

## Characterization of SnO<sub>2</sub> thin films grown by pulsed laser deposition under transverse magnetic field

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**ABSTRACT:** SnO<sub>2</sub> thin films were deposited on fused silica substrate by pulsed laser deposition under transverse magnetic field. We have explored the effects of magnetic field and ablation laser wavelength on the optical properties of laser-induced plasma plume and structural characteristics of the deposited SnO<sub>2</sub> films. Optical emission from the plume was monitored using an optical fiber to examine the influence of magnetic field on the population of the excited neutral and ionic species and their decay with times after laser ablation. Also, we employed photoluminescence, x-ray diffraction, and UV-Vis absorption to characterize SnO<sub>2</sub> films.

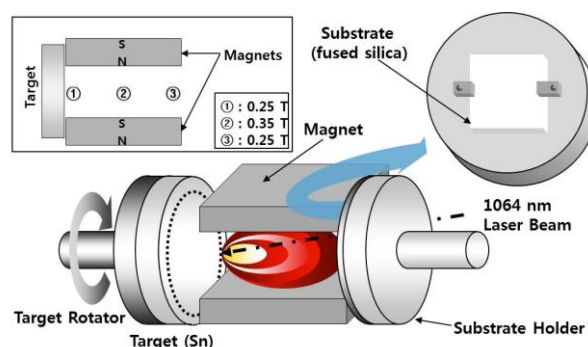
SnO<sub>2</sub> is n-type semiconducting material with a wide bandgap of 3.6 eV at room temperature. Since SnO<sub>2</sub> has high transparency in visible region and electric conductivity, it has diverse applications in gas sensors, solar cells, transparent conducting electrodes, and optoelectronic devices<sup>1-2</sup>. To fabricate SnO<sub>2</sub> thin films, various methods such as chemical vapor deposition (CVD)<sup>3</sup>, sol-gel processing<sup>4</sup>, hydrothermal method<sup>5</sup>, pulse corona discharge (PCD)<sup>6</sup>, and pulsed laser deposition (PLD)<sup>7</sup> have been adopted.

Among these, PLD has its unique advantage in that the experimental setup is extremely simple and the film thickness can be easily controlled. Besides, the ejected particles by laser ablation are highly directed with less consumption of material in PLD<sup>8</sup> and oxide and nitride films can be fabricated through reactive laser ablation. However, wide application of PLD has been limited due to high substrate temperatures ranging typically from 400 to 800 °C, which was considered to be indispensable to improve the crystalline quality of the films deposited.

In this regard, it is highly desirable to develop a new PLD method which makes low temperature growth possible. Previously, we have reported that the characteristics of the PLD-grown thin films were improved and the growth rate was enhanced when the plume was formed under transverse magnetic field during ZnO film deposition. Here, we applied PLD under transverse magnetic field to obtain high quality SnO<sub>2</sub> thin films (to be precise, SnO<sub>x</sub>, x=0, 1, 2) and analyzed the laser-produced plume to understand the role of magnetic field on the characteristics of the plume and the characteristics of the resultant films.

The experimental setup depicted in Fig. 1 is similar to the one employed in our previous work<sup>9</sup>. A Sn target (99.995%) with a

diameter of 25.4 mm was mounted on a target holder and rotated at 14 rpm to reduce target aging. Two permanent magnets were placed 15 mm apart in parallel to produce transverse magnetic field to the plume and the field strength was estimated to be 0.35 T. The target was irradiated by a Q-switched Nd:YAG laser (YG980, Quantel) at either 1064 nm or 355 nm to verify the effects of the ablation wavelength. The laser energy was 30 mJ/pulse. The laser beam was focused to give the spot diameter of 1.65 mm on the target surface, which corresponded to a laser fluence of 1.40 J/cm<sup>2</sup>, impinging on the target at 45°. Fused silica was used as a substrate and the distance between the target and the substrate was fixed at 30 mm. The reaction chamber was filled with oxygen and its pressure was maintained at 0.6 Torr. The deposition time was 30 min. To eliminate any geometrical influence from the magnets, they were replaced with the same sized stainless steel blocks when the effects of the magnetic field were investigated.

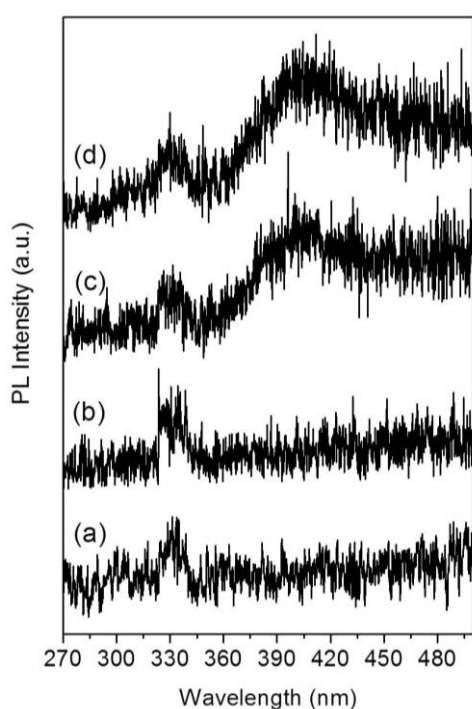


**Figure 1.** The experimental setup prepared for pulsed laser deposition under transverse magnetic field.

Optical properties of the SnO<sub>2</sub> thin films were examined by photoluminescence (PL), UV-Vis, and optical absorption and their crystallinity was measured by x-ray diffraction (XRD). To study expansion of the laser-produced plasma plume, time-resolved optical emission spectra at wavelengths corresponding to the emission of the electronically excited states of Sn I and Sn II as well as ordinary emission spectra at a position 1 cm away from the target surface with and without transverse magnetic field while irradiating the target at 90°. To detect optical emission, the optical emission was fed to a monochromator coupled with an intensified charge coupled device (ICCD, Andor, DH734) using an optical fiber after focusing with a lens.

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The PL spectra from the deposited SnO<sub>2</sub> thin films are shown in Fig. 2. A Q-switched Nd:YAG laser operating at 266 nm (Minilite II, Continuum) was used as an excitation source for PL measurement. When SnO<sub>2</sub> thin films were deposited by laser ablation at 355 nm, there was PL peak only at 330 nm. On the other hand, a broad emission was also observed at ~400 nm for the films prepared at 1064 nm. The peak at 330 nm corresponds to the band-to-band emission of 3.76 eV while the broad emission over the visible region stems from the defects such as oxygen vacancies and Sn interstitials<sup>10</sup>. Although the magnetic field did not show distinct effects of on the PL intensity and shape, there was slight increase in either UV or visible region for films prepared at 355 nm and 1064 nm, respectively.

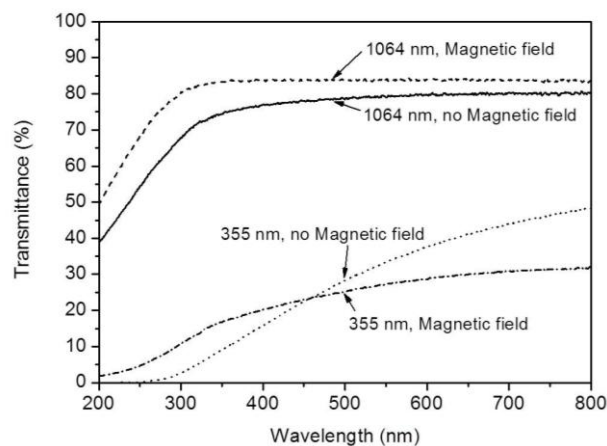


**Figure 2.** The PL spectra for the films deposited at (a) 355 nm, magnetic field off (b) 355 nm, magnetic field on (c) 1064 nm, magnetic field off (d) 1064 nm, magnetic field on.

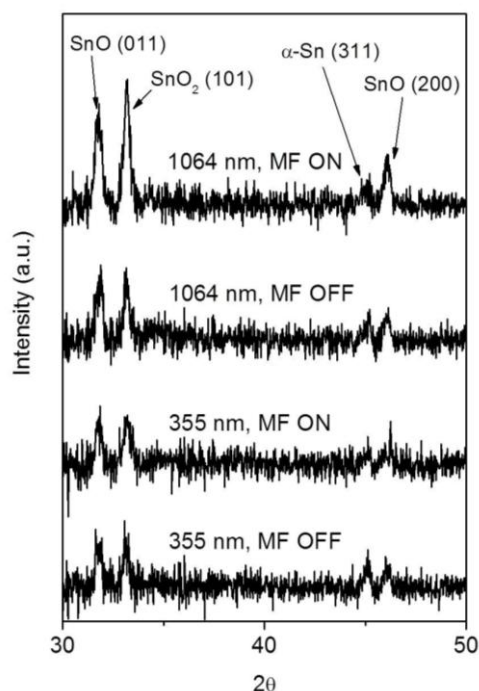
Figure 3 shows the UV-Vis transmittance spectra for the films deposited at 355 nm and 1064 nm with and without magnetic field. The film prepared at 1064 nm indicated maximum transmittance of 83% with the magnetic field on while it decreased slightly to 80% without field. At 355 nm, the overall transmittance in visible region dropped significantly compared to the case of 1064 nm and the transmittance for the films grown without field increased with wavelength rapidly.

The XRD spectra for the films grown either with or without magnetic field at 355 nm and 1064 nm are displayed in Fig. 4. For all the films so produced, diffraction peaks representing  $\alpha$ -Sn (311), SnO (011), SnO (200), SnO<sub>2</sub> (101) were observed. For the films prepared at 1064 nm under magnetic field, peaks related to SnO and SnO<sub>2</sub> were relatively enhanced compared to Sn peak, which implies that the

crystalline phase of SnO and SnO<sub>2</sub> in the films was most enriched over Sn among 4 different conditions.



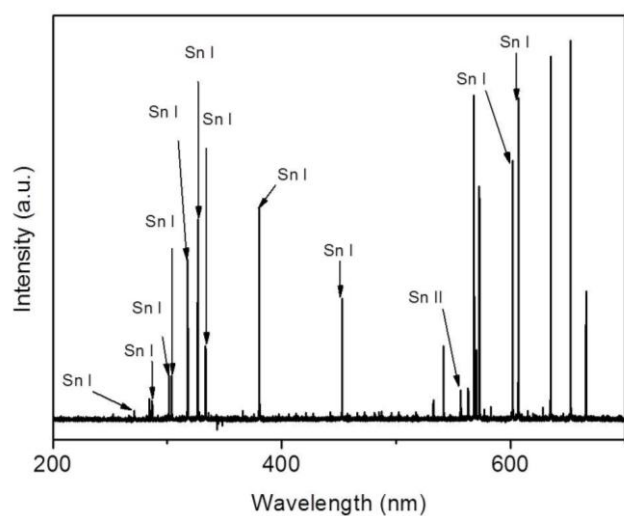
**Figure 3.** The UV-Vis transmittance spectra for the films prepared at 355 nm and 1064 nm with magnetic field on and off.



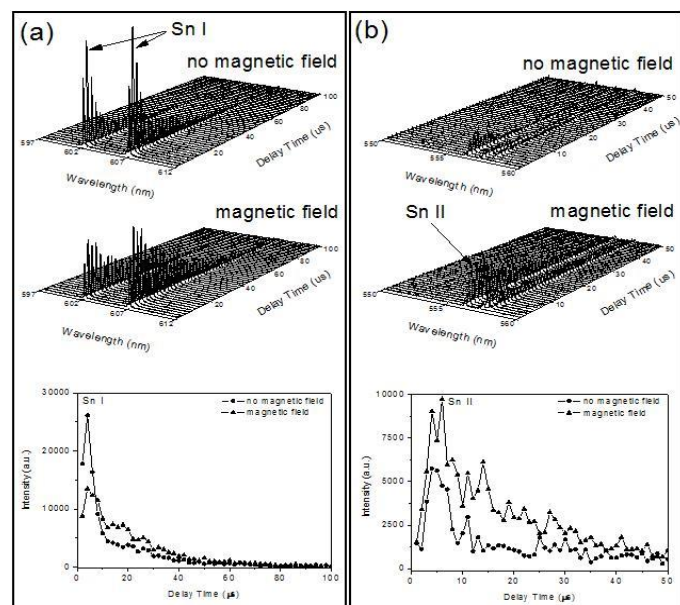
**Figure 4.** The XRD spectra of the films prepared at 355 nm and 1064 nm magnetic field on and off.

Figure 5 shows an optical emission spectrum in the range of 200 ~ 700 nm from the plume produced by irradiating Sn target in oxygen atmosphere. Emission peaks were mostly assigned to Sn I and only the peak at 556.19 nm corresponded to the emission from Sn II. When time-resolved optical emission spectra were obtained, the wavelength was scanned from 597 to 612 nm and from 550 to 560 nm for Sn I and Sn II, respectively, as shown in Fig. 6. For Sn I, the emission intensity decreased when the transverse magnetic field was applied, but that of Sn II was enhanced

drastically with magnetic field. For both Sn I and Sn II, the optical emission lasted longer by applying the magnetic field. Charged species are trapped when they cross the transverse magnetic field. The ions and electrons in the plasma plume experience Lorentz force and perform spiral motions in different directions, the frequencies of which are determined by their mass and charge. Accordingly, the kinetic energies of the charged species in the plume increases and the increased kinetic energy of the particles help increase the density of charged species due to energetic collisions, which brings about the decrease in the density of neutral species. Subsequently, the thermal energy of the plume increases through Joule heating effect. The number of excited Sn I and Sn II increases and their optical emissions last longer under magnetic field<sup>9,11-12</sup>.

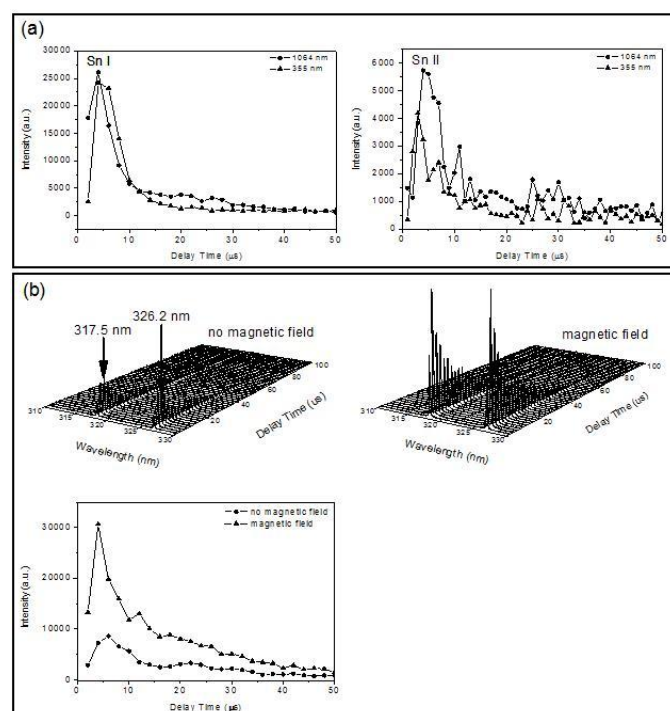


**Figure 5.** The optical emission spectrum from the plume formed by laser ablation of a Sn target in oxygen atmosphere.



**Figure 6.** Time-resolve optical emission spectra from the electronically excited Sn I and Sn II and their time decay profiles. With magnetic field on and off.

When there was no magnetic field, the emission intensity from Sn I was nearly the same for the two ablation wavelength, 355 nm and 1064 nm as shown in Fig. 7(a). For Sn II, the emission intensity for 355 nm irradiation was just 2/3 of that for 1064 nm. Besides, the emission lasted shorter without magnetic field for both Sn I and Sn II. Figure 7(b) shows the time-resolved emission spectra at 317.5 nm and 326.2 nm from the plume produced by irradiation at 1064 nm. These wavelengths were assigned to be emission lines from Sn I in NIST atomic spectra database and previous work. However, it is highly suspicious that these originate from Sn I because their intensities were enhanced as much as ~3 times under magnetic field, which manifests the behavior of ionic species, Sn II.



**Figure 7.** (a) The wavelength dependence of the time decay profiles for Sn I and Sn II optical emissions. (b) Time-resolved optical emission spectra and time decay profiles at 317.5 nm and 326.2 nm with magnetic field on and off.

SnO<sub>2</sub> thin films were grown on fused silica substrate by irradiation of a Sn target at 355 nm and 1064 nm in oxygen atmosphere under transverse magnetic field. In particular, when the film was deposited under magnetic field at 1064 nm, the amount of crystalline SnO<sub>2</sub> was fairly increased in the film, which is reflected in the increase of SnO<sub>2</sub> peaks in the XRD spectrum. This originates from the increased density of more reactive Sn II in the plume when it was formed under magnetic field. Besides, the PL intensity in the visible region was most intense in this deposition condition. This suggests that the overall crystallinity is not improved under magnetic field, which may stem from the faster growth rate of films when they were deposited under magnetic field.

**KEYWORDS:** laser ablation, SnO<sub>2</sub>, transverse magnetic field

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