Effects of pressure and substrate temperature on the growth of Al-doped ZnO films by pulsed laser deposition

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Abstract
Al-doped ZnO (AZO) thin films were deposited on p-Si (100) by pulsed laser deposition from a composite ceramic target (ZnO:Al₂O₃) by using 355 nm laser at different O₂ background pressure and substrate temperature. Upon ablation at laser fluence of 2 J cm⁻², plasma plume consists of Zn neutrals and ions, Al neutrals and O neutral are formed. As the O₂ background pressure increases from 3 Pa to 26 Pa, the energy of the plasma species are moderated. The results show that the ions density and velocity reduced significantly above 13 Pa. The velocity of the ions reduced from 14 kms⁻¹ to 11 kms⁻¹ at 13 Pa, while the ions energy reduced from 63 eV to 42 eV respectively. Below 13 Pa, crystalline and homogeneous AZO nanostructured films were formed. Above 13 Pa, the process results in low crystallinity films with higher porosity. The resistivity of the films also increases from 0.1 ohmcm to 24 ohmcm as the pressure increased. At fixed O₂ background pressure of 3 Pa, the adatom mobility of atoms on the substrates is altered by substrate heating. The resistivity of the films decreased to 10⁻³ ohmcm when the substrates are heated to 100 °C–300 °C during deposition. The films with highest carrier density of 10²⁰ cm⁻³ and carrier mobility of 13 cmV⁻¹ s⁻¹ are achieved at 200 °C.

1. Introduction
Zinc oxide (ZnO) based materials possess wide bandgap and is able to doped with a variety of element to achieve conductivity, bandgap, magnetic and sensing properties as shown by first principle calculation [1]. Recently, large ultrafast nonlinearities under both interband and intraband excitations are demonstrated in aluminium-doped zinc oxide (AZO) [2]. The results revealed special intrinsic properties of AZO which are useful for manipulating optical signal at high speed and sensing in addition to being promising alternatives to transparent conducting oxide. Such AZO films are grown by pulsed laser deposition, where the properties of the films are highly dependent on the growth parameters. Oxygen-deprived films with high density of oxygen vacancies are obtained by depositing the films in low oxygen pressure [3]. In pulsed laser deposition, the growth proceeds in three stages; namely laser ablation of target, plasma plume expansion and film growth on the substrate. Typically, in the first stage, the laser parameters are optimized to ensure congruent and sufficient ablation to produce the required plasma species. Subsequently, in the second stage, the plasma plume propagates and expands to reach the substrate where it can react with the background gas and attenuated by the background gas and its pressure. Finally, in the third stage, the films grow and this is affected by the properties of the plasma species as well as the substrates condition. The dependence on laser fluence on deposition of AZO has been widely studied. In order to obtain sufficient growth rate and high quality films, typical fluence of 2–3 Jcm⁻² for KrF [4–8] and 355 nm [8–11] lasers are used. At higher laser fluences, unwanted droplets are deposited [10, 12] and the morphology, optical, electrical properties of the films deteriorate [13]. ZnO is typically grown in the presence of O₂ to ensure stoichiometric films. The relation between the O₂ pressure and the structural-dependent electrical and optical properties of pulsed laser deposition of AZO nanostructures have been reported.
from 0.01–200 Pa (0.075–1500 mTorr) using a 266 nm laser [14]. As the pressure increases, the resistivity of the films increases. Another comprehensive report reveal that low O₂ pressure create vacancy that increase the carrier density in the films while substrate heating at optimized temperature produce smooth films with smaller grains by a 248 nm laser for applications in telecommunication wavelengths [3]. However, the effects of the background pressure on the plasma formation and expansion leading to deposition of AZO films by a 355 nm laser were not studied. In the first part of the current work, we investigate the effects of O₂ pressure on the plasma plume and on the deposition of AZO films by 355 nm laser. The laser fluence is fixed at 2 J cm⁻² while the O₂ pressure is varied. Plasma diagnostic consists of optical emission spectroscopy and ion probe measurements are

**Figure 1.** (a) OES and (b) time-of-flight signal and (c) ion velocity at different O₂ pressure.
performed to monitor the plasma generated in different background O\textsubscript{2} pressure and to ensure that sufficient species for growth on the substrate. Subsequently, in the second part, the effects of substrate temperature for films growth is studied and discussed at optimized O\textsubscript{2} background pressure.

2. Experiment

AZO thin films are grown by using Nd:YAG Laser (EKSPLA, NL301) at 355 nm; with a pulse length of 4.7 ns and 10 Hz repetition rate. The laser fluence is fixed at 2 Jcm\textsuperscript{-2}. Corning glass (Corning #26003) and p-type silicon (100) substrates are ultrasonically cleaned with acetone and isopropyl alcohol before deposition. The distance between a AZO target (KurtJ.Lesker 98% ZnO + 2wt% Al\textsubscript{2}O\textsubscript{3}) to the substrate is 5 cm in all the experiments. Prior to deposition, the vacuum chamber is evacuated to 1.33 × 10\textsuperscript{-4} Pa (1 × 10\textsuperscript{-5} Torr). The duration for deposition is fixed at 90 min (54000 pulses) for all deposition. In the first study, the deposition is carried out in 3 Pa to 26 Pa (23–200 mTorr) oxygen background pressure at room temperature. Optical emission spectroscopy and a home build ion probe are setup to detect the plasma species and the time-of flight signal at different background pressure. In the second study, the substrate temperature is varied from room temperature to 300°C at fixed laser fluence and pressure. The thickness of the AZO is measured by using a stylus profilometer (Mahr Perthometer S2). The morphology of the AZO is measured by using AFM. The resistivity of AZO is measured by
Figure 4. AFM images for size distribution in AZO thin films on glass substrate as a function of background pressure of (a) 3 Pa (23 mtorr); (b) 6 Pa (46 mtorr); (c) 13 Pa (100 mtorr); and (d) 26 Pa (200 mtorr).

Figure 5. The resistivity of the AZO films grown at different background pressure at room temperature.
four-point probe (Keithley 236 and probe station, Ohio) and Hall effects measurement with van der Pauw configuration (Lakeshore). The optical transmittance is measured by UV–vis spectrometer with a deuterium-halogen light source (Avantes, Oceanoptics S2000).

3. Result and discussion

3.1. Effects of O₂ background pressure
All the depositions were performed with laser fluence of 2 Jcm⁻² in O₂ background pressure of 3 Pa to 26 Pa. In order to investigate the effects of pressure on the plasma plume, optical emission spectra and ion velocity of laser ablation of AZO target are measured. The details of the measurement setup was described in our previous report [10].

Figures 1(a) and (b) show the optical emission spectra and ions signal in different O₂ background pressure. Zn, Al, and O species are detected for the pressure range 3 Pa to 13 Pa. For ions signal measurement, an ion probe is placed at the substrate position. The velocity of the detected ions is deduced from the time-of-flight information and the results are summarized in figure 1(c). The velocity of the ions reduces from 14 kms⁻¹ to 11 kms⁻¹ at 13 Pa, while the ions energy reduces from 63 eV to 42 eV respectively. The energy of the incident species is reduced due to scattering of the ablated material and the background gas. The ion signal at 26 Pa is too low to be measured, thus, the ion velocity at 26 Pa is expected to be less than 10 kms⁻¹ and the corresponding ions energy is <42 eV.
In our previous work, ions velocity of $\sim 10 \text{ km/s}$ was obtained when laser fluence of $1.4 \text{ J/cm}^2$ was used [10]. This fluence was lower than the typical fluence for the growth of ZnO based films, thus the growth rate was extremely low and the incorporation of Al species is uncertain [10]. Lower fluence was shown to be ineffective in producing plasma plume for AZO deposition, that results in low growth rate [13]. Moderation of ions velocity is thus better achieved by using higher background pressure. In the current work, the results show that background pressures up to 13 Pa can be used to moderate the ion velocity/energy while retaining the dopant ions.

The optical properties of the films grown at room temperature are not significantly affected by O$_2$ background pressure. The optical bandgap and transmittance of the samples grown in 3 Pa, 6 Pa, 13 Pa and 26 Pa O$_2$ are shown in figure 2. As the pressure increases from 3 Pa to 26 Pa, the transmittance in the visible for all the AZO films is $\sim 80\%$–$90\%$. The optical bandgap of AZO films are determined based on the Tauc plot:

$$(\alpha h\nu)^2 \approx (h\nu - E_g)$$

where $h\nu$ is photo energy and $\alpha$ is absorption coefficient. The optical bandgap obtained are 3.32–3.36 eV. The values are higher than an undoped ZnO of $\sim 3.3$ eV; indicate that the films are successfully doped with Al based on Burstein-Moss effect.

However, the crystallinity, morphology and resistivity of the films grown at room temperature are affected by O$_2$ background pressure. The XRD spectra of the films are shown in figure 3. The crystalline peak at (002) is detected at 34.3$^\circ$ for all the samples; while the intensity of the peak decreases with increasing background pressure. The crystallinity of the film started to degrade when the oxygen pressure is higher than 13 Pa and the
crystalline peak at 002 was not detected at 26 Pa. Similar results have been reported in KrF laser deposition of ZnO on sapphire [15]. Higher O–H defects were detected for the samples grown at oxygen pressure higher than 13 Pa (100 mTorr). The AFM images of the samples are shown in figure 4. The films consist of nanostructures and the size of the nanostructures increased with background pressure. ZnO films with larger grain size have been obtained at higher background pressure in the deposition by KrF laser [16]. In addition, the porosity of the films are also increased as the background pressure increased. In another report, O2 background pressure of 13–53 Pa (100–400 mTorr) was used to obtain thick nanoporous ZnO film as photoanode by using KrF laser at room temperature [17]. Figure 5 shows that resistivities of the films increased when deposited at high O2 background pressure. Similar trend has been observed in deposition of AZO by KrF laser at 250 °C [18]. It was ascribed to the increase of oxygen vacancy which in turn increases the carrier concentration of the films [18]. Oxygen-deprived films AZO films have been obtained at even lower O2 background pressure in order to obtain higher intrinsic carrier density [3]. It is noted that for the films deposited at 3 Pa (23 mTorr), the carrier density is in the range of $10^{18}$ cm$^{-3}$.

3.2. Effects of substrate temperature

From the results in the first study, O2 background pressure at 3 Pa (23 mTorr) was selected in order to obtain good quality AZO films. At fixed laser fluence and O2 pressure, it is expected that the same plasma species and kinetic energy are produced in the ablation; but by varying the substrate temperature from room temperature to 300 °C, the mobility of the depositing species on the surface of the substrate will be altered. The optical bandgap of the samples deposited at RT to 300 °C are plotted in figure 6. When depositions were performed at higher substrate temperature, the optical bandgap increased slightly from 3.36 eV to 3.38–3.42 eV. Figure 7 shows the XRD spectra of the samples, which indicate all the films grown are crystalline and with a preferential (002) orientation. The AFM images show that the size of the nanostructures increased slightly with substrate
### Table 1. Properties of AZO films.

| Substrate temperature (°C) | Thickness (nm) | Bandgap (eV) | XRD peak | Resistivity (Ω cm) | Resistivity (Ω cm) | Carrier density (cm⁻³) | Mobility (cmV⁻¹ s⁻¹) |
|----------------------------|----------------|--------------|-----------|--------------------|--------------------|------------------------|----------------------|
| 27                         | 75             | 3.36         | 002, 103  | $1.2 \times 10^{-1}$ | $5.9 \times 10^{-1}$ | $4.08 \times 10^{18}$ | 2.6                  |
| 100                        | 100            | 3.38         | 002, 103  | $6.3 \times 10^{-3}$ | $4.5 \times 10^{-2}$ | $1.34 \times 10^{19}$ | 10.5                 |
| 200                        | 125            | 3.38         | 002, 103  | $3.6 \times 10^{-3}$ | $2.9 \times 10^{-3}$ | $1.55 \times 10^{20}$ | 13.9                 |
| 300                        | 145            | 3.42         | 002, 103  | $3.9 \times 10^{-3}$ | $3.1 \times 10^{-5}$ | $1.89 \times 10^{20}$ | 10.7                 |
temperature (figure 8). The most significant effect observed is that the resistivity of the films reduces to $10^{-3}$ ohmcm when deposited above 100 °C. The results from 4-point-probe and van der Pauw technique are shown in figure 9. The carrier density increased by one order of magnitude. For the low resistivity films, the carrier density of $10^{20}$ cm$^{-3}$ and mobility of 10–14 cmV$^{-1}$s$^{-1}$ were obtained from Hall effect measurement. In particular, the carrier concentration is >25× higher at 200 °C and 300 °C as compared to deposition at RT.

The results are summarized in table 1. Such a trend has also been reported in KrF laser deposition of AZO where the carrier concentration increase >50× from RT to 300 °C [4]. With the same plasma content as precursors to the films in the deposition, the results suggest that the increase of carrier density may be due to better incorporation of dopant in the films indicated by the slight increase in bandgap from the Tauc plot. In addition, the increase of carrier density at high substrate temperature could also be related to oxygen in the films. The presence of adsorbed oxygen decreases the conductivity. As temperature increase, the rate of oxygen desorption from the surface of ZnO increases, and an increase in current was reported [19]. The effect may be limited to low substrate temperature deposition in PLD (<400 °C) because at higher substrate temperature, significant changes in properties like the crystallinity and morphology occurred [16, 20, 21] which can affect the electrical properties significantly.

4. Conclusion

In summary, deposition of AZO films at room temperature in O$_2$ background pressure < 13 Pa (100 mTorr) ensure better crystallinity, resistivity and also morphology of the films as compared to higher pressure range. When the O$_2$ background pressure increased, the plasma plume produced is subjected to increase collisions that results in lower ions intensity and ions energy for AZO films growth. Thus low O$_2$ background pressure (< 6 Pa/46 mTorr) is required to ensure good quality films. Subsequently, AZO films were grown at 3 Pa (23 mTorr) and substrate heating of 100 °C–300 °C further improved the resistivity of the films to $10^{-3}$ ohmcm. Both the carrier density and mobility increases when grown at 100 °C–300 °C where adatom mobility during films growth is enhanced.

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