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Al-doped zinc oxide (ZnO:Al) thin films by pulsed laser ablation[†]

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Abstract

Highly conductive and transparent aluminum-doped zinc oxide thin films were prepared by ablating the target containing 2 wt% Al_2O_3 with ArF excimer laser (λ=193 nm). The films were grown at a repetition rate of 10 Hz, energy density of 2–3 J/cm^2 and irradiation time of 10–60 min (6000–36000 laser shots). The optical and electrical properties of the films depend on the substrate temperature and oxygen pressure during film deposition. The lowest resistivity was found to be at 1.44 Ωcm for films deposited at 300°C and in 1mtorr of oxygen ambient. The average transmittance was found to be in the range of 84–92%. Sharp decrease in transmittance and sharp increase in reflectance near the plasma edge in the near-infrared range are due to impurity scattering, which is caused by aluminum doping.

1. Introduction

Transparent conducting oxide (TCO) films have found extensive applications in optoelectronic devices[1] (for example, solar cells,[2] liquid crystal displays, heat mirrors and multiplayer photothermal conversion system[3]). Zinc oxide has attracted attention as a transparent conducting oxide because of its (i) large bandgap (3.3 eV),[4] (ii) high conductivity, (iii) ease in doping, (iv) chemical stability in hydrogen plasma,[5] (v) thermal stability when doped with III group elements,[6] and (vi) abundance in nature and nontoxicity. In addition to potential use as transparent conducting oxide in optoelectric devices, ZnO thin films also find application as gas sensors,[6] because of their high electrical resistivity. The optoelectric properties of ZnO thin films depend on the deposition and postdeposition treatment conditions as these properties change significantly with (i) the nature of chosen doping element, (ii) the adsorption of oxygen that takes place during film deposition, (iii) film deposition temperature and (iv) desorption during annealing treatment in a reducing atmosphere.[7]

Several deposition techniques are used to grow aluminum-doped zinc oxide (AZO) thin films. These include chemical vapor deposition (CVD),[7,8] magnetron sputtering,[9–12] spray pyrolysis,[13,14] and pulsed laser deposition (PLD).[15,16] In comparison with other techniques, PLD has many advantages such as (i) the composition of the films grown by PLD is quite close to that of the target, (ii) the surface of the films is very smooth, (iii) good quality films can be deposited at room temperature due to high kinetic energies (>1 eV) of atoms and ionized species in the laser-produced plasma.[17]

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In the present study, we have investigated the effect of film deposition temperature and oxygen ambient on the optical and electrical properties of aluminum-doped zinc oxide thin films deposited by pulsed laser deposition. The purpose of this work is to determine the conditions that can produce highly conducting and transparent films for optoelectronic applications.

2. Experimental

Figure 1 shows a schematic diagram of the pulsed laser deposition system. AZO films were deposited on quartz and Corning 7059 glass by focusing an ArF (194 nm) laser on to a target rotating at 15 rpm. The ZnO (99.99% purity) target was 2″ in diameter and was doped with 2 wt% Al_2O_3 (99.99% purity). For all experiments, a repetition rate of 10 Hz and energy density of 2–3 J/cm^2 were maintained. The laser pulse duration was 20 ns. The distance between the target and the substrate was 30 mm. The films were deposited by ablating the target for 10–60 min (6000–36000 laser shots). The deposition cell was initially evacuated to the pressure of the order of 6×10^{-6} torr and film deposition was done at 0.1–5 mtorr of oxygen pressure. The substrate temperature was varied from 25 to 300°C. Film thickness was measured with a DEKTAK^3-ST profilometer. The transmission through the films, referenced to the quartz glass, was measured in the wavelengths from 200–2000 nm by a spectrophotometer (Hitachi-330). The reflectance spectrum was measured from 200–1800 nm with a CARY 5E UV-VIS-NIR spectrophotometer at an angle of incidence 10°. Electrical resistivity was measured by van der Pauw method. Hall voltage measurements were carried out to calculate the carrier concentration. Electrical and optical properties were measured as a function of oxygen pressure and substrate deposition temperature.

3. Results and discussion

3.1. *Film thickness*

AZO films with thickness varying from 120 to 580 nm were deposited in vacuum and 100 to 500 nm in oxygen ambient (1mtorr) by ablating the target for 10–60 min (6000 to 36000 laser shots) at 300°C. The thickness in the film decreases in the presence of oxygen ambient and is due to reduction in film growth rate. It is attributed primarily to increased collision of the ablated AZO particles with the ionized gas plasma during deposition. Zheng and Kwok[18] had reported a similar

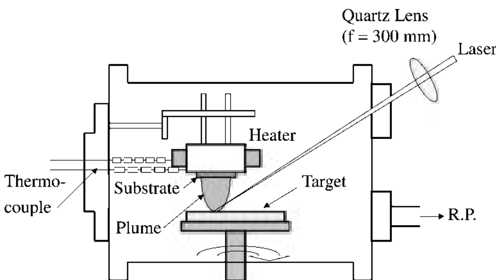

FIG. 1. Schematic diagram of pulsed laser deposition system.

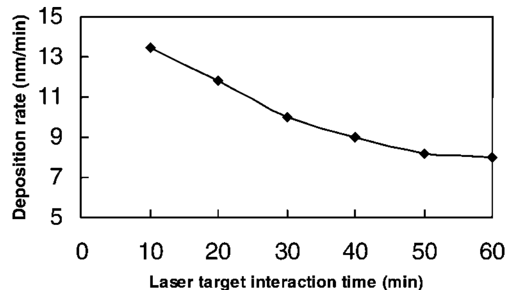

FIG. 2. Variation of film deposition rate with laser target interaction time 10–60 min(6000–36000 laser shots) for the films deposited at 300°C in 1 mtorr of oxygen ambient.

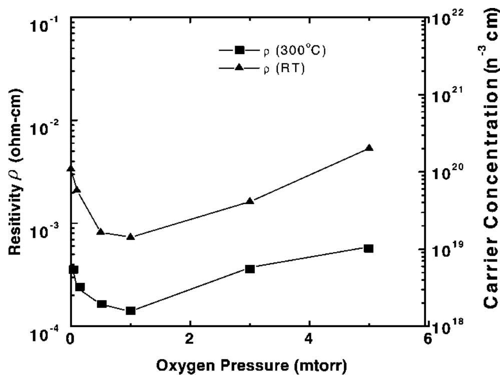

Fig. 3. Effect of oxygen pressure on the variation of the resistivity (ρ) of AZO thin films deposited at room temperature and 300°C.

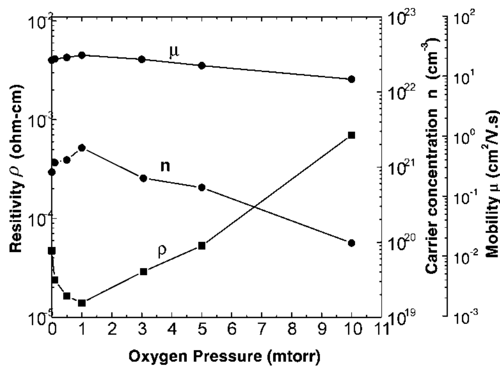

Fig. 4. Variation of resistivity, carrier concentration and Hall mobility of AZO film as a function of oxygen pressure deposited at 300°C.

effect of oxygen partial pressure on the film thickness and growth rate of ITO films deposited by PLD. Figure 2 shows the effect of variation of film deposition rate on laser target interaction time for films deposited at 300°C in 1 mtorr of oxygen ambient. Deposition rate decreases and shows saturation with increase in laser–target interaction time. This decrease in the deposition rate is linked directly to a reduction in the amount of target material being vaporized.[19] The amount of target material that vaporizes decreases due to the formation of cones on the target surface. As the size of the cones increases the laser fluence incident on the target decreases, hence the deposition rate decreases. This saturation phenomenon of the deposition rate can be due to the complete formation of cones on the target surface.[20] In the saturation region, the deposition rate is found to be 8 nm/min for films deposited in oxygen ambient at 300°C.

3.2. *Electrical properties*

The resistivity of AZO films deposited at room temperature is very sensitive to oxygen pressure (Fig. 3). High resistivity films were obtained at low oxygen pressure (< 0.5 mtorr) which rapidly decrease to a lowest value of 7.3×10^{-4} Ω -cm at 1 mtorr of oxygen pressure. As the pressure increases further, resistivity increases rapidly and the film prepared in 10 mtorr of oxygen pressure showed insulating behavior. The resistivity of AZO films deposited at 300°C is less dependent on oxygen deposition pressure. At 300°C the lowest resistivity (1.44×10^{-4} Ω-cm) is also observed at 1 mtorr of oxygen pressure. It appears that at nearly 1 mtorr, sufficient oxygen vacancies exist in the film, which give rise to lowest resistivity. At lower pressure (< 1 mtorr), the resistivity is high due to deficiency of oxygen vacancies. This is confirmed by the black color of the films deposited in vacuum and in low oxygen pressure. The sharp increase in resistivity with increase of oxygen pressure (>1 mtorr) can be explained by the fact that the increase of oxygen pressure in this range may reduce the number of oxygen vacancies in these films. The decrease of oxygen vacancies reduces the carrier concentration resulting in increase in resistivity.

Figure 4 shows resistivity, carrier concentration and Hall mobility of AZO film as a function of oxygen pressure at 300°C. As the oxygen pressure increases from 0–1 mtorr, sharp decreases in resistivity and sharp increase in carrier concentration with slight increase in Hall mobility were

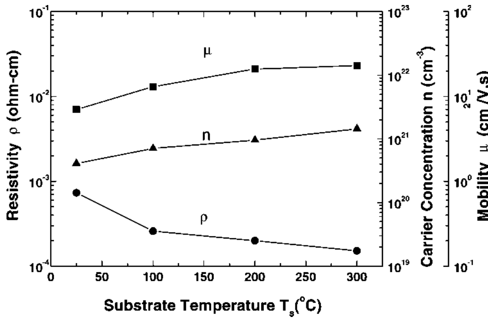

FIG. 5. Resistivity, carrier concentration and Hall mobility of AZO films as a function of substrate temperature deposited at 1 mtorr of oxygen pressure.

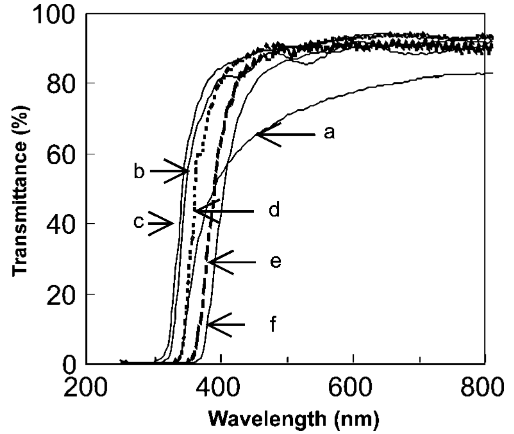

FIG. 6. Optical transmittance spectra in the wavelength range of 200–800 nm as function of wavelength for AZO films prepared at 300ºC for different oxygen pressures: (a) vacuum, (b) 0.5 mtorr, (c) 1 mtorr, (d), 3 mtorr,(e) 5 mtorr and (f)10 mtorr.

observed. With increase in the oxygen pressure from 1 to 10 mtorr, resistivity increases, and carrier concentration and Hall mobility decrease. The decrease in resistivity can be due to increase in the carrier concentration, which can be due to decrease in carrier concentration with increase in oxygen pressure (>1 mtorr). The decrease in the carrier concentration can be due to the suppression of oxygen vacancies in films prepared in oxygen pressure range (>1 mtorr). The decrease of oxygen vacancies reduces the carrier concentration resulting in increase in resistivity. Slight increase in mobility is due to improvement in crystallinity with increase in oxygen pressure (0 – 1mtorr) and decrease in mobility is due to degradation of crystallinity with increase in oxygen pressure (> 1mtorr).[21]

Figure 5 shows resistivity, carrier concentration and Hall mobility film as a function of substrate temperature of AZO films deposited in 1 mtorr of oxygen pressure. The carrier concentration increases at first up to 200ºC and is almost constant despite further increase in substrate temperature. Hall mobility also showed a similar tendency. Resistivity decreased rapidly up to 100ºC and then gradually with increase in substrate temperature. It is worth noting that the films prepared at low substrate temperature of 100ºC showed a low resistivity value of 2.75×10^{-4} Ω-cm. The lowest value of resistivity (1.44×10^{-4} Ω-cm) was observed at 1 mtorr of oxygen pressure at 300ºC.

3.3 *Optical properties*

Figure 6 shows optical transmittance (200–800 nm) as function of wavelength for AZO films prepared at 300ºC at different oxygen pressures. The films deposited in vacuum were black in color and showed low transmittance. The coloration of the film is due to excessive zinc in the film. The low value of transmittance may be because of excessive zinc ions existing at interstitial sites that probably absorb light.[22] High transmittance (above 90%) was exhibited by films prepared at 0.5–10 mtorr of oxygen pressure. However, films deposited in 10 mtorr of oxygen ambient

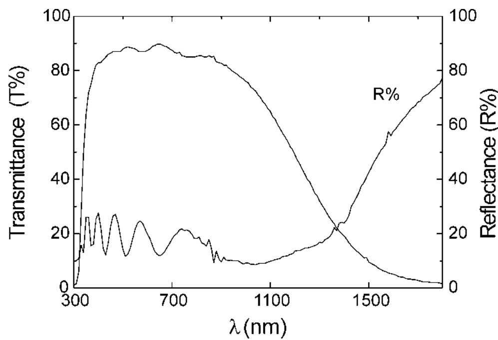

FIG. 7. Transmittance and reflectance spectra of AZO film deposited at 300ºC.

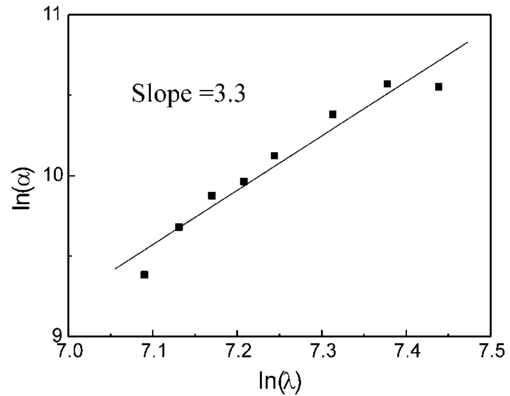

FIG. 8. Variation of ln(λ) and ln(α).

showed slight decrease in transmittance. A shift in the absorption edge was observed with increase in oxygen pressure. The shift in the absorption edge is due to well-known Brustein–Moss shift and is related to carrier density.[23] This change in the absorption edge (small band gap widening) is important in window layer coating since it can help prevent unwanted absorption in luminous spectra range.

It is observed that the average transmittance decreases from 92% to 84% as the thickness increases from 100 nm to 550 nm for films deposited by ablating the target 10–60 min at 300ºC in 1 mtorr of oxygen ambient. However, the transmittance increases continuously with increase in the substrate temperature for films in 1 mtorr of oxygen ambient.

It is observed that in the infrared region, films behave like metals and have high reflectance. In the visible region films, are highly transparent and their spectra are like those of dielectrics. The crossover between these two behaviors is at the plasma frequency. Figure 7 shows the reflectance and transmittance spectra of the AZO film. In the visible range, transmittance is high and constant, while the reflectance is low. In the near IR range, transmittance decreases while reflectance starts increasing. Minami *et al.*[24] also reported such a behavior. Figure 7 shows that one of the samples prepared at 300ºC exhibits a minimum in the reflectance spectra. Such a minimum is expected to take place near the plasma frequency. The plasma frequency ω_p is related to the reflectance minimum by the relation[25]

$$\omega_{\min} = \omega_p(\varepsilon_\infty/\varepsilon_\infty - 1)^{\frac{1}{2}}. \quad (1)$$

Hence, by determining $\omega_{\min}$ from the reflectance minimum, ω_p can be calculated by using the relation as predicted by Drude theory[26,27]

$$\omega_p^2 = N_e e^2/\varepsilon_0 m_e^*(\varepsilon_\infty - 1) - \gamma^2 \quad (2)$$

where ε_∞ is the high-frequency dielectric function, e, the electron charge, m_e^*, the effective mass of the electron in the conduction band, m_e, the mass of the electron and γ, the Drude scattering frequency where γ is given by the relation

$$\gamma = e/m^*_e\mu \quad (3)$$

and μ is the mobility of the electrons. The values of ε_∞ and m^*_e are 4 and 0.3 m_e.

Substituting the value ω_p, ε_∞, γ^2 and m_e^* into eqn (2), the carrier density is calculated to be of the order of 1.5×10^{21} cm^{-3} in our films. This is in good agreement with that stimated from the Hall mobility and the conduction data.

The free carrier absorption coefficient (α) is related to wavelength (λ) (near-infrared), and it varies as λ^p, where p lies between 1.5 and 3.5.[28] If $p=1.5$, the changes in the optical properties are due to scattering by acoustic phonons, if $p=2$ it could be assigned to optical phonons and in case $p=3-3.5$ it is normally associated with impurity.

Figure 8 shows the variation of ln(λ) and ln(α). The relationship between them is linear and the slope is found to be 3.3. This suggests that in our films the changes in the optical properties are mainly due to ionized (Al) impurity scattering.

4. Conclusions

In this study, we found that oxygen affects significantly the deposition rate, optical and electrical properties of AZO films. Good-quality (highly conducting and transparent) AZO thin films can be prepared in a narrow range of oxygen pressure between 0.5 and 1 mtorr. By controlling the oxygen pressure, coloration of the films, caused by the lack of oxygen, could be prevented. An average transmittance of about 91% in the visible range and a minimum resistivity of 1.44×10^{-4} Ω-cm were obtained for 2 wt% AZO films prepared in 1 mtorr of oxygen pressure at 300°C. With increase in film thickness, transmittance decrease was observed. The study of variation of absorption coefficient α with wavelength λ reveals that aluminum atoms in the films not only produce conduction electrons, but also ionize impurity scattering centers. An infrared wavelength cutoff property is attributed to light absorption by impurity scattering in our films.

Acknowledgement

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