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Electrical and Optical Properties of Ga-doped SnO_2 Thin Films Via Pulsed Laser Deposition

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Abstract

Ga_2O_3-doped SnO_2 thin films were grown by using pulsed laser deposition (PLD) technique on glass substrate. The optical and electrical properties of these films were investigated for different doping concentrations, oxygen partial pressures, substrate temperatures, and film thickness. The films were deposited at different substrate temperatures (room temperature to 600°C). The best opto-electrical properties is shown by the film deposited at substrate temperature of 300°C with oxygen partial pressure of 80 m Torr and the gallium concentration of 2 wt%. The as obtained lowest resistivity is 9.57×10^{-3} Ω cm with the average transmission of 80% in the visible region and an optical band gap (indirect allowed) of 4.26 eV.

Keywords: Transparent conducting oxide, Ga_2O_3: SnO_2 thin films, Pulsed laser deposition

1. Introduction

Highly transparent and electrically conducting metal oxide based coatings are very interesting because of their wide variety of technological applications in flat-panel displays, light emitting diodes, touch panels and solar cells[1]. Recently, many deposition techniques have been used to grow the SnO_2 films, such as chemical vapor deposition[2], sol gel[3], sputtering and pulsed laser deposition (PLD). Among all, PLD is an efficient technique to produce good quality of thin films with low resistivity. Many research groups have reported the films grown by using PLD[2,4,5]. Sn-doped In_2O_3 (ITO) have been paid more attention because of its outstanding resistivity ρ (2×10^{-4} Ω cm) and visible transmittance (80-90%)[6]. The development of TCOs has become hotspot in this era. However, ITO, which is the most widely used TCO, is not available easily nowadays; therefore, efforts are being directed towards searching alternative materials. Tin, zinc and titanium are being studied for the best alternative products[7]. As compared to used ITO; SnO_2 films are chemically steady in acidic, thermally stable in oxidizing environments at high temperatures, and also mechanically hard. So, SnO_2 is key material in the field of TCOs and need more study. However, very few reports focus on the use of Ga as doping materials with SnO_2. In case of Ga, the lattice parameters is increasing due to the smaller size of ionic radius than Sn^{4+} (0.069 nm), it causes the incorporation of Ga ions in the interstitial positions[8].

In this paper, we studied the electrical and optical properties of Ga_2O_3-doped SnO_2 thin films deposited using PLD on glass substrate. Systematic investigation about structural, electrical and optical properties of as deposited films were carried out as function substrate temperature, oxygen partial pressure, film thickness and doping concentration.

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2. Experimental Details

The Ga_2O_3-doped SnO_2 thin films were prepared by using PLD (KrF excimer laser, $\lambda = 248$ nm) on glass substrate. The laser was operated at 2 Hz and energy density of 1.0 J/cm^2 maintained at the target surface. The target was prepared by conventional solid state reaction method. The stoichiometric amounts of high-purity analytical grade (99.99%) SnO_2 and Ga_2O_3 powder were mixed completely in a ball milling for 24 h to achieve homogeneity, and then pressed into a 1 inch diameter pellet at 10,0001b. Finally, the pellets were sintered at 1,250ºC for 12 h. The distance from the target to the substrate which is 10 mm × 10 mm glass was approximately 35 mm. The substrates were completely cleaned in an ultrasonic cleaner for 30 min. with acetone and then ethanol. Thin films were deposited in oxygen partial pressure ranging from 20 m Torr to 100 m Torr at the substrate temperatures (ranging from room temperature to 600°C).

The structural properties of the films were analyzed by using X-ray diffraction (XRD) (Cu Kα1, $\lambda =$ 0.15406 nm) with 0.02°θ step size in the 2θ range of 20~80°. The electrical properties were checked by four probe sheet resistance (Mitsbishi Loresta MCP-T610 TFP) and Hall measurement. The optical properties of the films were studied at room temperature by using a UV-VIS-NIR spectrometer in the wavelength range of 300~800 nm.

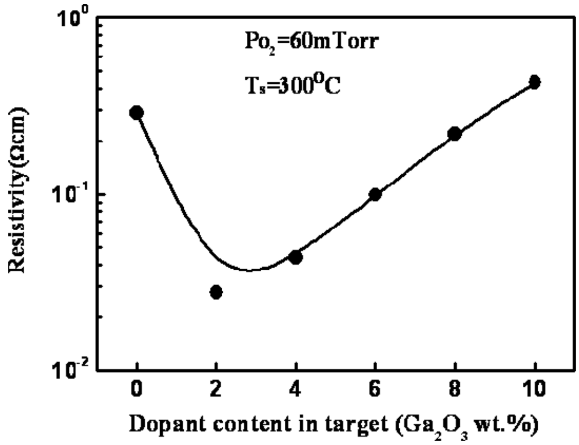

Fig. 1. Variation of electrical resistivity as a function of Ga_2O_3-doping level in the target.

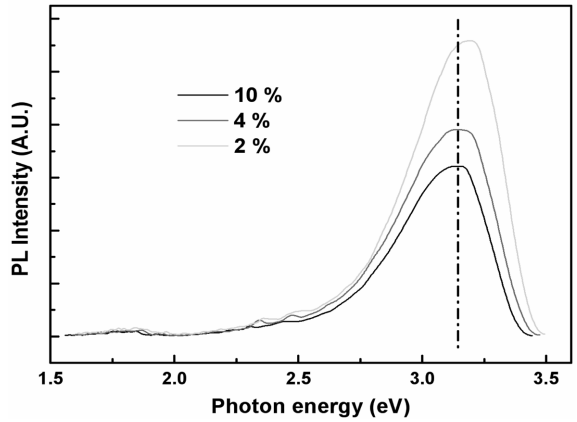

Fig. 2. Photoluminescence spectra of Ga_2O_3-doped SnO_2 (SnO_2: Ga_2O_3) thin films with different doping level.

3. Results and Discussion

In order to obtain low resistivity of SnO_2: Ga_2O_3 films, the doping concentration, oxygen partial pressure, substrate temperature and films thicknesses are optimized respectively. Fig. 1 shows the electrical properties of SnO_2: Ga_2O_3 films as function of doping concentration. The lowest resistivity ($\rho \sim 2.1 \times 10^{-2}$ Ω cm) was observed at 2 wt% doping of Ga_2O_3, and it is increasing with further increasing of the Ga_2O_3 doping concentration. It is possible to interpret that decreasing resistivity is due to an increase in free carrier concentrations as a result of the donor electrons from the Ga dopant. Because of the substitutional incorporation of Ga^{3+} (0.062 nm) ions at Sn^{4+} (0.069 nm) cation sites as their ionic radii are matching, resistivity was decreased, but after 2 wt%, resistivity was rapidly increased until end of 10 wt%. This is due to the high doping, cause's structural distortion in the SnO_2: Ga_2O_3 films[9]. In order to optimize the other conditions have effects characteristic of films, further investigation proceed as follows.

Fig. 2 shows the room temperature PL spectra of Ga_2O_3 doped SnO_2 films. It can be seen from the PL spectra that PL intensity is decreasing with increasing the doping concentration. The decline of the PL intensity with increasing the doping concentration is due to the enhancement of the crystallites carried out in the high doping level and they may be related to crystal defects with increasing doping concentration and the position of the UV-violet peak for Ga_2O_3-doped SnO_2 (Fig. 2, curves a, b, and c) appears some blue shift.

Fig. 3(a) shows that resistivity, hall mobility and carrier concentration depending on oxygen partial pressures for SnO_2: Ga_2O_3 films with 2 wt% of Ga_2O_3 doping at 300°C of substrate temperature. It was observed that the resistivity is very sensitive to the oxygen partial pressure. Resistivity continuously decreased from 20 to 80 m Torr, the lowest resistivity

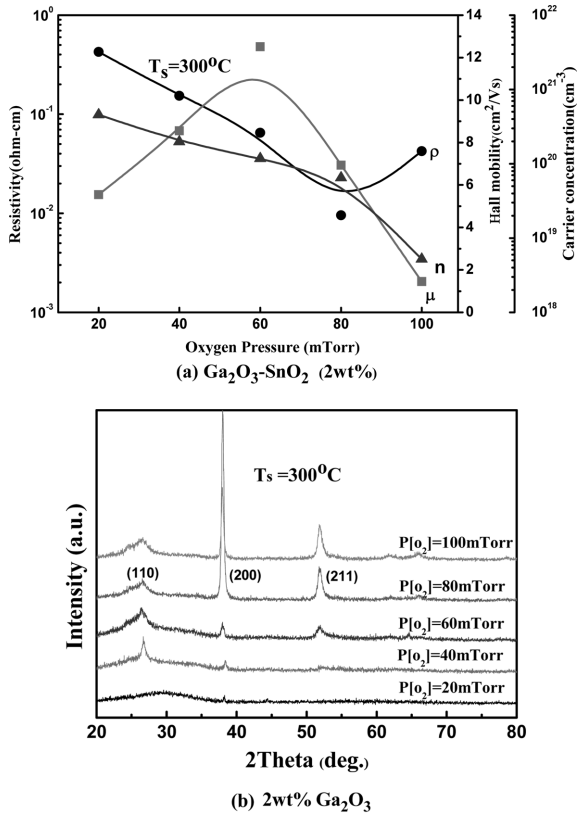

Fig. 3. (a) Variation of resistivity (ρ), mobility (μ) and carrier concentration (n) of thin films with different oxygen pressures, (b) XRD patterns of thin films with different oxygen pressure.

was found to be $\rho \sim 2.1 \times 10^{-2}$ Ω cm at 80 m Torr. According to the increase of oxygen partial pressure, deficiencies i.e. oxygen vacancies were decreased with improving crystallinity as seen in the Fig. 3(b). As the result, mobility of carriers was increased with decreasing the resistivity of the SnO_2: Ga_2O_3 films. Therefore, resistivity decreases with oxygen partial pressure from 20 to 80 m Torr, reaches a minimum at 80 m Torr, and then increases at oxygen partial pressure above 80 m Torr. Since, electrons in the SnO_2: Ga_2O_3 films are supplied from oxygen vacancies and gallium atoms in the films, it can be thought that an increase of oxygen content might cause a decrease of the oxygen vacancies, results in increase of resistivity[10].

Fig. 3(b) shows the XRD patterns of the SnO_2: Ga_2O_3 films as a function oxygen partial pressure. At 80 m Torr of oxygen partial pressure, the electrical resistivity has the lowest value. It can be explain in terms of crystallinity of the films, it is clearly observed that the film became crystalline at 80 m Torr and was found amorphous at 20 m Torr. This is the reason that crystallization of the films has an

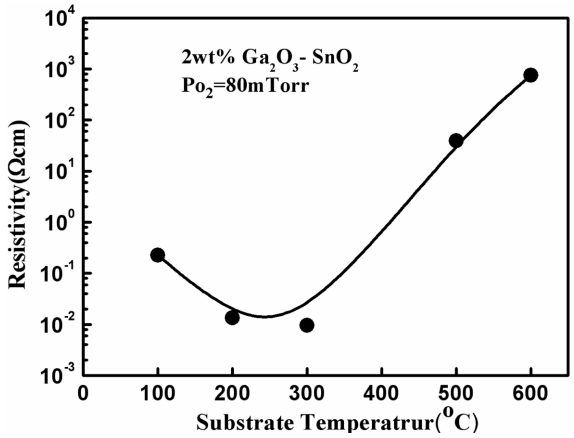

Fig. 4. Variation of electrical resistivity as a function of substrate temperature for SnO_2: Ga_2O_3 films.

effect on the resistivity of the films.

Fig. 4 shows the resistivity as a function of substrate temperature for SnO_2: Ga_2O_3 films. It was observed that substrate temperature (Ts) has influence on the resistivity of the films during deposition, it reaches a minimum at 300°C ($\rho \sim 9.57 \times 10^{-3}$ Ω cm), and increase at higher substrate temperature (>300°C). As further Ts increased, the opposite behavior was observed. When Ts < 300°C, the decrease in resistivity originates from the improvement in crystallization and enhanced substitutional doping. When Ts > 300°C, high substrate temperature, reducing the grain boundary scattering and increasing the resistivity. Beside the grain boundary scattering another factor affect the resistivity is contamination of alkali ions and C from quartz glass substrates at Ts > 300°C. The C contamination was found to be increased with increasing substrate temperature may be due to the remainder on substrate after cleaning process. Therefore, the increase in the resistivity Ts > 300°C is also attributed to the increase of alkali ions and C contamination[11].

Fig. 5 shows the electrical properties of the films as a function of the films thickness. It was observed that the first resistivity was decreased with film thickness until 500 nm and then again increased. The highest value of mobility (9.4 cm^2/Vs) and carrier concentrations (6.6×10^{19} cm^{-3}) obtained at the film thickness of 500 nm. This is due to the increasing of hall mobility and carrier concentration. With increasing films thickness, the increase in mobility is attributed to the improved crystallinity and increased crystallite size of the films, which weakens the inter-crystallite boundary scattering[12-14].

Fig. 6 shows the dependence optical transmittance of the films as function of the film thickness,

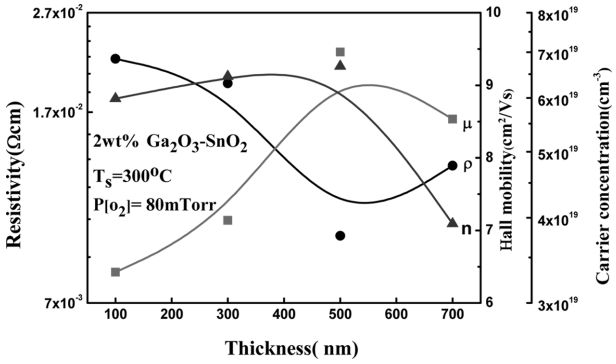

Fig. 5. Resistivity (ρ), Hall mobility (μ) and carrier concentration (n) as a function of films thickness for SnO_2: Ga_2O_3 films.

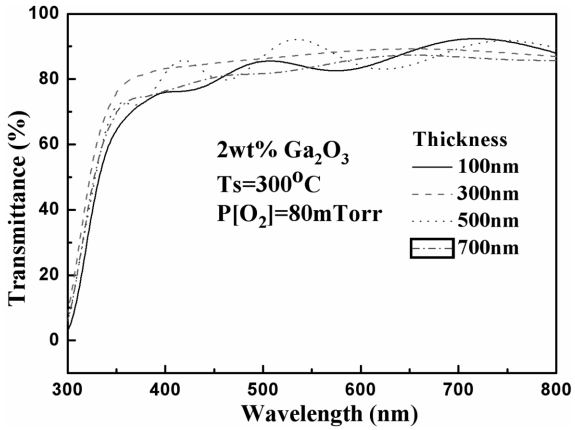

Fig. 6. The optical transmittance spectra of Ga_2O_3-doped SnO_2 thin films with different thickness.

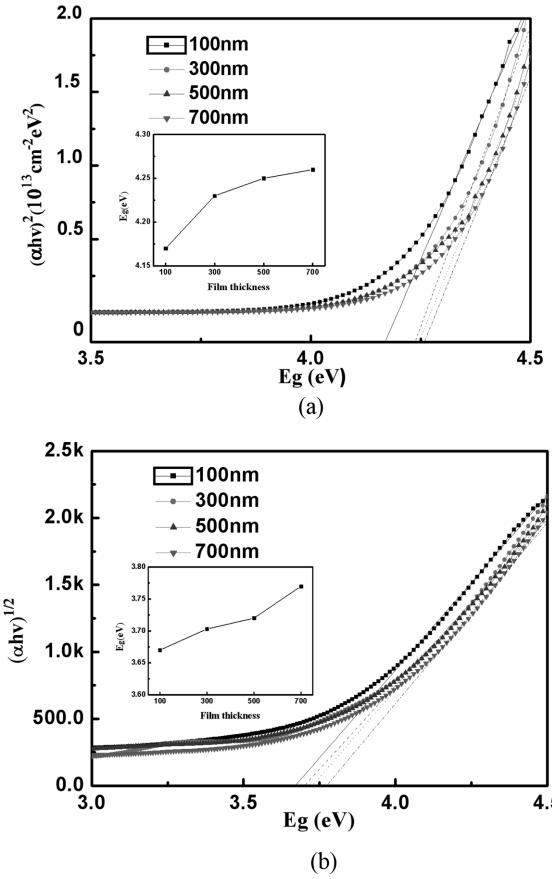

Fig. 7. (a) The Tauc plots (n = 2) of Ga_2O_3-doped SnO_2 thin films with different thickness, (b)The Tauc plots (n = 1/2) of Ga_2O_3-doped SnO_2 thin films with different thickness.

deposited at 300°C of substrate temperature and 80 m Torr of oxygen partial pressure. All films show the average transmittance higher than 80% in visible range. The band gap energy (E_g) of these films was calculated from absorption data using the Tauc's equation:

$$\alpha h\nu = A(h\nu - E_g)^n$$

where, α is absorption coefficient and *n* is a constant which depends on the probability of transition; it takes values 1/2, 3/2, 2, and 3 for direct allowed, direct forbidden, indirect allowed, and indirect forbidden transitions, respectively.

Fig. 7(a) and 7(b) show $(\alpha h\nu)^2$ vs. hν and $(\alpha h\nu)^{1/2}$ vs. hν plots for SnO_2: Ga_2O_3 thin films with various film thickness. The optical band gap (E_g) of the films was determined by extrapolating the linear region of $(\alpha h\nu)^2$ vs hν and $(\alpha h\nu)^{1/2}$ vs hν plots. The value of E_g (indirect allowed) varies from 4.17 to 4.26 eV, according to the film thickness. Also, the Eg (direct allowed) of the Ga_2O_3-doped SnO_2 is found to increase from 3.67 to 3.78 eV with an increase in the film thickness, as shown in Fig. 7(b) Thus, Ga_2O_3 doped SnO_2 films show a blue shift in band gap energy with an increase in the film thickness.

4. Conclusions

In summary, transparent and conducting SnO_2: Ga_2O_3 films have been deposited on glass substrates by PLD technique. The electrical, structural, and optical properties of the SnO_2: Ga_2O_3 films have been investigated as a function of doping concentrations, substrate deposition temperatures, and oxygen partial pressures. The lowest electrical resistivity ($\rho \sim 9.57 \times 10^{-3}$ Ω cm) was obtained with 500 nm thickness, 2 wt% Ga_2O_3 doping, 300°C of substrate temperature and 80 m Torr of partial pressure for the SnO_2: Ga_2O_3 film. The average transmittance ~80% was found for all films in the visible region. The Eg (direct allowed) of the SnO_2: Ga_2O_3 film is found to increase from 3.67 to 3.78 eV with an increase in the film thickness.

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