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Laser Ablation of a ZnO:P_2O_5 Target under the Presence of a Transverse Magnetic Field

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From time-resolved optical emission spectra, we have investigated the effects of a transverse magnetic field on the expansion of a plasma plume produced by laser ablation of a ZnO:P_2O_5 ceramic target in oxygen active atmosphere. The emission spectra of Zn^+*, P^+*, and Zn* neutrals in the presence of magnetic field turn out to be considerably different from those without magnetic field. The characteristics of the deposited films grown on amorphous fused silica substrates by pulsed laser deposition (PLD) are examined by analyzing their photoluminescence (PL), X-ray diffraction (XRD), and UV-visible spectra.

Key Words: P-doped ZnO, Laser-induced plasma, Transverse magnetic field

Introduction

Zinc oxide (ZnO), a crystal of hexagonal wurtzite structure with the lattice constant of $a = 0.3249$ nm, $c = 0.5207$ nm, has been intensively studied as a promising material for applications in transparent electronics, ultraviolet (UV) light emitters, piezoelectric device, chemical sensors, and spin electronics.[1-3] ZnO, a II-VI compound semiconductor, has a wide band gap of 3.37 eV with a high exciton binding energy of 60 meV at room temperature (RT), which is much higher than that of ZnSe (20 meV) and GaN (21 meV). Besides, ZnO can be prepared at lower temperature compared to ZnSe and GaN. Owing to these properties, ZnO is regarded, in particular, as the most attractive UV or blue emitting material.[4-5]

Recently, it is also expected that it can be employed as a material for semiconductor devices operating in harsh environments, such as space and nuclear reactors as ZnO is more radiation resistive than Si, GaAs, SiC, or GaN.[6] However, there are certain bottlenecks to be overcome for realization of p-n junctions, in particular, for nano LEDs or lasers.[7] Unless intentionally doped, ZnO generally exhibits n-type conductivity with an electron density on the order of 10^{16} cm^{-3} up to 10^{18} cm^{-3} due to the presence of native defects.[7-9] The most promising dopants for p-type material are the group V elements, which have good p-type electrical properties including high carrier concentration good mobility, and low resistivity.[10]

ZnO films can be deposited by diverse techniques such as chemical vapor deposition, vapor phase epitaxy, molecular beam epitaxy, RF sputtering, and pulsed deposition (PLD). Among these, PLD has apparent advantages over the others in that the dopant level can be easily controlled in ZnO films just by adjusting the composition of the target material. In PLD, the quality of the deposited films is determined by the characteristics of the laser produced plasma plume formed by irradiation of solid target using a focused pulsed laser beam.

To prepare high-quality thin oxide films by PLD, there are two important factors to consider seriously: one is the ambient oxygen and the other is the density of ions with proper kinetic energy. During preparation of films, ambient oxygen scatters, enervates, and reacts with the ablation plume to form oxides and possibly clusters which may aid oxygen incorporation into the growing films. As the amount of ablated species increases with time, gas dynamic effects are thought to play a vital role in determining the spatial and velocity distributions of the vaporized materials.[11]

Among many species in the plume such as electrons, atoms, ions, and molecules including clusters, energetic ions are the most important species for deposition of high quality thin films. In this regard, it is beneficial to be able to control the density and kinetic energy of ions in the plume. PLD parameters like laser fluence and its wavelength may well be adjusted to this purpose. Also, magnetic field can be applied during laser deposition with a goal to enhance the activation and/or ionization of the ablated species while they are transported from the target to substrate.[12] Magnetic field has strong effects on the formation and expansion of plume through interaction of current density with magnetic field. PLD in the presence of a magnetic field (MF-PLD) turned out to be superior to the conventional PLD in producing high-quality films.

Here, we adopt MF-PLD to fabricate P-doped ZnO films at room temperature and present experimental results related to the effect of the transverse magnetic field on the expansion dynamics of the Zn plume in oxygen atmosphere as well as on the photoluminescence (PL) of the deposited films. Also, we attempted to elucidate the highly complicated phenomena occurring in a laser-produced plasma under the presence of magnetic field by analyzing the effects of the magnetic field on the optical emission at a given position of the plume. Time-resolved spatial distributions of Zn*, Zn^+*, and P^+* were separately monitored by coupling of an intensified charge coupled device (ICCD) with interference filters.

Experimental

The schematic view of the MF-PLD setup is illustrated in Fig. 1. The target was a high purity ZnO:P_2O_5 ceramic disk with 1.0 wt % P_2O_5, whose diameter was 1.0. The target was mounted in between the poles which were apart by 1.0 cm. The mag-

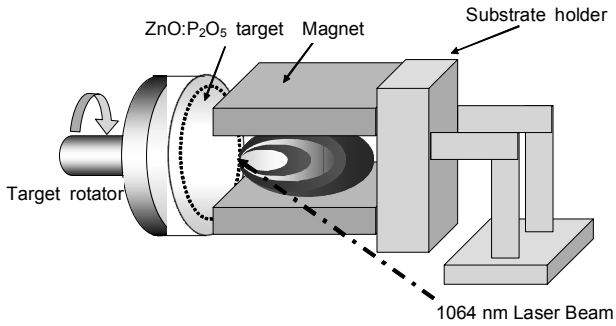

Figure 1. A schematic diagram of PLD experiment setup. The magnets were mounted facing each other and the distance between them was 1.0 cm. In case of magnetic field off, the magnets were replaced by the Al blocks of the same size. The laser fluence was 1.29 J/cm^2.

netic field was minimum (0.19 - 0.29 T) at the center and maximum (0.30 - 0.32 T) near the poles along the pole direction. A Q-switched Nd:YAG laser (Continuum 980 C, λ = 1064 nm, pulse duration = 6 ns) operating at 10 Hz was employed for PLD. The diameter of the focused laser spot was 1.2 mm and the laser fluence on the target surface was 1.29 J/cm^2 (15 mJ/pulse). The target was rotated by a standard rotary motion feed through. The deposition was performed for 30 min in oxygen reactive atmosphere. Oxygen gas (99.999%) was fed to the chamber by a needle valve and the pressure was measured by a full range gauge (Balzers PKR250). The structures of ZnO thin films were studied by X-ray diffraction (XRD) measurements (Rigaku, DMAX-IIIA). Optical band gap of the films were measured by using UV-vis spectrophotometer (HP, 8452A). The photoluminescence spectra were obtained using a He-Cd laser (325 nm, Kimmon IK3252R-E) as an excitation source at room temperature.

To examine the effects of magnetic field on the expansion of the plume and deposition of thin films, the magnets were placed between the target and substrate. In case of magnetic field off, the magnets were replaced with the Al blocks of the same size. Optical emission was studied in the oxygen active atmosphere on the laser generated plume of the ZnO:P_2O_5 ceramic target. Optical emission from the electronically excited states of Zn, Zn^+ and P^+ in the plume was collected using a lens of 5 cm focal length. The optical emission was detected by an ICCD detector (Andor, DH 734) coupled with a monochromator *via* an optical fiber bundle (Spex 700FB). The gate width of the ICCD was fixed at 10 ns. The diameter of the entrance of optical fiber bundle was 0.8 mm.

Results and Discussion

We investigated the plume dynamics of the ejected material accompanying laser ablation of the ZnO:P_2O_5 ceramic target by adopting time-resolved optical emission spectroscopy in order to obtain information on the nature of the ejected species. The emission spectra of the plume produced by laser ablation of the ZnO:P_2O_5 ceramic target were recorded in the presence and absence of the magnetic field at various oxygen pressures as shown in Fig. 2. The emission was recorded at 8 mm away from the target and the laser energy was increased to 40 mJ/pulse. All emission lines originate from the electronically excited Zn atoms

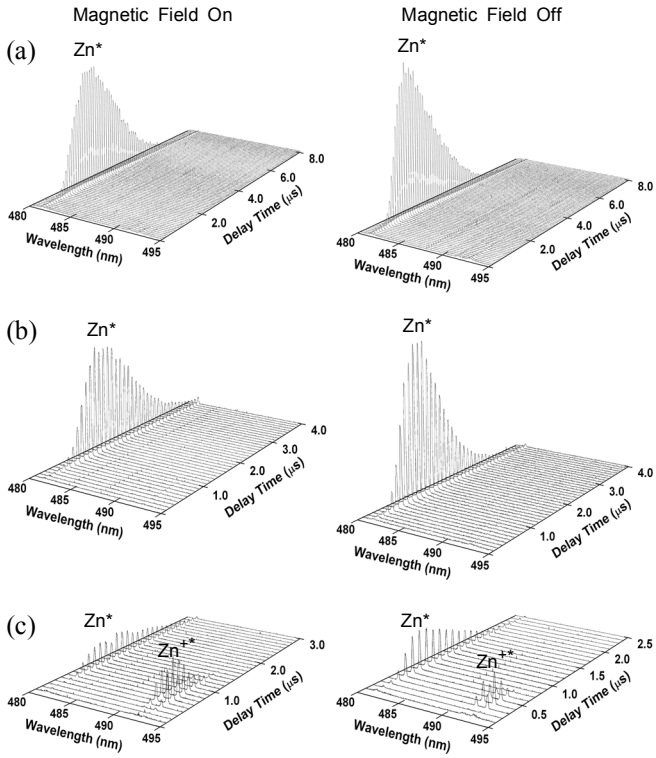

Figure 2. Time-resolved optical emission spectra of Zn* and Zn^+* at various delay times. (a) 1 Torr oxygen partial pressure, (b) 100 mTorr oxygen partial pressure, and (c) 1 mTorr oxygen partial pressure with magnetic field on and off. Optical emission was recorded at 8 mm away from the target.

or singly charged cations- henceforth represented as Zn* and Zn^+* respectively. The emission peak observed at 481.05 nm is for Zn* neutral, peaks at 491.16 and 492.40 nm representing singly charged Zn^+*. Claeyssens *et al.*[13] reported that the electronically excited species are formed by recombination between electrons and atomic species bearing a positive charge of one higher than that of the observed species *via* electron-ion recombination scheme:

$$Zn^{m+} + e^- + M \rightarrow Zn^{(m-1)+}* + M,$$

where M is the third body. This recombination process contributes to the formation of Rydberg atoms and ions, which decay *via* subsequent collisions or by photon emission, through a radiative cascade including transfer through the observed transitions. Consequently, the emission from Zn^+* generates actually a signature of the propagation of the Zn^{2+} species and similarly the Zn* emission is a signature of the Zn^+ species.[14] During ablation, the ionization potential of atomic Zn is much lower than those of the other atomic species in the plume (9.39 eV for atomic Zn, 13.62 eV for atomic O, and 27.36 and 48.74 eV for the respective double ionizations: $Zn^+ \rightarrow Zn^{2+}$ and $O^+ \rightarrow O^{2+}$). Therefore, Zn^+ ions are the dominant cationic species in the dense plasma.[13]

At lower pressures, we got optical emission from both Zn* neutral and singly charged Zn^+*. On the other hand, at higher pressures, we could detect emission from Zn* neutral only. But in the absence of magnetic field, the emission intensity from

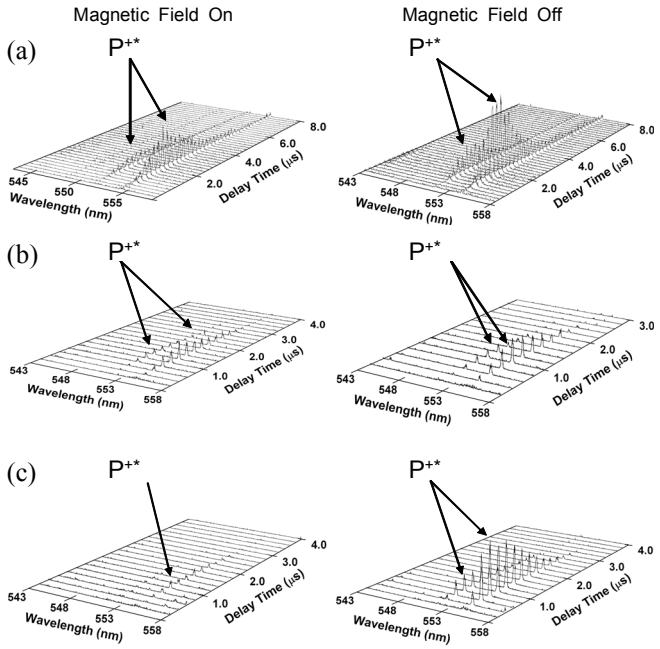

Figure 3. Time-resolved optical emission spectra of P^+* at various delay times. (a) 1 Torr oxygen partial pressure, (b) 100 mTorr oxygen partial pressure, (c) 1 mTorr oxygen partial pressure with magnetic field on and off. Optical emission was recorded at 8 mm away from the target.

Zn* was higher compared to the presence of magnetic field. Neogi *et al.*[15] reported that the emission intensities from both carbon atoms and ions increased significantly in the presence of magnetic field. But in case of our experiment, the optical emission peak of Zn* neutral was higher in the absence of magnetic field in comparison to the presence of magnetic field. To the contrast, the optical emission peak of singly charged Zn^+* was smaller when the magnetic field was off. Since the ionization potential of Zn (9.39 eV) is relatively small compared to that of carbon (11.26 eV),[12] Zn atoms are ionized relatively easily through energetic collisions in the presence of magnetic field.

Generally, the presence of magnetic field confines the plasma and increases the effective density of the plasma in the confinement region. This may cause self-absorption of the emission coming out from the plasma, leading to an observation of saturation in the signal. As a result, a strong saturation occurred in the emission intensity with increase in the oxygen partial pressures and the optical emission was less intense in the presence of magnetic field, which indicates a loss of plasma energy. The generation of instabilities and high energy particles in the plasma along with self-absorption of the emission by the plasma may be the process for loss of plasma energy.[16]

At higher pressures, either magnetic field on or off, the kinetic energy of the plasma particles decreases. Therefore, ionization of Zn atoms became less efficient and emission peaks only from Zn* species were observed. At lower pressures, however, the particles in the plume are liberated instead of being confined in the presence of magnetic field. At low pressures, even with magnetic field, plasma density was not so high as in the case

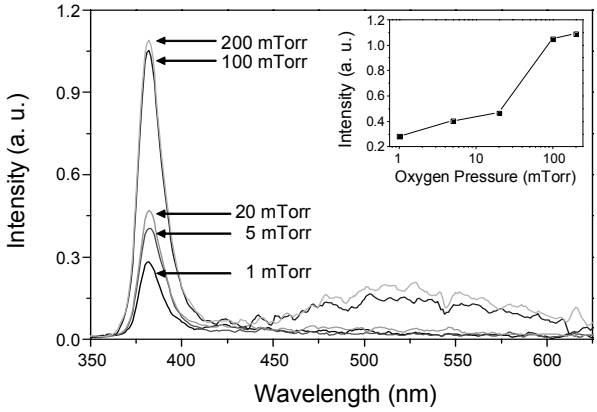

Figure 4. PL spectra of P-doped ZnO thin films on amorphous fused silica substrates by PLD at various oxygen pressures in the presence of magnetic field. The inset shows the PL peak intensity as a function of pressure.

of high pressures. That is why Zn atom could be easily ionized at low pressures in spite of the presence of magnetic field. The facile ionization together with reduced confinement effect at low pressures is considered to be responsible for the generation of both Zn* and Zn^+*.

The time-resolved optical emission spectra of P^+* in the plume with magnetic field on and off are shown in Fig. 3. The emission peaks recorded at 554.114 nm and 551.497 nm correspond to P^+* species. No optical emissions from P* were detected, presumably due to its low ionization energy (6.95 eV).[17] As the plasma has a high temperature and high density during or just after the laser irradiation,[16] P atoms were easily ionized at an initial stage of plume formation and thus optical emission from P^+* was just observed. At higher pressures, we got P^+* peak with higher emission intensity than at lower pressures. In the presence of magnetic field, the optical emission peaks became smaller compared to the absence of magnetic field.

V. N. Rai *et al.*[16] reported that the presence of magnetic field confines the plasma and increases the effective density of the plasma in the confinement region which decreases the "effective" emission intensity. The ionization induced by magnetic field does not contribute as much as in the case of Zn since the ionization potential of P is rather small. As a result of the confinement of plasma in the presence of magnetic field, we got P^+* emission peaks in lower intensity in the presence of magnetic field in comparison to the absence of magnetic field either at high pressures or low pressures. Thareja *et al.*[18] reported that at pressures 1 Torr and above, the initial plume expansion is spherical whereas at pressures 100 mTorr and less, the plume expansion is conical. They also reported that the plasma-gas interface shows distortion in the plume front and becomes instable at pressures 1 Torr and above. In case of our experiment, we found that this instability of the phosphorus plume at higher pressures (with magnetic field on) was responsible for the emission peaks at higher intense.

The PL spectra of the phosphorus doped ZnO thin films on amorphous fused silica prepared *via* pulsed laser deposition at room temperature are shown in Fig. 4. All the spectra are do-

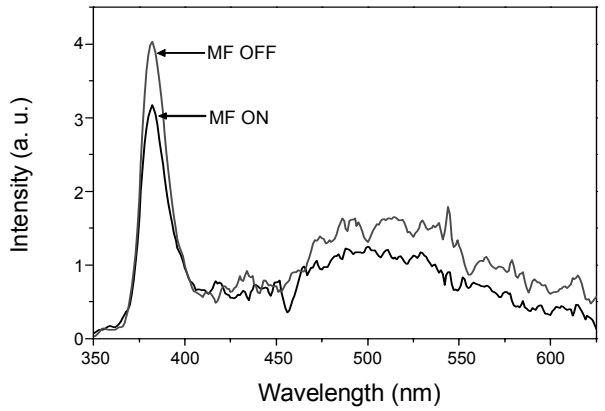

Figure 5. PL spectra of P-doped ZnO thin films on amorphous fused silica substrates by PLD at 100 mTorr oxygen partial pressure with magnetic field off and on.

minated by strong UV emission and wide visible emission and the PL intensity turns out to increase with the oxygen pressures, which may originate from the improved crystalline structure of the films. However, it is of note that films thickness is another parameter which can influence the intensity of the PL spectra. The room temperature UV emissions in the PL spectra, peaked at 3.24 eV, were produced from free excitonic emission because of the high exciton binding energy of ZnO.

Besides, we observed that the FWHM of UV emission peaks ranged from 14.2 nm to 16.8 nm with the increase of oxygen pressures. This narrow FWHM represents a good optical quality of the deposited films.[19-20] At higher oxygen pressures, the intensity of the visible emission peaks, which are indicative of the deep level emission, was larger. This manifests that the films grown at high pressures contain more structural defects.[21-23] Recently, many researchers reported about the origins of the visible emission of the P-doped ZnO films. Vanheusden *et al*.[24] has found a strong relationship between the visible emission and singly ionized oxygen vacancies. They reported that ionized oxygen is responsible for this visible emission. However, the XRD patterns of the P-doped ZnO thin films at various oxygen pressures with magnetic field on and off have no peak in the X-ray diffractograms, which indicates that the prepared films were mostly amorphous.

Fig. 5. shows the PL spectra of P-doped ZnO thin films at 100 mTorr of oxygen partial pressure with magnetic field on and off at room temperature. In case of magnetic off, the PL peak of the film was higher compared to the presence of magnetic field. The current which flows inside the plume interacts with the magnetic field giving rise to $\mathbf{J} \times \mathbf{B}$ term which decelerates the flow, where **B** is magnetic field and **J** is the charge current density.[15] Magnetic field confines the particles of the plume and increases the density of the plume in the magnetic confinement region. As a result, the average kinetic energy of Zn^+ becomes smaller with magnetic field on and the quality of the film deteriorates.

The band gap and PL peak energies of P-doped ZnO films at various oxygen pressures with (a) magnetic field on and (b) magnetic field off are shown in Fig. 6. The peak of near band edge emission (NBE) shifted to red with increase in the pressure

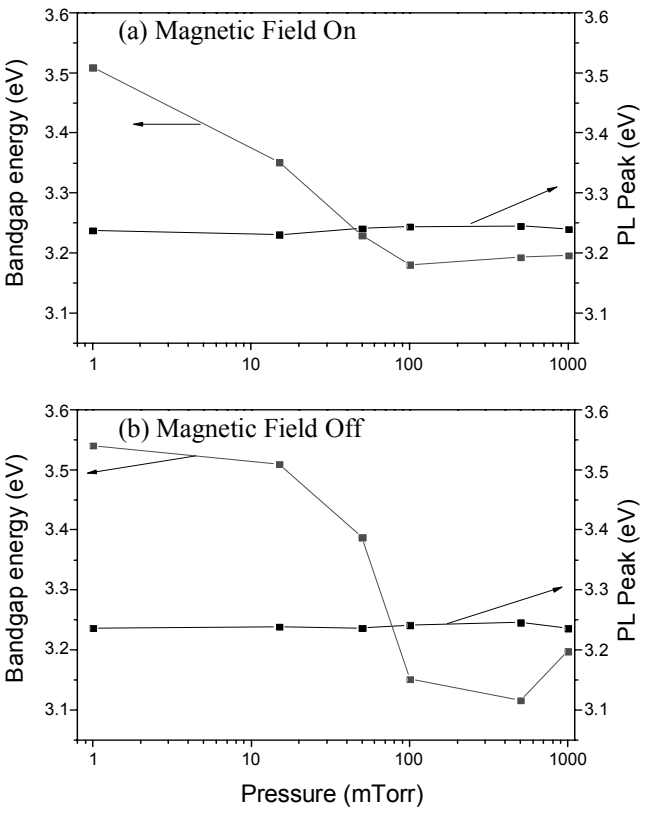

Figure 6. The band gap and PL peak energy of the P-doped ZnO films deposited by laser ablation of ZnO:P_2O_5 ceramic targets with magnetic field on (a) and off (b). The difference between two energies corresponds to the Stokes shift.

both in the presence and absence of magnetic field, while there was no apparent change in the PL peak energy with the oxygen pressure. At pressures below 100 mTorr, the band gap energy was larger when the films were grown without magnetic field. The Stokes shift, defined as the energy difference between the PL peak energy and the UV absorption energy,[25-26] was clearly observed in our experiment as shown in Fig. 6(a) and 6(b). The Stokes shift decreased with increase in pressures up to 100 m Torr and then saturated with increase in pressure in the presence of magnetic field. But in case of magnetic field off, the energy difference of NBE emission decreased with increase in oxygen pressures but not so linearly as in the case of magnetic field. Many reasons are related for occurring Stokes shift; electron-phonon coupling, lattice distortions, interface defects and point defects may cause the red shift of emission from the absorption edge. The red shift of band gap energy is thought to originate from the residual stress along *c*-axis due to the lattice distortion.[21,27-29] P. Sagar *et al*.[21] reported that the decrease in the band gap energy is attributed to the increase in the grain size, which conforms to our results considering the effects of pressure on the grain size.

Conclusions

We have investigated the plasma plume produced by laser ablation of a ZnO:P_2O_5 ceramic target by analyzing the optical emission spectra. The transverse magnetic field across the plume

had a significant effect on the optical emission from both neutral atoms and ions. We noted that the optical emission intensity from Zn* is reduced with magnetic field on, which indicates that the ionization of Zn atoms is more facilitated by the increase of energetic collisions. In case of P^{+}*, a plume confinement effect induced by magnetic field is dominant over the ionization due to its small ionization energy and accordingly the emission intensity decreased with magnetic field on. With increase in the oxygen pressure, the band gap energy of P-doped ZnO film decreased significantly, while the PL peak energy remained nearly unchanged.

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