THE EMISSION SPECTRA AND ICCD IMAGES OF LASER ABLATION PLASMA FOR ZnO THIN FILM PREPARATION

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Abstract

We report structural and optical properties of ZnO thin films deposited on Si (100), quartz, sapphire, and Corning glass substrates by pulsed laser deposition technique. ZnO plasmas created from the target surface under various conditions were investigated by optical emission spectroscopy. We have studied the influence of deposition parameters, such as substrate temperature and ambient oxygen gas pressure, on the properties of the grown films.

1. Introduction

In late eighties, since pulsed laser deposition (PLD) succeeded in the preparation of high quality superconducting thin films [1-3], it has been approved 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]. However, not much work has been reported on correlation between laser-produced plasma and the deposited thin film. We have undertaken a systematic study to understand the correlation between ZnO plasma plume and ZnO films. ZnO is a II-VI semiconductor which has a direct band gap and unique properties relevant to photonic material with crystal structure similar to GaN. In general, II-VI semiconductors are attractive, because they have a 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 [5]. However, almost devices using the conventional II-VI materials degrade during their operation due to generation of defects in the material. In addition to a direct band gap of 3.37 eV at a room temperature (RT), large bond strength with large exciton binding energy (\(E_b=60\) meV), ZnO has a high melting temperature of 2248 K. It is expected that degradation due to the defects produced by the device operation will not become a serious problem.

Various techniques 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 pulsed laser deposition (PLD) [6,7]. In
PLD energy of the species in the plasma plume is reasonably large, the film deposition can be carried out at a low substrate temperature and high ambient gas pressures. 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 [8-10].

2. Experimental Details

An experimental layout used for investigating laser-ablated plumes and depositing thin films is shown in Fig. 1. Details of the ablation system are published in elsewhere. A KrF excimer laser was used to ablate a stoichiometric ZnO (purity 99.9 %) target. Laser fluence at the target was in the range of 1-4 J/cm². The films were grown at different pressures of ambient oxygen (purity 99.9 %) on Si (100), quartz, sapphire and Corning glass substrate at varying temperatures. Structures and properties of as-grown film were investigated using X-ray diffraction (XRD) and atomic force microscope (AFM), and UV-visible spectro-photometry (UVV).

Emission spectra of the plasma plumes produced in deposition of ZnO thin films were recorded using a monochromator (Acton Research, SpectraPro-308i) equipped with the ICCD (Princeton Inc., ICCD-576G) camera and the detector controller (Princeton Inc., ST-138S) connected to a PC. The spectra at a delay time from 50 ns to 500 ns after ablation were measured with constant ICCD gate width of 20 ns using the delay pulse generator (Princeton Inc., PG-200). Plasma emission was also recorded at distances of 1-10 mm from the target surface at laser fluence of 1-4 J/cm².

3. Results and Discussion

The emission spectra from various positions of the ZnO plasma plume were recorded under different laser fluence in the oxygen gas of 2, 5, and 10 mTorr at various delay times with respect to the laser pulse. Figure 2 shows the emission spectra recorded at 5 mm away from the target surface and from parallel direction to the target with laser fluence of 2 J/cm² and oxygen at pressure of 5 mTorr. The spectra were recorded at time delays varying from 50 ns to 300 ns. Table 1 shows identified emission lines using the spectral data available in the literature [11]. At low laser fluence and a small delay time, three peaks corresponding to green emission around 510 nm, red emission around 650 nm, and UV emission around 390 nm were observed. However, at higher laser fluence used for the film deposition, atomic and ionic lines of Zn predominate the spectra. Intensities of the emission lines decrease 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
Fig. 2. Temporal change of emission spectra of ZnO plasma plume at laser fluence of 2 J/cm² in ambient oxygen gas pressure of 5 mTorr.

Ablation. Several theoretical investigations have been reported to understand the formation and evolution properties of laser ablated plasmas [12-15]. The plasma expanding in a background gas has been studied using fluid dynamic models and it has been shown that the so-called knudsen layer modifies the distribution of the species to a drifted (shifted) maxwellian distribution [12]. The collisions between the expanding plasma species and the gas molecules are shown to result in a shock wave [16-18]. 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 [18]. To understand the dynamics of the laser ablated plumes 2d-images of the expanding plumes in different environments were recorded at various delay times. The evolution of the plume is simulated using hydrodynamical model [13]. It is assumed that the initial expansion is unaffected by the presence of ambient gas. However, at later times, collisions

| Table 1. Identified emission spectral lines from ZnO plasma plume. |
|-----------------------|-----------------------|
|                       | Wavelength (nm)       |
| Zn                    | 301.835, 303.578, 307.206, 307.590, 301.835 |
|                       | 330.294, 334.502, 334.557, 334.593, 468.014 |
|                       | 472.216, 481.053, 518.200 |
| Zn⁺                   | 317.218, 368.347, 319.629, 329.939, 330.596 |
|                       | 338.104, 368.347, 379.391, 380.638, 384.034 |
|                       | 384.226, 398.923, 405.771, 491.166, 492.404 |
| O                     | 382.347, 394.733, 423.332, 496.876, 532.898 |
|                       | 532.959, 533.066, 543.576, 543.683 |
| O⁺                    | 407.216, 411.922, 434.944, 464.915, 466.165 |
|                       | 467.625 |

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between the ambient gas and dominant species in the plume attenuates and slows down the plume. Figure 3 shows 2d-iced images of the plume in oxygen at pressure of 5 mTorr at various delay times. Figure 4 shows the variation of plume front edge position with time in vacuum, 5 and 10 mTorr of oxygen. The increased collisions due to increase in ambient pressure decreases the propagation range of the plume. The velocities of $1.53 \times 10^4$ and $1.68 \times 10^4$ m/s at 300 ns of the expanding front at pressures of 5 and 10 mTorr respectively are estimated.

The crucial parameters in PLD are the deposition temperature, the pulse repetition rate, and the pressure of the background gas during deposition. XRD results of all the grown films in the whole range of deposition parameters used in this study show strong c-axis orientation in (002) and (004) planes. Increasing the substrate temperature enhanced the crystallinity of the film irrespective of the substrate. The width of diffraction peaks and hence size of the nanocrystallites is highly influenced by the temperature of the substrate. Figure 5 shows XRD of ZnO films grown on Si (100) and quartz.

Fig. 3. 2D-images of ZnO plasma plume at laser fluence of 2 J/cm² at ambient gas pressure of 5 mTorr at various time delays.

Fig. 4. Position of plume front as a function of delay time at different ambient gas pressures.
substrates at various pressures of oxygen at substrate temperature of 550 °C. As film quality improves, evidenced by reduced FWHM, the position of the (002) peak tends towards higher angles. It may be due to development of micro-strain arising from mismatch in thermal expansion coefficients (TEC) between the substrate and the film. The mismatch enlarges the ZnO a-b plane leading to larger (002) peak angles as the substrate and film are cooled from higher temperatures.

Systematic shift in the peak position is seen at higher temperature where film quality is better. Increasing substrate temperature also increased the transparency of the films. Surface morphologies of the films were measured using AFM in air. Film samples were scanned over areas of 1×1 m² at several different locations on the film surface. Surface morphology varied among the films grown at various different ambient pressures. The films grown at higher oxygen pressures were smoother than those grown at lower pressures.

The variation in FWHM of XRD at different pressures can be understood by considering (Zn, O) plume size, reactive oxygen density, density of particulates generated at the target that reach the substrate, surface mobility, and Si diffusion into the newly formed ZnO layers. Oxygen molecules in the ambient atmosphere react with plasma (Zn, O) and transfer energy by inelastic collisions with plasma species. Regardless of growth technique of ZnO films, they are always oxygen deficient. This deficiency (to reduce number of oxygen vacancies) can be compensated from reactive oxygen created from ambient atmosphere. It follows from the spectra at various pressures that the number of particles reaching the substrate decreases with the ambient pressure. At sufficiently high ambient gas pressures, ZnO plasma does not reach substrate. The plasma density decreases exponentially as the pressure increases, with distance and the relative density ratio of Zn and O elements may not be good for high quality films. This also explains the roughness and grain size behavior.

4. Conclusions

ZnO thin film deposition using PLD is discussed. It is observed that temperature of the substrate improves the crystallinity of the film. The variation in FWHM of XRD at different
pressure is attributed to (Zn,O) plume size, reactive oxygen density, density of particulates generated at the target that reach the substrate, surface mobility, and Si diffusion into the newly formed ZnO layers. Spectroscopic investigations revealed that luminescence is observed only at low laser fluence and earlier times. At the fluence commonly used for thin film deposition the spectrum is dominated with atomic and ionic transitions of Zn.

5. References