550°C on: (a) quartz, (b) Si (100). Inset shows 0-rocking curves.

Fig. 7. AFM of ZnO films deposited at pressures of 2.5, and 10 mTorr on quartz at RT.
surface. Thus, the available ZnO, needed for high quality film decreases as the ambient pressure increases. Moreover, if the target-substrate distance is much larger than plume size, the ZnO arriving at the substrate further decreases. However, at low ambient pressures, plasma species have large energy and hence low density of ZnO. Therefore, there exists an optimum value of ambient pressure beyond which the film quality deteriorates drastically.

The band edge of the film was estimated using the relation where absorption coefficient is a parabolic function of the incident energy and the optical band gap, \( \alpha(h\nu) = A'(h\nu - E_g)^{1/2} \), where \( A' \) is a function of refractive index of the material, the reduced mass, and the speed of light in vacuum. Using this relationship, the band edge of ZnO is evaluated by plotting \( \alpha^2 \) as a function of the energy of the incident radiation and extrapolating the linear part of the curve to intercept the energy axis. Fig. 8 shows transmission and absorption of the films deposited at various pressures at RT. From the variation of \( \alpha^2 \) as a function of the energy of the incident radiation, we observe that band gap does not depend significantly on the pressure of the ambient gas. However, the films deposited at a temperature of 550°C gives band gap of 3.23 eV, close to the crystalline value. The corresponding curves are given in Fig. 9. An average transmittance greater than 80% in visible region with sharp absorption edge near 385 nm is observed.

4. Conclusions

ZnO thin film deposition using PLD is discussed. It is observed that temperature of the substrate improves the crystallinity of the film. Observed band gap energy also improves with temperature, however, no significant effect of pressure is observed on band gap energy of the films deposited at RT. Spectroscopic investigations revealed that luminescence is observed only at low fluence and at
earlier times. At the fluence commonly used for thin film deposition, the spectrum is dominated with atomic and ionic transitions of Zn.

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