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# Ambient Oxygen Effects on the Growth of ZnO Thin Films by Pulsed Laser Deposition

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**Abstract** ZnO thin films were prepared by pulsed laser deposition on amorphous fused silica substrates at different ambient $O_2$ pressures varying from 0.5 to 500 mTorr, to observe the effect of ambient gas on their crystalline structure, morphology and optical properties. Results of X-ray diffraction, scanning electron microscopy, atomic force microscopy and photoluminescence studies showed that crystallinity, surface features and optical properties of the films significantly depended on the oxygen background pressure during growth. A low oxygen pressure (0.5 mTorr) seems to be suitable for the growth of highly c-axis oriented and smoother films possessing a superior luminescent property. The films grown at the higher $O_2$ pressures (50-500 mTorr) were found to have many defects probably due to an excessive incorporation of oxygen into ZnO lattice. We speculate that the film crystallinity could be affected by the kinetics of atomic arrangement during deposition at the higher oxygen pressures.

**Key words** ZnO thin film, pulsed laser deposition, film growth.

## 1. Introduction

Wide-band-gap semiconductor materials are of great technological importance as they can be used in the optoelectronic devices such as light emitting diodes (LEDs) and laser diodes (LDs). ZnO is a II-VI group semiconductor, has now been recognized as a promising candidate for making blue and UV lighting devices owing to its wide bandgap ($E_g = 3.37$ eV) at room temperature and large excitonic binding energy (60 meV).1) This higher excitonic binding energy plays a positive role in making more efficient short-wavelength LEDs and LDs. Making *p*-type ZnO is the key issue for the fabrication of LEDs or LDs based on ZnO, which is still thought to be a difficult task. Previous attempts to achieve p-type doping with high hole concentration have been unsuccessful2,3) due to the compensation effect by a large background electron concentration and also few other results have proven difficult to reproduce.4-6) It is known that free electrons in ZnO are mainly generated by oxygen non-stoichiometry (possibly by the formation of oxygen vacancies). Thus, oxygen vacancies must be removed or suppressed as low as possible in order to achieve more reliable *p*-type doing in ZnO.

There are many reports concerning the growth of ZnO thin films by various techniques including molecular beam epitaxy,7) metal-organic chemical vapor deposition,8) radio frequency sputtering9) and pulsed laser deposition (PLD).10) In the present study PLD technique was used to grow ZnO thin films. PLD has some advantages over other techniques such as being able to employ a relatively high oxygen partial pressure, to control the plasma density by changing oxygen pressure and to obtain high quality crystalline films with relatively high deposition rate at low temperatures.11) In PLD, a higher ambient oxygen pressure appears more favorable to reduce the oxygen vacancies in ZnO films. However, in general, the crystallinity of oxide films grown by PLD is also quite sensitive to the oxygen pressure employed during film growth. This implies that an optimization of the oxygen pressure is required simultaneously considering both the suppression of the oxygen vacancies and the improvement of the film crystallinity.

In this article, we report the growth of ZnO films by pulsed laser deposition on fused silica substrates, which is a typical amorphous material. The structural, morphological and optical properties of the ZnO films were studied particularly as a function of ambient oxygen pressure.

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## 2. Experimental Procedure

ZnO thin films have been deposited on fused silica substrates using PLD under different $O_2$ pressures in order to investigate their properties while changing the $O_2$ pressure during film growth. The pressure of the ambient $O_2$ in the growth chamber was varied as 0.5, 50 and 500 mTorr. A pulsed KrF excimer laser (248 nm, 30 ns duration) operated at 5 Hz was line-focused onto a ZnO target rotating at 8 rpm. The laser beam energy was typically set at 150 mJ/pulse, yielding an energy density of about 3 J/cm$^3$. The target was fabricated by sintering ZnO powder for 12 h at 1100°C in air. Degreasing of the substrates was carried out in an ultrasonic bath using trichloroethylene, acetone and ethanol, in sequence. The substrates were positioned 4 cm away from the target and 1.5 cm off from the center to avoid direct exposure to the plume. The chamber was pumped to a base pressure of ~$10^{-6}$ Torr prior to back filling it with the different $O_2$ pressures. The growth temperature and deposition time were set as 600°C and 30 minutes, respectively. The film thickness was measured by using a surface profiler and further confirmed by cross-sectional scanning electron microscopy (SEM). The crystalline quality of the grown ZnO films was determined by X-ray diffraction (XRD). Surface morphology was analyzed by SEM and atomic force microscopy (AFM). The optical property of the films was studied by photoluminescence (PL) measurements.

## 3. Results and discussion

X-ray diffraction measurements were carried out to investigate the structural properties of the ZnO films grown at different $O_2$ pressures. The results are displayed in Fig. 1. The inset of Fig. 1 shows the variation in the integrated intensity of the (002) reflections as a function of $O_2$ pressure. All of the ZnO films show *c*-axis orientation in nature and no trace of differently aligned planes irrespective of the $O_2$ pressures used. It is noted that the low integrated intensity for the films grown in the higher $O_2$ pressure regime (50-500 mTorr) indicates deterioration in the crystallinity of the films grown at that higher $O_2$ pressures, compared with the ZnO film grown at the lowest $O_2$ pressure of 0.5 mTorr showing a high intensity. This deterioration in crystallinity is presumably due to an excessive incorporation of oxygen into ZnO lattice. The *c*-axis orientation indicates self-textured preference in the normal direction and this *c*-axis orientation is generally ascribed to the lowest surface free energy of the (001) basal plane of ZnO, leading to a preferred growth in that direction.

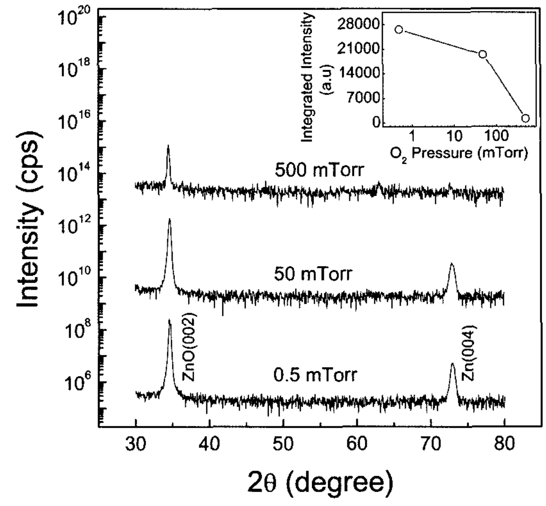

**Fig. 1.** X-ray diffraction patterns of the ZnO films grown on fused silica at 500, 50 and 0.5 mTorr $O_2$ pressure. Note that the scale of the intensities is logarithmic. The inset shows the variation in the integrated intensity of the (002) reflections as a function of $O_2$ pressure

Fig. 2 shows the SEM micrographs of the ZnO films. As can be seen from the figures, unevenly packed and bumpy like surface features are observed for the films grown in the higher $O_2$ pressure regime (50-500 mTorr) indicating inferior quality of the films. On the other hand, the ZnO film grown at the lowest $O_2$ pressure (0.5 mTorr) obviously exhibits well-packed and regular grains. The SEM observation consequently suggests that the surface morphology of the films depends on the $O_2$ pressure in the growth chamber and also it may be controlled by adjusting the $O_2$ pressure during growth. The cross-sectional microstructures observed by SEM, not presented here, showed a dense and columnar-grained structure for the film grown at the lowest $O_2$ pressure whereas the films grown at the higher $O_2$ pressures show grain boundary voids. In addition, the surface feature of all the ZnO films was also analyzed by AFM and root mean square (rms) roughness values for the films were measured. The variation in rms roughness of the ZnO films in respect of various $O_2$ pressures is shown in Fig. 3 and the

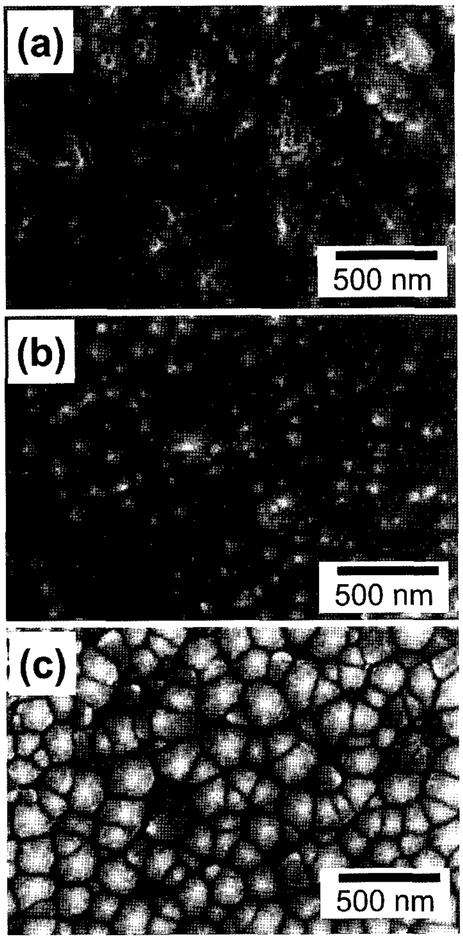

**Fig. 2.** SEM micrographs of the ZnO films grown on fused silica at different $O_2$ pressures (a) 500 mTorr, (b) 50 mTorr and (c) 0.5 mTorr.

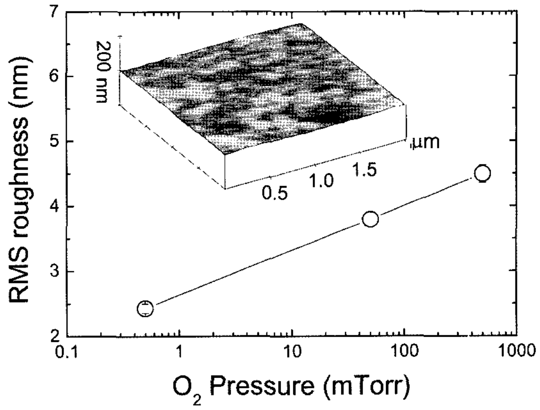

**Fig. 3.** Variation in RMS roughness values of the ZnO films in respect of different $O_2$ pressures. The inset shows a three-dimensional AFM image of the ZnO film grown at 0.5 mTorr $O_2$ pressure.

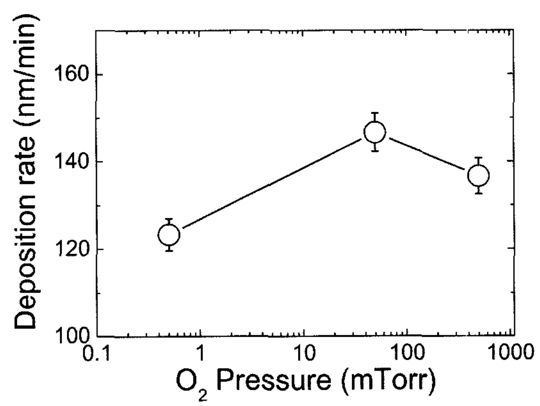

**Fig. 4.** Deposition rate of the ZnO films as a function of $O_2$ pressure.

inset in Fig. 3 shows a three-dimensional AFM image of the ZnO film grown at 0.5 mTorr $O_2$ pressure, as an illustration of surface smoothness. The surface roughness of the ZnO film grown at the lowest $O_2$ pressure is much smaller and it increases considerably with increase in $O_2$ pressure, which is consistent with the SEM observation. The increase in surface roughness with increasing $O_2$ pressure is attributed to an enhanced particulate formation in the laser-induced flume, which is a typical characteristic of high-pressure laser ablation.[12]

The variation in deposition rate depending on $O_2$ pressure is shown in Fig. 4. The deposition rate increases as $O_2$ pressure increases from 0.5 to 50 mTorr and it starts to decrease slightly for further increase in $O_2$ pressure to the highest value of 500 mTorr. The number of particulates arriving at the substrate decreases as the pressure of an ambient gas increases that presumably cause for the slight decrease in deposition rate at the highest $O_2$ pressure.[13] Also, the excessive high ambient pressure compresses the ablation plume in size and deteriorates the film uniformity in thickness.[14] The higher deposition rate at the higher $O_2$ pressures may yield a more oxygen incorporation in the ZnO lattice, consequently leading to an inferior crystallinity and more structural defects. From our experimental results, it is apparent that the lowest $O_2$ pressure (0.5 mTorr) is more favorable for the growth of high quality ZnO films.

Fig 5 shows room temperature PL spectra of the ZnO films using a continuous wave He-Cd laser (325 nm) as the excitation source and the inset in Fig. 5 shows the variation in the integrated intensity of the UV emission peaks as a function of $O_2$ pressure. Significantly pronounced visible emission, often attributed to structural defects in ZnO, is observed for the films

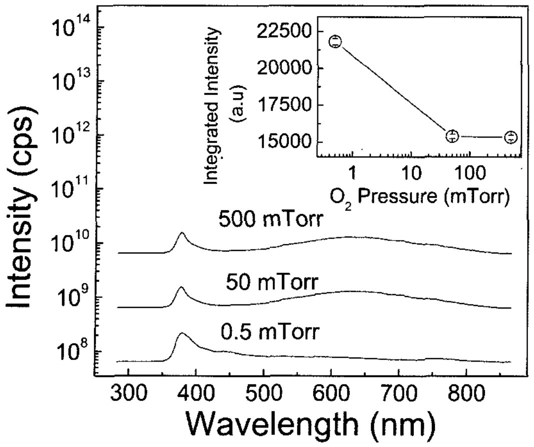

**Fig. 5.** Room temperature PL spectra of the ZnO films grown on fused silica at 500, 50 and 0.5 mTorr $O_2$ pressure. The inset shows the variation in the integrated intensity of the UV peaks as a function of $O_2$ pressure.

grown in the higher $O_2$ pressure regime (50-500 mTorr), again indicating a deterioration in the film crystallinity. On the other hand, the strong band edge emission, generally ascribed to excitonic emission, with no significant visible emission is observed for the film grown at the lowest $O_2$ pressure (0.5 mTorr), strongly indicating less structural defects in the film. Also, it is seen from the inset in Fig. 5, the integrated intensity of the UV emission for the film grown at the lowest pressure shows the maximum, but it decreases as the $O_2$ pressure increases further than 0.5 mTorr, again indicating a deterioration in the film quality at the higher $O_2$ pressures. It is well known that the deep-level emissions, i.e., the green and red emissions are closely related with structural defects such as oxygen vacancies,[15] while the UV emission is ascribed to the excitonic process.[16] The degree of structural defects in ZnO is often evaluated by comparing the relative PL intensity ratio of the UV emission to the deep-level emissions. In general, the PL spectra of the epitaxial thin films of ZnO grown by MBE, MOCVD and PLD techniques on the well lattice matched single-crystalline substrates show weaker deep-level emissions at room temperature because of reduced structural defects.[17] Conversely, the films grown on polycrystalline substrate show stronger deep-level emissions than the UV emissions. Therefore, we believe that the ZnO film grown at the lowest $O_2$ pressure has lower structural defects than those grown at the higher $O_2$ pressures, which is consistent with the XRD results.

In addition to the excessive oxygen incorporation at the higher $O_2$ pressures, we speculate that the film crystallinity may also be affected by the kinetics of atomic arrangements during deposition. In case of a film with high crystalline quality, there must be sufficient time for deposited atoms to undergo surface diffusion to thermodynamically stable sites before being covered by the next layer. Both the substrate temperature and the energy of deposition flux determine the diffusion kinetics during film growth. According to Chrisely and Hubler,[18] the average energy of atoms in a PLD plume is on the order of 10 eV, and is degraded by collisions with the ambient gas. Hence, the energy of the deposition flux is controlled by means of the ambient gas pressure and thus a high pressure causes a lower deposition energy, which may be one of the reasons for the deterioration of the ZnO films grown at the higher $O_2$ pressures. Concludingly, our experimental results show that ZnO films of good quality can be grown by keeping the $O_2$ ambient pressure towards the lowest value of 0.5 mTorr.

## 4. Conclusions

It was investigated the effects of ambient $O_2$ pressure on the properties ZnO films grown on fused silica substrates, while applying different ambient $O_2$ pressures in a pulsed laser deposition process. The XRD results showed that the film grown at the lowest $O_2$ pressure of 0.5 mTorr was highly *c*-axis oriented whereas the higher $O_2$ pressure regime (50-500 mTorr) led to a deterioration in the film crystallinity. The SEM observation confirmed that the surface features of the films could be controlled by adjusting the ambient $O_2$ pressure during film growth. From the PL measurements, it was observed that the intensity of UV emission decreased as the $O_2$ pressure increased. At the lowest $O_2$ pressure of 0.5 mTorr, the ZnO film exhibited strong excitonic emission characteristics with no deep-level emission. An excessive incorporation of oxygen into the ZnO lattice and the kinetics of atomic arrangements during deposition at the higher oxygen pressures were believed a cause of the deterioration in the film quality. This work demonstrates that the control of the ambient $O_2$ pressure during deposition is a key parameter for the growth of ZnO films with high quality by PLD and in particular lower $O_2$ pressures are more desirable.

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