Correlation between the OES plasma composition and ZnMnO films properties during pulsed laser

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Abstract. Manganese doped zinc oxide was ablated on (100) silicon using the fundamental harmonics of Nd:YAG laser at various oxygen ambient gas pressures and temperature substrate was kept at room temperature during the deposition. In all experiments we used ZnMnO target. Optical emission spectroscopy (OES) is used to survey the plasma composition during deposition. The intensities of the ZnI and ZnII emission lines are correlated to the oxygen gas pressure and composition and morphology of the films deposited. Strong emission lines of ZnI, Zn II and neutral oxygen are observed. Oxygen and Mn emission lines in its atomic or ionic states have not been detected in this investigation, which is thought ZnMnO as being exclusively produced on the substrate surface and not generated into the plasma, which is in agreement with previous studies of ZnO plasma plume. Atomic Force Microscopy (AFM) is used to study the influence of oxygen gas pressure on the ZnMnO film morphology. An X-ray diffraction was tried to verify a crystal structure of the sample. We have demonstrated that gas pressure is an important parameter for the quality and performances of ZnMnO structures obtained by pulsed laser deposition.

1. Introduction
Pulsed Laser Deposition (PLD) of material processing is a technique which has given good results for various applications of thin films of wide range materials [1]. In PLD, a pulsed laser is focused onto a target of the material to be deposited. For sufficiently high laser energy density, each laser pulse vaporizes or ablates a small amount of the material creating a plasma plume. The ablated material is ejected from the target in a highly forward-directed plume. The ablation plume consists primarily of excited atomic, diatomic, ionic and others species. The plasma properties of the plume largely determine the quality of the thin films deposited on the substrate. Most of the work about PLD is now devoted to improve the quality of the deposited films. To this end, it is of great importance to understand the ablation process and the transport phenomena of materials from the target to the collecting substrate. The stream of atoms, ions, molecules, and clusters ejected from the target surface emit radiation that can be analyzed using optical emission spectroscopy to gather information about the composition and dynamics of the plasma plume.

ZnO is a semiconductor possessing a large number of interesting properties that have been the focus of intensive research for many years. Due to recent and exciting developments in several key areas, pure or doped ZnO films appear to be a highly promising new and advanced functional material. Initially interest in oxide based in semiconductors was stimulated by the theoretical prediction of Dietl et al [2] that ZnO would exhibit ferromagnetism at room temperature after doping with Mn. Until now
several research groups attempted to obtain experimental evidence for such ferromagnetism in thin films form of ZnO doped with transition metals. Thin Films of ZnO and ZnO-related compounds have been grown by a wide a variety of chemical as well as physical methods: sol-gel synthesis [3], chemical vapour deposition [4], magnetron sputtering [5], molecular beam epitaxy (MBE) [6] and Pulsed Laser Deposition [7].

In this work we report the analysis of plasma generated by pulsed laser ablation using fundamental wavelength (1064 nm) of Nd:YAG (neodymium-doped yttrium aluminum garnet) laser. The effect of O2 gas pressure on plasma plume and some thin films were studied comparatively.

2. Experimental methods

The plasma plume was produced by ablating a ZnMnO target using a Nd:YAG laser (wavelength: 1064 nm, pulse width: 9 ns, repetition rate: 10 Hz) at various oxygen ambient pressures from 13 to 95 mTorr. The ZnMnO target was mounted on a holder rotated at a constant rate of 2.2 rpm so that the laser beam continuously irradiated a fresh region on the surface. The laser beam was focused onto the target at an incident angle of 45° with respect to the target surface at power of 1.2 W. The optical emission spectra from plume were measured using a spectrometer (Jobin Yvon Triax550) with a wavelength resolution of 2 nm and 1200 grooves/mm grating attached to a CCD camera. The ablation was done in O2, atmosphere at pressures ranging from 13–95 mTorr.

The surface morphology and crystallite size of ZnMnO in the films were recorded by atomic force microscopy (AFM). Also, other properties of thin films were observed by X-ray diffraction (XRD).

3. Analysis of the plasma

To investigate the plume dynamics of the ejected material accompanying laser ablation of the ZnMnO target, OES measurements were carried out, obtaining information on the nature of the ejected species. The optical emission spectra of plasma plume were recorded in the wavelength range from 400 to 800 nm at various gas pressures and substrate temperature.

![Figure 1](image-url)

Figure 1. Typical optical emission spectra of the plume accompanying the 1064 nm pulsed laser ablation of the ZnMnO target in oxygen atmosphere at a pulse power of 1.2W.

Strong blue light emission from the plasma due to the emissions from the neutral Zn atoms could be observed. Typical emission spectra of the plasma plume formed during laser irradiation in an O2 atmosphere and at a laser power 1.2 W are shown in figure 1. These spectra showed that the plasma emission in mainly due to atomic and singly ionized Zn. These results are similar to those previously
reported for pulsed-laser ablation of ZnO [8–10] and, Saji et al [11] who only observed zinc atoms and ions during the ablation of a sintered ZnO target by Q-switched third harmonic Nd:YAG laser (355 nm) at different oxygen partial pressures. Strong emissions were observed around 481.05 and 636.23 nm from the neutral Zn atoms (Zn I) and 773.25 from the singly ionized Zn atoms (Zn II) in the all gas pressure, others neutral spectral lines such as 468.01, 472.1, and the ionic line 492.4 appear in all pressures except at 13 mTorr. Practically at 13 mTorr there are a few presences of Zn emission lines.

The peaks of the neutral and ionized Mn atoms and O species could not be observed, possibly due to a lower density of these compared with that of the neutral Zn atoms. On the other hand, 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), [9]. Therefore, Zn species are the dominant in the dense plasma. Significant variations in the intensities of emission lines of various atomic and ionic species of the plasma were observed with changes ambient gas pressures, it is observed that both electronically excited Zn atoms and the singly ionized Zn atoms peaks increase linearly with gas pressure as shown in figure 2. The intensities of the emission lines corresponding to the Zn I and Zn II reach maximum values at 95 mTorr. The intensity increase of the spectral lines is due to the effect of cooling by the background gas resulting in confinement of the plasma plume. The strongest observed emission lines are listed in table 1 with corresponding spectroscopic data. From figure 2, it is seen that the emission intensity of strongest lines increase with Oxygen gas pressure.

Table 1. The strongest observed emission lines of the plume accompanying the 1064 nm pulsed laser ablation of the ZnMnO target in oxygen atmosphere at a pulse power of 1.2W.

| Lines ZnO | ZnII | 492.4 nm | 4d2D5/2-4f2F7/2 |
|-----------|------|----------|----------------|
| ZnI       | 468.01 nm | 4s4p3P0-4s5s1S1 |
| ZnII      | 472.21 nm | 4s4p3P1-4s5s1S1 |
| ZnI       | 481.05 nm | 4s4p3P1-4s4d1D2 |
| ZnI       | 636.23 nm | 4s4p3P1-4s4d1D2 |

Figure 2. (color online) Variations of Intensity emission lines of the plume corresponding to ZnI (481.05 nm, 636.23 nm) and ZnII (773.25 nm) with increase of oxygen pressure.

4. Deposition of ZnO films

ZnMnO thin films were deposited on silicon (111) substrate at room temperature, various gas pressure from 13 to 95 mTorr by PLD using a Nd:YAG laser with 1.2W per pulse. The focused laser radiation illuminated a rotating target at an incident angle of 45°. The target was 99.9% pure ZnO doped with 0.05wt% Mn. The distance target-substrate was 5.5 cm.
4.1. XRD analysis
The ZnMnO thin films grown at room temperature on various oxygen gas pressures have been characterized with regards to the structure by XRD. Amorphous films were obtained, except the film grown at 95 mTorr as shown in figure 3. This suggests that the ablated species reaching the substrate may not have the minimum energy required for crystallization and thereby getting amorphous films. The X-ray diffraction peak corresponding to ZnO (002) plane is observed. Observation of the (002) plane indicates that the film is c-axis oriented. This indicate that the surface energy of (002) plane is the lowest in ZnO crystal [12]. It is known that the number of particulates arriving at the substrate is decreased as the pressure of an ambient gas increases. Deposited particulates in a ZnO film degrade film quality. Therefore, the crystal quality is improved as the ambient gas pressure increase [13].

![XRD plot](image)

**Figure 3.** XRD θ scan of film deposited on Silicon (100) substrate at room temperature for 95 mTorr oxygen pressure by PLD.

4.2. Surface morphology by AFM
Films deposited under different oxygen pressures at room temperature were also evaluated by AFM. The scanning area was 1 μm×1 μm.

Figures 4a) to 4e) show the surface morphology of these samples as seen by AFM. The images show the effect of gas pressure on the surface roughness and grain size. It is seen that the grain size increase with oxygen gas pressure, with a grain-size distribution between 15.9 and 44.6 nm for the samples grown at room temperature. In contrast, the roughness behaves very different; there is no a clear trend of increasing roughness with increasing gas pressure.

| Oxygen Pressure (mTorr) | rms surface roughness (nm) | Grain size (nm) | Thickness (nm) |
|-------------------------|---------------------------|----------------|---------------|
| 13                      | 0.55                      | 15.89          | 65.9          |
| 32                      | 2.87                      | 19.90          | 360.0         |
| 46                      | 1.20                      | 26.57          | 97.8          |
| 64                      | 2.74                      | 40.16          | 267.0         |
| 95                      | 3.92                      | 44.59          | 180.0         |

**Table 2.** Structural parameters for the ZnMnO samples obtained from AFM at RT.

Table 2 summarizes the results of AFM measurements on ZnMnO thin films grown at different pressures. The results can be understood by considering the ZnMnO plume size. As the ambient pressure increases, the number of particles arriving on the substrate decreases, resulting in deterioration of the deposited film.
5. Conclusions

We observed that only at 95 mTorr ZnMnO crystalline films was grown. Optimization of the deposition conditions makes it possible to produce high-quality thin films. Structure and surface morphology of all obtained samples demonstrated the strong influence of the gas pressure. OES investigations are in agreement with the studies of films, showing plasma richer in Zn species. Our studies evidenced the prevalent presence of ZnI in the plasma generated under action Nd:YAG laser operated at 1064 nm.

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