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The Effects of Transverse Magnetic Field on Pulsed Laser Deposition of Cd-doped ZnO Films

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Laser ablation of a solid target has been a research topic of wide interest since the advent of various lasers in 1960s.[1] It is certainly intriguing to explore the laser ablation of solid surfaces with high-power pulsed lasers since it reveals fundamental mechanisms regarding light-matter interaction.[2,3] Not only for unraveling problems hidden in nature, pulsed laser ablation is also an attractive green technology to fabricate thin films including multi-elements.

Pulsed laser deposition (PLD) is particularly a convenient and useful method to form oxide and nitride films via laser ablation of a target in either oxygen or nitrogen atmosphere, which is called *reactive laser ablation*.[1] When a solid surface is irradiated by a high-power laser in vacuum or gaseous atmosphere, a laser-induced plasma plume (plume, in short) is generated. In reactive laser ablation, chemical species including ions and neutrals in the plume encounter gaseous molecules like oxygen or nitrogen as they expand toward a substrate mounted facing the target.

Recently, ZnO thin films have been grown successfully employing PLD.[4-6] Although ZnO films can be grown at relatively low temperatures in PLD compared to chemical vapor deposition, the inclusion of impurities into the films is to be further avoided in case the deposition is performed at room temperature (RT). In this respect, external field such as magnetic field (MF) was applied during PLD with a goal to promote the reactive chemical reactions in the plume with the help of orbital motions of ions as well as their increased concentration under MF.[4,7] This turned out to be highly successful in PLD of ZnO and the photoluminescence (PL) intensity increased drastically with the aid of MF.[4,7]

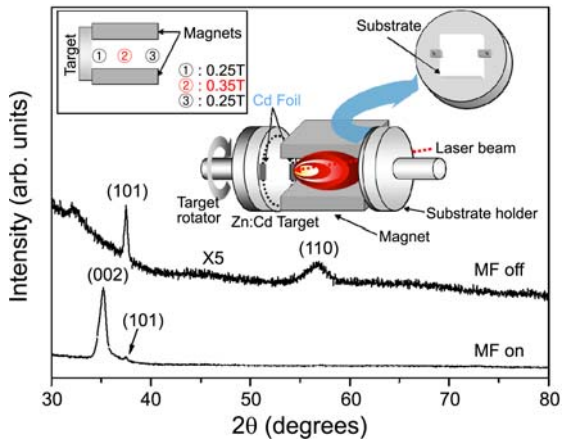

Figure 1. The XRD spectra of undoped ZnO films prepared by PLD at room temperature with and without transverse magnetic field. The inset illustrates the experimental setup.

Here, we report experimental results on pulsed laser deposition of ZnO films at RT by laser ablation of Zn target in oxygen atmosphere under *transverse* magnetic field (tMF). A significant change in X-ray diffraction (XRD) spectrum as well as in PL was observed as ZnO films were formed under tMF. This is the first, to the best of our knowledge, direct observation which explains the PL enhancement in view of the crystallinity of ZnO.

The experimental setup is depicted in the inset of Figure 1. Briefly, the target consists of a Zn disk (99.99%) and Cd foils. The length of the Cd foil along the irradiation trajectory roughly determines the concentration of Cd atoms ablated and doped in ZnO film. Since the ablation efficiencies of metals are not too different with each other, the concentration of the doped Cd atoms can be loosely considered to be proportional to the length of Cd foil over the circumference of the laser irradiation trajectory on the Zn target surface.[5] The laser ablation was done using focused Nd:YAG laser (Quantel YG980, 1064 nm, pulse width = 7 ns, 10 Hz, fluence = 3.5 J/cm^2) in oxygen atmosphere at 15 m Torr. Two magnets were mounted facing each other so that they can produce a tMF for the incident chemical species produced by laser ablation. The intensity of the field was as large as 0.35 T at the center. To elucidate the effects of the tMF on the laser ablation and the resultant films deposited on the substrate (fused silica, 10 mm × 10 mm) at RT, the two magnets were replaced with Al blocks of the same size when laser ablation was performed without tMF. Besides, optical time-of-spectra were obtained using an optical fiber installed on a three dimensional stage.[8] The temporal optical emission signal collected from a selected position of the plume was fed to a monochromator and stored by a storage oscilloscope.

The XRD spectra with and without tMF are shown in Figure 1. When tMF was not applied, the diffraction peaks were small and the (002) peak, which has to do with the ZnO crystal grown in the c-axis direction, was hardly observable. This indicates that ZnO films grown by PLD at RT have poor crystallinity. Surprisingly, however, the (002) peaks became quite clear and other diffraction peaks were nearly invisible when laser ablation was carried out under tMF. Now, it is of no doubt that tMF plays a central role to improve the crystal properties in room temperature PLD.

As illustrated in Figure 2, the PL intensity of 1% Cd-doped ZnO film grown by PLD at room temperature increased

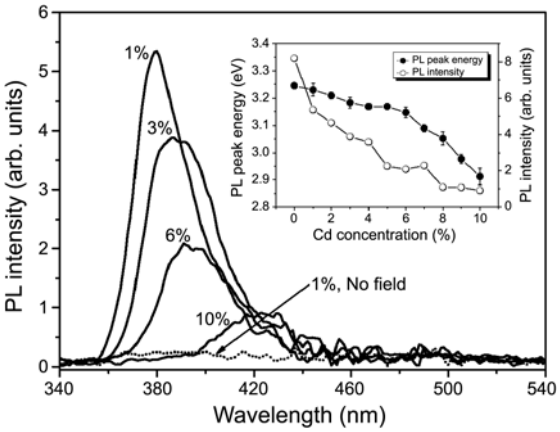

Figure 2. The PL spectra of Cd-doped ZnO films deposited by tMF-PLD. The effect of tMF on the PL intensity is clearly shown for the 1% Cd-doped films. The inset shows the intensity of PL and its peak shift with the increase in Cd contents in ZnO films.

dramatically as tMF was applied. This makes sense as we consider the anomalous improvement of the crystalline quality of ZnO film when it was formed by tMF-PLD. Also, it is highly gratifying that we could clearly show the relevance of PL and XRD results. The PL intensity decreased significantly, however, as the contents of Cd increased from 1 to 10%, presumably due to the strong mismatch in the radii of Zn^{2+} and Cd^{2+}, which are 0.74 Å and 0.97 Å, respectively. The PL peak energy decreased with the increase in the Cd concentration as shown in the inset of Figure 2. This reflects the red shift of band gap energy with Cd-doping and also suggests that RT band gap engineering of ZnO films can be facilitated by tMF-PLD.

Why is the crystallinity of the PLD-grown film improved under tMF? It is well approved that the characteristics of the films deposited by PLD are affected by the plume properties as well as the substrate temperature. The application of tMF to the plume is expected to increase the density of ions, which is critical to the deposition of high-quality films. The ions so produced will be further energized by the transient local electric field produced through plume expansion.[2] Figure 3 shows the optical time-of-flight spectra of Zn I (481.0 nm), Zn II (492.4 nm), Cd I (508.6 nm), and Cd II (553.7 nm) either with tMF or without.[8] For neutrals such as Zn I and Cd I, the optical emission is delayed and dispersed over the time without prominent change in its overall intensity. On the contrary, ions such as Zn II and Cd II were greatly enriched in the plume as tMF was applied.

In summary, we have shed light on the phenomena of PL enhancement in ZnO films deposited via tMF-PLD by analysis of both XRD and PL results. The relative enrichment of ionic species in the plume strongly contributes to the structural integrity of the ZnO films showing well-oriented growth. The red shift of PL peak energy with Cd doping manifests that tMF-PLD can be employed as a clean deposition technique for convenient RT band gap engineering.

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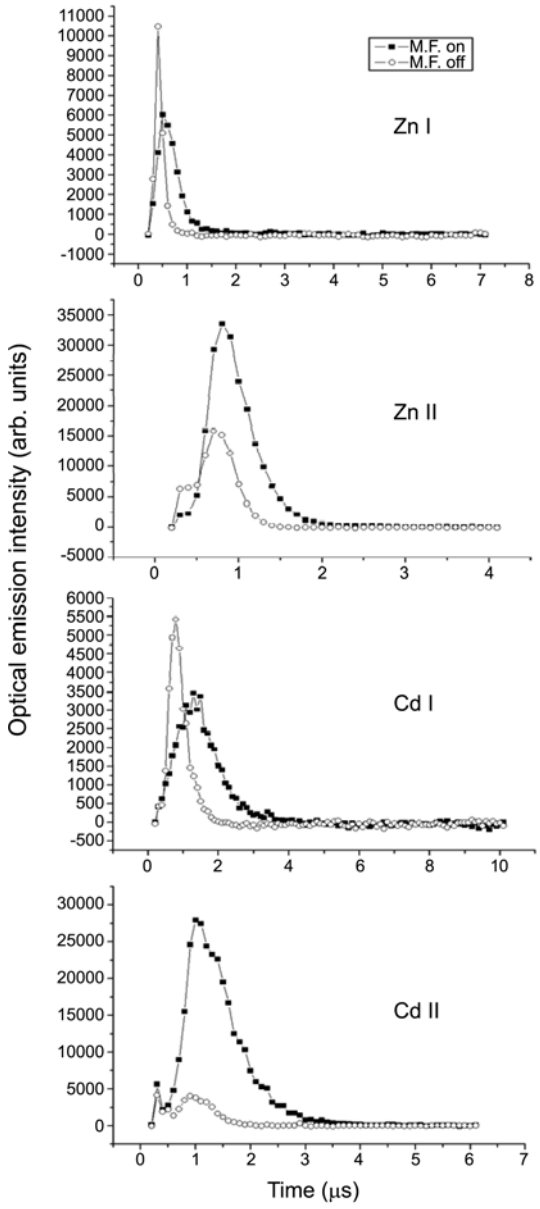

Figure 3. The optical time-of-flight spectra of Zn I, Zn II, Cd I, and Cd II with and without transverse magnetic field obtained at a position 10 mm away from the target surface.

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