ELSEVIER

Applied Energy 65 (2000) 19–28

APPLIED ENERGY

www.elsevier.com/locate/apenergy

Effects of temperature and r.f. power sputtering on electrical and optical properties of SnO_2

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Abstract

Electrical and optical properties of SnO_2, which is a photovoltaic material for solar energy conversion to electricity, have been investigated. Semi-conducting SnO_2 has been grown by r.f. sputtering.We report the influence of process variables, such as substrate temperature and r.f. power. The film resistivity decreases with increasing temperature, but rises with increasing r.f. power: these can be related to crystallite size and the film orientation respectively. From the optical measurements, we deduce a variation of band-gap energy with substrate temperature. We show that the substrate temperature has a subsequent influence on the electrical and optical properties of this material.

1. Introduction

For some years, important developments have been achieved with respect to thin films of semi-conductor transparent oxides, notably due to their remarkable optical and electrical properties. In particular, ITO and ZnO films are competitive because of their abundance in nature and its relatively low cost.

The tin-oxide thin film is a degenerate n-type semi-conductor with a large band-gap of $3.6\ eV < Eg < 4.0\ eV$: thus it has a strong transmission in the visible range (0.4–0.8 μm) and a high absorption coefficient in the UV range (104–105 cm^{-1}).

Several authors [1,2] have studied SnO_2 and shown that it has a weak resistance when its constituents are not in stoichiometric proportions, such that SnO_{2-x}, $x < 1$. Its electrical resistivity can vary by several orders of magnitude following according to the deposition technique adopted. For the utilisation of SnO_2 in photovoltaic applications, one needs to have specimens with weak resistivity values. It resists chemical attack, its adhesion to glass is very great [2]. Tin oxide crystallises in a

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0306-2619/00/$ - see front matter
PII: S0306-2619(99)00045-8

tetragonal rutilated structure, when it is deposited under optimal conditions, which allows it to have a weak shear resistance thereby giving it weak losses by Joule dissipation across electrical contacts.

To improve SnO_2 films, one could employ r.f. sputtering, vapour deposition (C.V.D.) or spraying. The aim is to improve its photovoltaic properties. In the case of SnO_2, as for other metallic oxide drivers, an excess of tin or a deficit of oxygen contibutes to the improvement of its properties. Annealing, and the doping by Sb, F, P or In are means for achieving these improvements.

Studies made on the evolution of tin-oxide films, prepared by r.f. sputtering, have revealed that substrate temperature, r.f. power, pressure and gas debit (e.g. argon/oxygen quotient) have considerable effects on the optical and electrical properties. The growth can be random or preferential. For solar cells, the SnO_2 has been used in different forms: e.g. with a transparent conductive window such as a $Si:H/SnO_2$/glass or $MOS:SnO_2/SiO_2/Si(n)$.

2. Experimental details

Thin SnO_2 films have been prepared by r.f. sputtering: a target of 8 cm diameter has been sintered with 99.99% pure SnO_2 powder.

The films are deposited in a high-purity argon atmosphere; an approximately 2×10^{-5} torr vacuum being obtained before introducing the argon gas. The working pressure and the target substrate distance were respectively 25 mTorr and 5 cm. A Corning glass substate was used.

In the first stage, the power was maintained at 150 W, for a deposition time of 60 min, and the substrate temperature could be varied from 50 to 350°C.

In the second stage, the temperature was fixed at 300°C, whereas the power was varied from 50 to 200 W in proportion to the time in order to always achieve the same film thickness.

The resistivity has been obtained at room temperature according to the Valdes conditions [3] using four equidistant and aligned probes.

The average transmission in the U.V. and visible ranges has been measured using a unique beam spectrophotometer.

The crystallographic structure of the film is examined by X-ray diffraction. The crystallite sizes were observed via a scanning electron-microscope. Using the Manifacier [4] and Tauc [5] models, we have deduced the optical thickness, the average transmission, the absorption coefficient and the optical band-gap.

3. Results and discussions

3.1. Films crystallographic properties

Electrical properties of the films depend on crystallographic structure. To evaluate the effects of substrate temperature and power on the opto-electrical properties, we

have examined the deposited films by X-rays. Most of the films have a preferential orientation along the (101) axis. The orientation becomes random for powers exceeding 100 W. Other information can be extracted from these spectra, especially regarding the crystallite size, which can be estimated by the Sherrer Bragg relationship of $[D_{hkl}] = 0.94\lambda/B\cos\theta_B$ where λ is the length of wave of the furrow, Cu(K) = 1.54 Å, B being the width at middle height of the pic and θ_B the Bragg angle.

Figs. 1 and 2 show the evolution of average size according to the temperature substrate and r.f. power: these have a net effect on the crystallite size, which increases from 40 to 110 nm.

3.2. Electrical properties

Fig. 3 shows the variation of the resistivity according to the substrate temperature: the resistivity decreases with the substrate temperature until 250°C at which temperature it tends to stabilise. The resistivity is dictated by the concentration of the carriers, the microstructure of the layer and the number of defects. The increase of

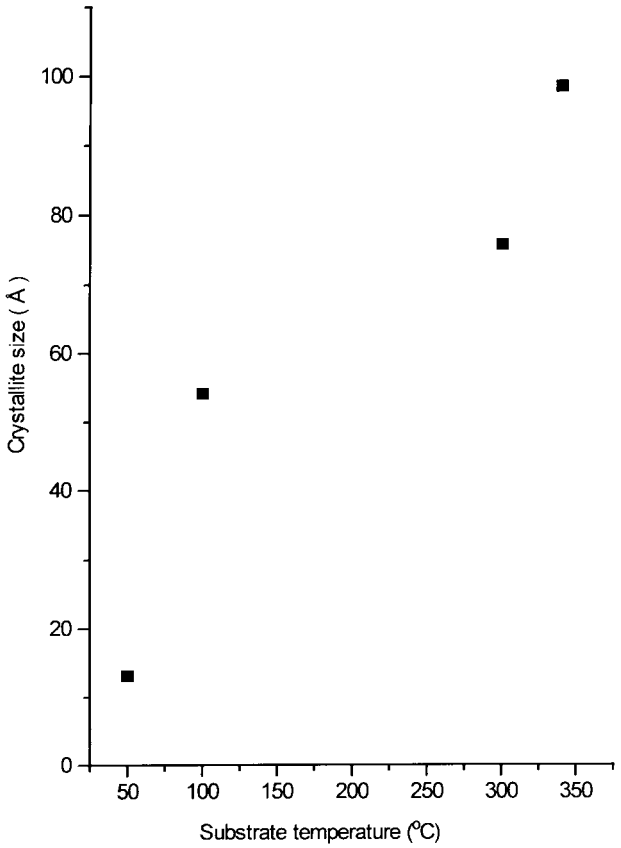

Fig. 1. Crystallite size of SnO_2 as a function of substrate temperature.

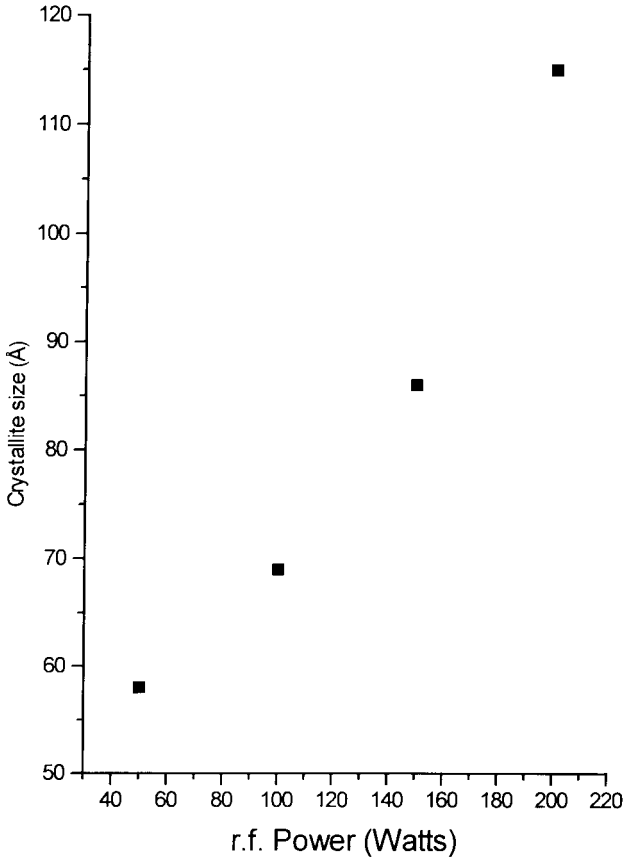

Fig. 2. Crystallite size of SnO_2 as a function of r.f. power.

the resistivity according to the r.f. power cannot been explained by the increase of the grain size, but by the poor orientation at high powers (Fig. 4).

3.3. Optical properties

The optical layer transmission (T_{mes}) is defined by

$$T_{mes} = T/T_s \tag{1}$$

where T is the transmission of the system film-substrate, and T_S is the transmission of the substrate only [6].

3.4. Methods of calculation

The refractive index can be deduced from the equation:

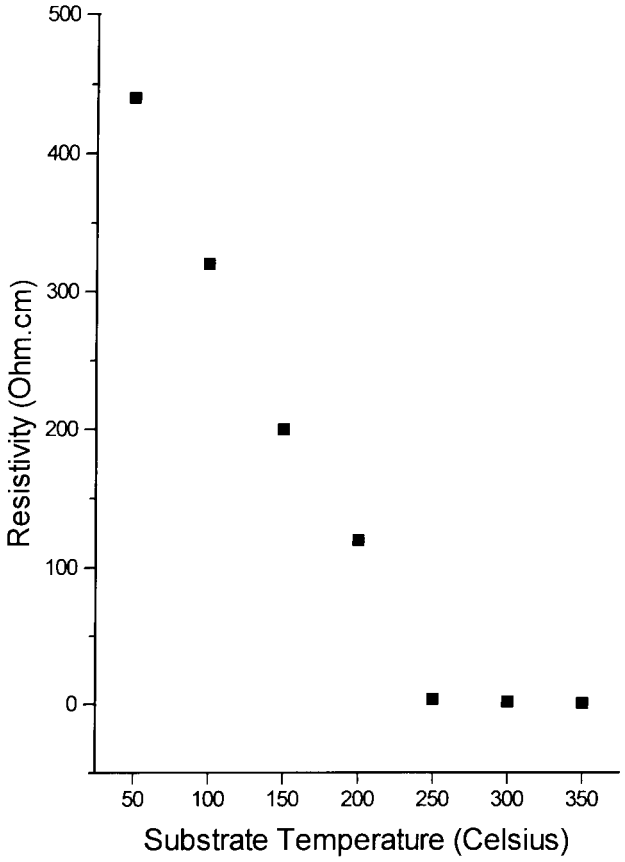

Fig. 3. Resistivity of the SnO_2 films as a function of substrate temperature. R.f. power = 150 W, sputtering time = 1 h, Ar pressure = 25 mtorr.

$$n = \left[N + \left(N^2 - n_0^2 n_1^2\right)^{1/2}\right]^{1/2} \tag{2}$$

where

$$N = \left(n_0^2 + n_1^2\right)/2 + 2n_0 n_1 (T_{\max} - T_{\min})/T_{\max} T_{\min} \tag{3}$$

where $T_{\max}$ and $T_{\min}$ are the values of asymptotic approached maximum and the minimum of the transmission curve, respectively.

On the other hand in the transparency zone (0.4–0.6 μm), we can deduce the thickness e of the specimen by application of the relationship

$$e = M\lambda_1\lambda_2/(2[n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1]) \tag{4}$$

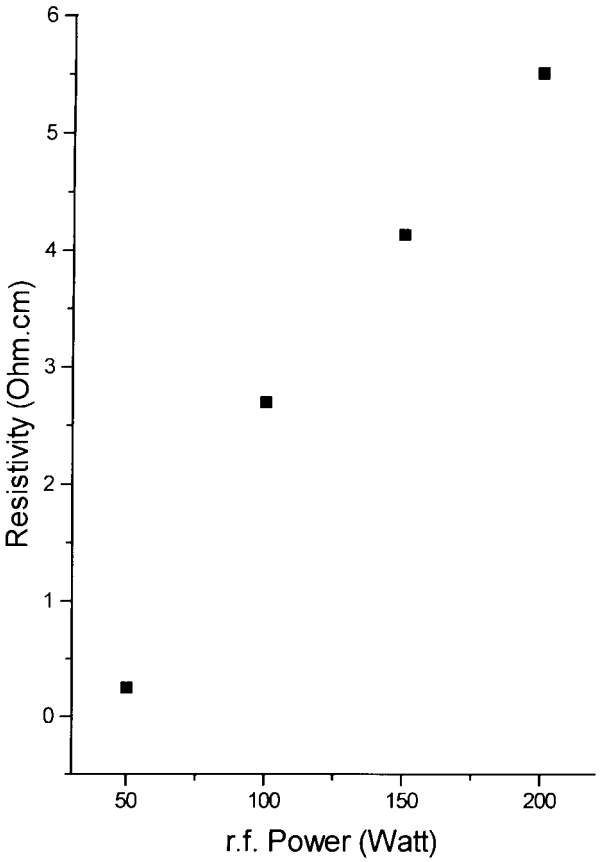

Fig. 4. Resistivity of the SnO_2 films as a function of r.f.power. $T_S = 300°C$, Air pressure = 25 mtorr.

where M is the number of oscillations, and λ_1, λ_2, $n(\lambda_1)$ $n(\lambda_2)$ are wavelengths and refractive indexs corresponding to two successive extremums.

The average can be calculated from superior and inferior envelopes T^+ (T_{max}) and T^- (T_{min}) by the relationship of the arithmetic average:

$$T_{ave} = (T^+ + T^-)/2 \tag{5}$$

3.5. Average transmission

A slight increase of the average transmission occurred with the temperature of the substrate when it was increased from 50 to 200°C (Fig. 5). However, the transmission decreased when the power was raised. The layer exhibited a brownish tint at 150 and 200 W which was attributed to the accumulation of tin.

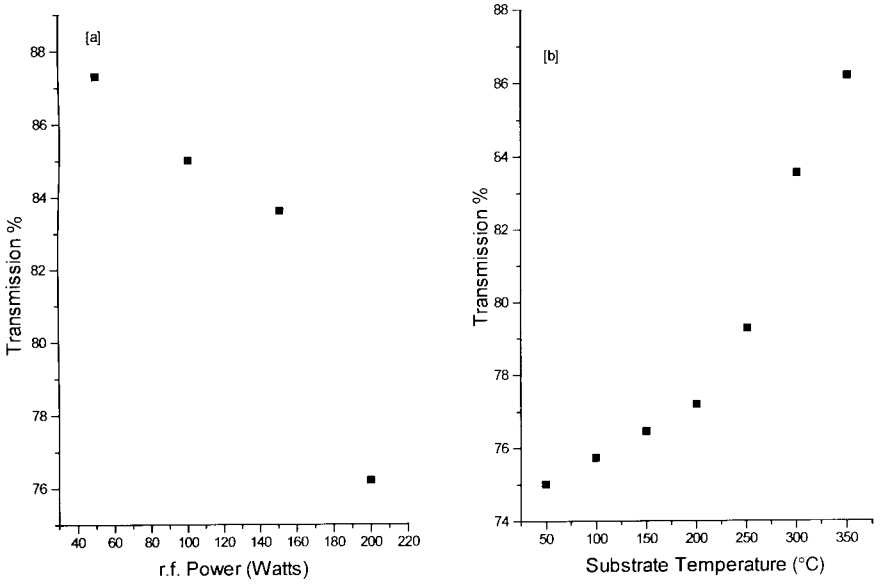

Fig. 5. Dependence of the transmittance on: (a) r.f. sputtering power, (b) the substrate temperature.

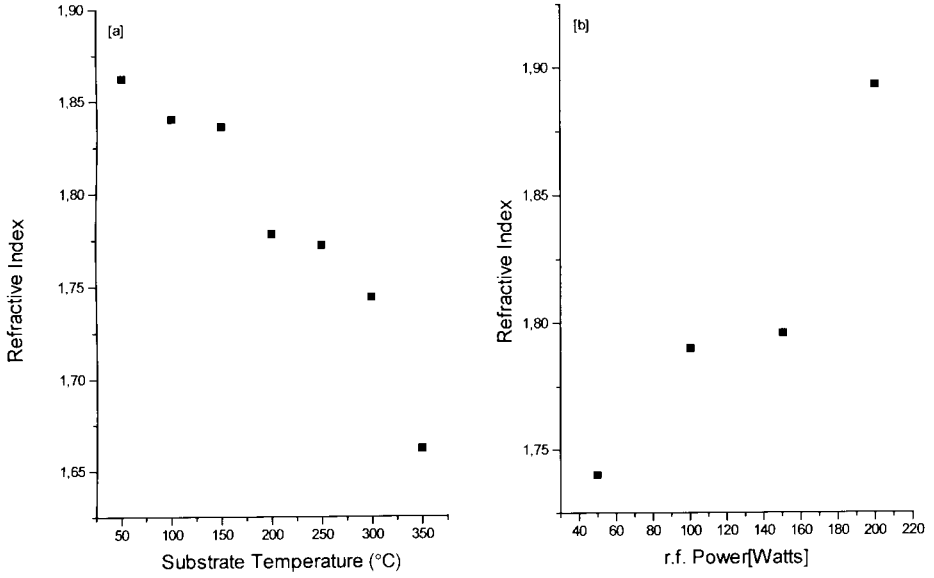

Fig. 6. Refractive index n versus: (a) r.f. sputtering power, (b) the substrate temperature of the SnO_2 film.

3.6. Refractive index

The refrative index rises with the r.f. power, and diminishes according to the temperature. The best crystallisation was achieved at around 300°C at which the refractive index was approximately 1.7 (Fig. 6).

3.7. Absorption coefficient

The coefficient of absorption α is expressed by the following relation [7]:

$$\alpha = (h_v - E_g)^{\gamma}$$

where h_ν is the radiation energy.

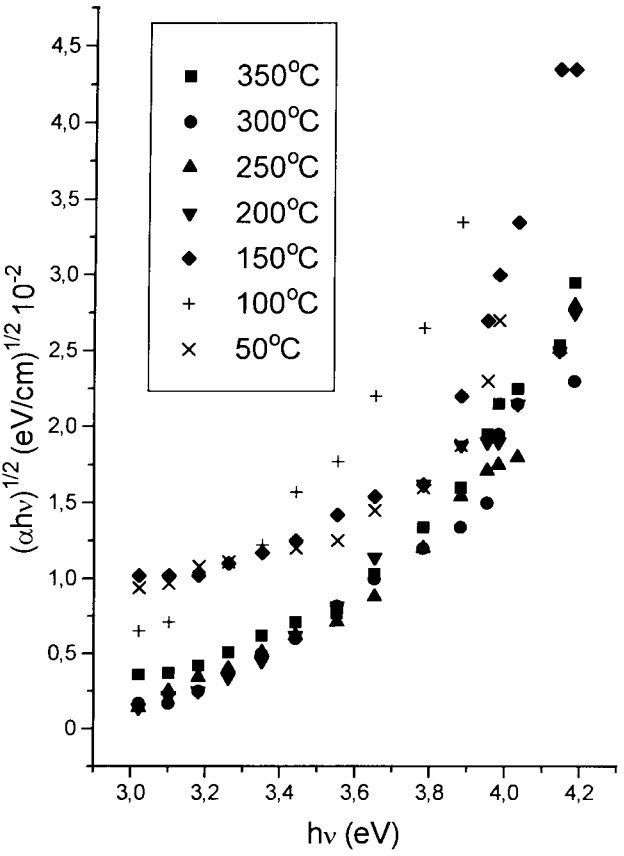

Fig. 7. $(\alpha h\nu)^{1/2}$ versus the photon energy h_ν for the tin-oxide films deposited at different substrate temperatures.

$$\text{where } \gamma = \begin{cases} 1/2 \text{ for allowed direct transitions} \\ 3/2 \text{ for forbidden direct transitions} \\ 2 \text{ for forbidden transitions} \end{cases}$$

The variation of the coefficient of absorption according to h_v is given by:

$$\alpha = 1/e\mathrm{Ln}\frac{\left[\left((1-R_1)^2(1-R_2)^2+4R_1R_2T^2\right)^{1/2}-(1-R_1)(1-R_2)\right]}{2R_1R_2} \tag{6}$$

where e and T are the thickness and the film transmission respectively, and

$$R_1 = (n_1 - n_0)/(n_1 + n_0) \text{ and } R_2 = (n_2 - n_1)/(n_2 + n_1)$$

where n_0 is refractive index of the air which equals unity, n_1 refractive index of the layer, and n_2 the refractive index of the substrate and equals 1.53. Melshmeir et al. [8] have demonstrated that for the polycrystalline structure undoped SnO_2

$$\alpha h\nu = Cte\left(h_v - E_g\right)^2 \tag{7}$$

On the other hand for SnO_2 of amorphous structure

$$\alpha h\nu = Cte\left(h_v - E_g\right)^3 \tag{8}$$

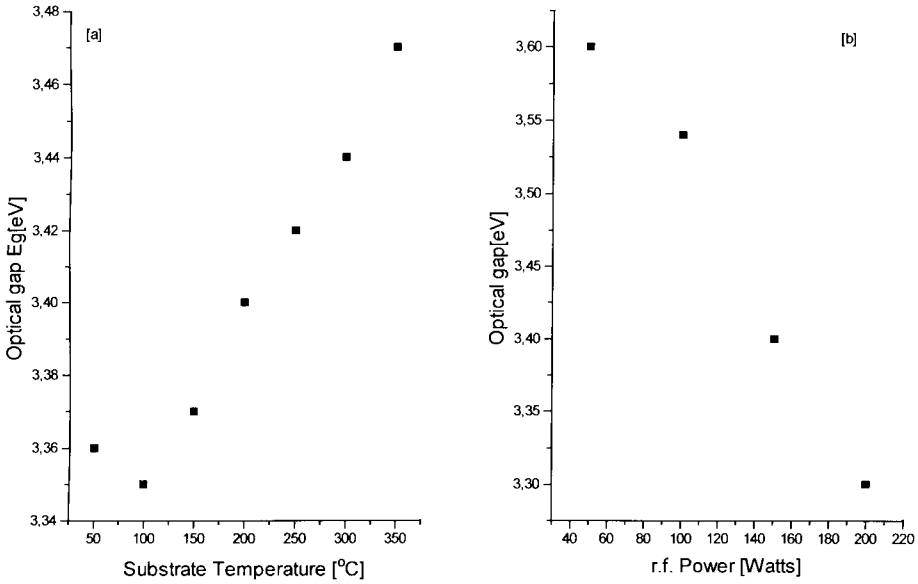

Fig. 8. (a) The optical gap shown as a function of a substrate temperature for tin-oxide films. (b) Optical gap of SnO_2 as a function of the r.f. power.

where $E_g = E_c - E_V$ (9)

One can determine therefore the optical gap by the extrapolation of the linear part of $(\alpha h\nu)^{1/2}$ (Fig. 7) until its intersection with the energy axis.

We observe according to Fig. 8a and b that the direct optical-band-gap varies slightly with the temperature of the substrate, whereas it declines with the r.f. power and increases with the thickness. This is due to the energy-level populations of and the increase of the number of defects.

4. Conclusion

Undoped tin-oxide films were prepared by r.f. sputtering. The films crystallise and grains grow with substrate heating. The electrical resistivity of SnO_{2-x} films decreases by orders of magnitude as a result of the substrate. The drop in the resistivity is attributed to the disappearance of the localised electron traps via crystallisation as well as a slow increase of charge-carrier concentration after heating the substrate. The effective band-gap increases from 3.36 eV for the as-deposited tin oxide film, to 3.6 eV for the 300°C heated one. The same reasons are responsible of the transmittance gain of the heated films. The loss of the transmittance with r.f. power can be explained by the introduction of more defects with more energetic deposited atoms.

Acknowledgements

This work is supported by the JICA (Japan International Cooperation Agency) office.

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