SnO2 thin films grown by pulsed Nd:YAG laser deposition

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Abstract

SnO₂ thin films have been deposited on glass substrates by pulsed Nd:YAG laser at different oxygen pressures, and the effects of oxygen pressure on the physical properties of SnO₂ films have been investigated. The films were deposited at substrate temperature of 500°C in oxygen partial pressure between 5.0 and 125 mTorr. The thin films deposited between 5.0 to 50 mTorr showed evidence of diffraction peaks, but increasing the oxygen pressure up to 100 mTorr, three diffraction peaks (110), (101) and (211) were observed containing the SnO₂ tetragonal structure. The electrical resistivity was very sensitive to the oxygen pressure. At 100 mTorr the films showed electrical resistivity of $4 \times 10^{-2} \Omega$ cm, free carrier density of 1.03×10^{19} cm⁻³, mobility of $10.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with average visible transmittance of ~ 87%, and optical band gap of 3.6 eV.

Introduction

SnO₂ is an n-type semiconductor with a wide band gap of 3.6 eV at room temperature. It belongs to the important family of oxide materials that combine low electrical resistance with high optical transparency (>80%) in the visible range (VIS) of the electromagnetic spectrum. These properties are sought in a number of applications. Notably as electrode materials in solar cells, light emitting diodes, flat panel displays and other optoelectronic devices where an electric contact needs to be made without obstructing photons from either entering or escaping the optical active area, and in transparent electronics such as transparent field effect transistors [1–4]. Another



property of SnO₂ as Transparent Conductor Oxides (TCOs) is that although they are transparent in the visible light, they are highly reflective for infrared light. This property is responsible for today's dominant use of SnO_2 as an energy conserving material. For instance, SnO₂ coated architectural windows allow transmitting light but keeping the heat out in the building depending on the climate of region. More sophisticated architectural windows, the socalled smart windows, depend of electrical contact of TCOs films with electrochromic films that change their coloring and transparency by applying a voltage across the films [5-7].

There are many different techniques used for deposition of SnO₂ films: spray pyrolysis [8], reactive electron beam evaporation [9], rf-sputtering [10, 11], dcmagnetron sputtering [12], chemical vapor deposition [13], reactive ion assisted deposition [14], filtered vacuum arc deposition [15] and pulsed laser deposition (PLD) [16]. However, all methods require high substrate temperature or post-annealing in order to fabricate good-guality polycrystalline films. PLD has emerged as one of the simplest and most versatile methods for the deposition of thin films of a wide variety of materials [17]. In all the techniques used for the fabrication of SnO₂ thin films, it has been found that the structural, optical and electrical properties depend critically on the oxygen partial pressure (PO_2) and the substrate temperature (T_s) [18, 19].

Laser	Nd: YAG ($\lambda = 1064 \text{ nm}$)		
Laser density energy	$2 \mathrm{J}\mathrm{cm}^{-2}\mathrm{shot}^{-1}$		
Repetition rate	5 Hz		
Target-to-substrate distance	60 mm		
Target rotation	30 rpm		
Target	SnO_2 powder 99.999% (disk with thickness of 5 mm and diameter of 15 mm)		
Substrate	Corning No. 7059 $(25 \times 25 \text{ mm}^2)$		
Substrate temperature (T_s)	500°C		
Base pressure	10^{-6} Torr		
Oxygen pressure range (PO_2)	Between 5.0 and 125 mTorr		
Ablation shots	4000		



In particular PLD in oxidizing atmosphere is one of the promising methods of preparing complex oxide films, and has been applied to the deposition of TCOs films as various high-quality SnO₂ thin films with low resistivity [20–22]. Efficient ablation of the target material requires the non-equilibrium excitation of the ablated volume to temperatures well above that required for evaporation. This generally requires a laser pulse of short duration, high energy density, and highly absorbed by the target material. For ceramic targets, this is most easily achieved via the use of short wavelength lasers operating in the ultraviolet region. Highenergy ultraviolet laser pulses can be readily provided via excimer lasers or frequency-tripled or quadrupled Nd:YAG (Neodymiumdoped Yttrium Aluminum Garnet) solid-state lasers. Each ablation pulse typically provides enough material for the deposition of only a sub-monolayer of the desired phase. The amount of film growth per laser pulse depends on multiple factors, including target-to-substrate distance, background gas pressure, laser spot size and laser energy density. Under typical conditions, the deposition rate per laser pulse can be ~ 1 Å per pulse [23]. As such, PLD enables laser shot-to-shot control of the deposition process that is ideal for multilayer and interface formation where sub-monolayer control is needed.

In this study SnO₂ thin films were prepared with a pulsed Nd:YAG laser ablation in oxygen gas background. The oxygen pressure dependence on the structural, optical and electrical properties of the SnO₂ thin films is discussed.

Experimental procedure

SnO₂ thin films were deposited on 25 × 25 mm² glass substrates (Corning 7059) using a Nd:YAG laser (λ = 1064 nm,10-ns full width at half maximum) at a repetition rate



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of 5 Hz on a target with rotation of 30 rpm in order to avoid pitting of target at any given spot and to obtain uniform thin films. The substrate was attached with a stainless steel mask to the substrate holder which was heated by a tungsten lamp. The laser was focused through a 50-cm focal length lens onto a rotating target at 45° angle of incidence. The energy density of the laser beam on the target surface was maintained at ~2.0 J/cm². The target-to-substrate distance was 60 mm. Before laser irradiation the deposition chamber is evacuated down to a base pressure of 10⁻⁶ Torr using a diffusion pump and a rotary pump. The target was prepared with SnO₂ powder (5N) and sintered (thickness of 5.0 mm and diameter of 15 mm). During deposition, high purity oxygen (99.997%) was introduced into the chamber at different pressures (ranging from 5.0 to 125 mTorr). Substrate temperature for all growths was maintained at 500°C. The ablation shots for all films were 4000. The substrates were carefully cleaned in ultrasonic bath for 10 min with acetone and methanol, rinsed in deionized water, and subsequently dried in air before deposition. Details of the growth conditions of SnO₂ thin films are given in Table 1.

The structural properties were determined by measurements in the grazing incidence geometry with an inclination of 1° in the X-ray diffraction beam (XRD) using Cu K_{α} wavelength monochromatic radiation ($\lambda = 1.5405$ Å), at 40 kV with 35 mA and an aperture diaphragm of 0.2 mm, using a D5000 Siemens X-ray diffractometer. The thickness (*d*) of the films was measured by a surface profilometer Dektak-8, Veeco. The electrical properties were determined at room temperature by Van der Pauw–Hall method. For an uniform thickness, the electrical resistivity (ρ) can be determined using the relation $\rho = R_{\text{Sheet}}d$, where R_{Sheet} is the sheet resistance. All sheet resistance and



resistivity values were determined as the average of three measurements of three different films deposited at same conditions. The optical transmittance measurements were performed using VISnear-IR spectrophotometer. The value of the direct band gap was calculated by using transmittance measurements and the Tauc formalism for direct transitions and parabolic bands [24]:

$$\left\{hv\ln\left[\frac{T}{T'}\right]\right\}^2 = (Ad)^2(hv - E_g) \tag{1}$$

where T is the film transmittance, T' is the substrate transmittance, A is a constant that depends on the material, *d* is the film thickness, hv the photon energy and E_g the band gap energy. In $\{hv \ln[\frac{T}{T'}]\}^2$, *hv* coordinates in expression (1) is a straight line. The line intercept corresponds to the band gap energy.

Results and discussion

Figure 1 shows the XRD patterns of films at 500°C for different PO_2 . The films deposited between 5.0 to 50 mTorr show evidence of three diffraction peaks around 20 at 26.6° (110), 33.8° (101) and 51.7° (211), and when increasing the PO_2 up to 100 mTorr these orientations become more evident. All the films up to 100 mTorr were polycrystalline and contain the SnO₂ tetragonal structure [25]. The effect of PO_2 on the crystallinity of the SnO₂ films is observed: the intensity of (110) and (101) diffraction peaks increases with increasing PO_2 , but the (110) diffraction peak decreases for PO_2 = 125 mTorr, increasing the (101) diffraction peak. A strong peak signal of the (110) was observed for the 100 mTorr film, while the less intense signal was for the film prepared at 125 mTorr. Additional information is obtained from the XRD measurements by



calculating the crystal size of SnO₂ film by using Scherrer's formula [26]:

$$\left\{hv\ln\left[\frac{T}{T'}\right]\right\}^2 = (Ad)^2(hv - E_g) \tag{1}$$

where λ is the X-ray wavelength (1.5402 Å), β is the (110) peak width (in radians), D is the crystal size, and θ is the Bragg diffraction angle. Table 2 shows that the crystal size increases from 20.51 nm at 5 mTorr to 24.19 nm at 50 mTorr, and then decreases gradually for films prepared above 50 mTorr. This suggests that the structural quality of the films changes with the increase in PO₂ above 50 mTorr. The excess oxygen might have induced defects in the films, which influenced the nucleation and growth of the films and resulted in the change of the structural quality. The films showed less volume of the cell unit, than SnO₂ powder (71.55 Å³), by indicating a compression of the unit cell due to the oxygen vacancies (V₀) formation and as consequence an effective generation and/or reduction of the residual donor-type defects on growth of SnO₂ films.



A thickness variation of the films is shown in Fig. 2. The rate deposition is affected by the scattering of the ablated species, the films show a thickness variation between 41 and 258 nm. The thickness of the films was reduced significantly when increasing PO_2 . The reduction in the rate deposition is attributed primarily to collisions of the ablated tin and oxygen atoms with the ionized gas plasma during deposition [27]

The electrical conductivity of *n*-type SnO₂ thin film depends on the carriers' density in the conduction band and on their mobility: $\sigma = \mu ne$, where μ the electron mobility, *n* is the carriers' density and *e* is the electron charge. Due to E_g > 3.0 eV separating the valence band from the conducting band, the conduction band cannot be thermally populated at room temperature ($kT \sim 0.03$ eV, where *k* is Boltzmann's constant); hence, the stoichiometric crystalline SnO₂ are good insulators [28].

Table 2 Structural properties of SnO₂ films on glass substrates at $T_s = 500^{\circ}$ C as a function of PO₂

PO ₂ (mTorr)	Cristal size (nm)	a = b (Å)	c (Å)	V (Å ³)
SnO ₂	_	4.7382	3.1871	71.55
5	20.51	4.7305	3.1779	71.12
10	20.74	4.7315	3.1915	71.45
50	24.19	4.7333	3.1834	71.32
100	11.62	4.7479	3.1670	71.39
125	10.76	4.7262	3.1731	70.88



Fig. 2 Thickness of the of PLD SnO₂ films as a function of PO₂



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In the case of intrinsic materials, the density of conducting electrons has often been attributed to the presence of unintentionally introduced donor centers, usually identified as metallic interstitials (M_i) or V₀ that produce shallow donor or impurity states located close to the conduction band. The excess of donor electrons are thermally ionized at room temperature, and move into the host conduction band. In SnO₂, the important role of Sn interstitial (Sni) in population of the conduction band, in addition to the V₀, has been conclusively supported by first-principle calculation of Kiliç and Zunger [29]. They showed that Sn_i and VO, which dominated the defect structure of SnO₂ due to the multivalence of Sn, explain the natural non-stoichiometry of this material and produce shallow donor levels, turning the material into an intrinsic *n*-type semiconductor. The electrical resistivity of films is shown in Fig. 3. For films deposited between 5.0 and 50 mTorr, the resistivity is ~8 × 10¹ Ω cm. Increasing *PO*₂ at 100 mTorr the resistivity decreases abruptly at minimum value of 4 × 10⁻² Ω cm, and increasing again *PO*₂ the value of the resistivity increases reaching values of ~4×10⁻¹ Ω cm.

The oxygen pressure between 50 and 100 mTorr reduces lattice structural disorders and hence increases the conductivity in the films. However, oxygen pressure above 100 mTorr produces less oxygen vacancies and decreases the conductivity of the films as was observed in XRD analysis. Low resistivity films can be obtained at 100 mTorr of oxygen, the Hall coefficient measured by Van der Paw electrode configuration for these films grown at 100 mTorr, gives the value of $-0.261 \text{ cm}^3 \text{ C}^{-1}$, suggesting that the conduction is *n*-type, and combining the Hall coefficient and conductivity measurements results in a carrier density of $1.03 \times 10^{19} \text{ cm}^{-3}$ and mobility of the electrons of $10.26 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.





Fig. 3 Electrical resistivity as a function of PO2 for SnO2 films



Fig. 4 Optical transmittance spectra of SnO_2 films under the different PO_2

The optical transmittance of the thin films as a function of wavelength in the VIS region of spectrum solar is shown in Fig. 4. The optical transmittance of the thin films increases with increasing PO_2 , high transmittance (~87%) in VIS region was exhibited by the thin films prepared under PO_2 of 100 mTorr and higher. The optical band gaps of these films were ~3.6 eV corresponding to band gap of the SnO₂. Lowering PO_2 resulted in translucent films with light yellow color. As we can see, the samples A, B and C have a similar transmission spectrum; the edge absorption is typical of the SnO₂ thin



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films. However, some interference with maximum and minimum transmittance can be observed in the visible region (VIS). These interferences were not observed in the samples D and E corresponding at PO₂ of 100 and 125 mTorr respectively, but the edge absorption shows a little shift toward a lower wavelength with an average transmittance of ~87% in the visible region. The optical E_g values for the sample grown at 100 mTorr were calculated by extrapolation of the linear region of the plot of square of the absorption coefficient as a function of the photon energy as shown in the inset of Fig. 4 of the transmittance spectrum. As is known, the transmission in the VIS region is limited by the SnO₂ band gap ($E_g = 3.6 \text{ eV}$), and photons with energy larger than Eg are absorbed. The wide SnO₂ band gap should not absorb photons in the transmission "window" in the VIS-NIR region. However, there are no "ideal" SnO₂ thin films; and even if such films could be deposited, reflection and interference would also affect the transmission. The optical properties of SnO_2 thin film as the transmission, reflection and absorption, are determined by its refraction index, extinction coefficient, E_{g} , and geometry. Geometry includes film thickness, thickness uniformity, and film surface roughness. Transmission, reflection and absorption are intrinsic, depending on the chemical composition and solid structure of the material, whereas the geometry is extrinsic, depending on the control of deposition parameters. On the other hand, it is known that the width of the VIS transmission window of an SnO₂ film with thickness deposited on a transparent substrate is affected not only by the optical parameters of the SnO_2 film but also by the optical properties of the substrate. The refractive index of the most common substrates is ~1.45 for fused silica and ~1.6 for various glasses. The extinction coefficient of the substrate is generally ~10-7, hence any light absorption



would take place in the SnO₂ films. Due to this, several interference bands are formed in the SnO₂ films producing these maximal and minimal values of transmission when either the wavelength or thickness is varied, as can be observed in Fig. 4.

Conclusion

Tin oxide thin films have been deposited by Nd:YAG-PLD on glass substrates. The physical properties of these films were investigated as a function of the oxygen pressure. The XRD results indicate that the preferential orientation of the films is changed from the (110) plane for low oxygen pressure to the (101) plane for higher pressure. As can be seen, the electro-optical properties of the SnO₂ are closely related to their stoichiometry. A low stoichiometry leads to the appearance of ionized defects which play the same role as ionized impurities. These defects are the Sn_i and/or V₀. For our films, the electron concentration varies with the PO₂ and reaches minimum values depending on this parameter. This suggests that the increase and decrease of electron concentration is caused by generation and reduction of V_0 ; also it is suspected that this behavior is due to the reduction of Sn_i as has been observed in SnO₂ films grown by pulsed laser deposition [30, 31]. The oxygen pressure between 50 and 100 mTorr reduces lattice structural disorders and hence increases the conductivity of the films. However, oxygen pressure above 100 mTorr produces less oxygen vacancies and decreases the conductivity of the films. The optical transmittance in visible region of the films increases with an increasing of PO_2 , and it exhibits high values (~87%) by the films prepared under oxygen pressure of 100 mTorr and higher. Finally, we confirm that the oxygen partial pressure induces defects which have influenced the nucleation and



growth of the films, demonstrating that it is effective to increase donortype defects of the thin films deposited by Nd:YAG PLD.

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