

Properties of tin doped indium oxide thin films prepared by magnetron sputtering

Swati Ray, Ratnabali Banerjee, N. Basu, A. K. Batabyal, and A. K. Barua

Indian Association for the Cultivation of Science, Calcutta-700 032, India

(Received 9 November 1982; accepted for publication 26 January 1983)

Indium tin oxide (ITO) films have been prepared by the magnetron sputtering technique from a target of a mixture of In_2O_3 and SnO_2 in the proportion 9:1 by weight. By optimizing the deposition conditions it has been possible to produce highly transparent (transmission $\sim 90\%$) and conducting (resistivity $\sim 10^{-5} \Omega \text{ cm}$) ITO films. A resistivity $\sim 10^{-4} \Omega \text{ cm}$ has been obtained for films of thickness $\sim 1000 \text{ \AA}$ at a comparatively low substrate temperature of 50°C and without using oxygen in the sputtering chamber. To characterize the films, the following properties have been studied, viz., electrical conductivity, thermoelectric power, Hall effect, optical transmission, and band gap. The effect of annealing in air and vacuum on the properties of the films have also been studied.

PACS numbers: 81.15.Ef

I. INTRODUCTION

In recent years various methods of preparation have been tried¹ for developing transparent conducting oxide films owing to their many practical applications. Usually, doped indium oxide and tin oxide films are used for this purpose. These oxide films are used in solar cells to serve simultaneously as conducting electrode and antireflection coating. Indium tin oxide ITO/ $p-i-n$ and $\text{SnO}_2/p-i-n$ structure solar cells have been fabricated^{2,3} in which the ITO or SnO_2 layer serves as a transparent window and antireflection coating. These films are also used as selective filters for solar thermal collectors and in liquid crystal displays.

Several authors have reported properties of indium tin oxide films prepared by spray pyrolysis⁴, reactive evaporation,^{5,6} and reactive sputtering.^{7,8} In these methods, the parameters like deposition rate, oxygen background pressure, substrate temperature, and/or annealing temperature have to be controlled carefully to produce films of proper stoichiometry. To have conducting oxide films, the material should be anion deficient.

Deposition of conducting oxide films by rf or dc sputtering of oxide targets have also been reported.⁹⁻¹¹ By these methods films having a resistivity $\sim 10^{-4} \Omega \text{ cm}$ have been obtained for thicknesses greater than 2000 \AA . The substrate or the annealing temperature had to be made quite high and in some cases a small amount of oxygen had to be introduced together with argon at the time of deposition for obtaining high conductivity and transmissivity. However, for use as antireflection coating, the thickness of the ITO layer on the top of the solar cell is $800-1000 \text{ \AA}$. The use of high substrate temperature and the presence of oxygen during sputtering are likely to affect the solar cells adversely.

More recently, the rf magnetron sputtering method, in which the films are likely to be damaged less than in ordinary diode sputtering methods has been tried.¹² By using oxygen, ITO films having a resistivity $\sim 4 \times 10^{-4} \Omega \text{ cm}$ have been obtained with the substrate temperature in the range $40-180^\circ \text{C}$. In view of the encouraging results obtained with the magnetron sputtering methods we have thought it worth-

while to investigate systematically the effect of various deposition parameters.

We have prepared ITO films by sputtering $\text{In}_2\text{O}_3:\text{SnO}_2$ targets. The effects of varying the different deposition parameters, viz., substrate temperature, argon gas pressure, rf power, and substrate-target spacing have been investigated. The properties which have been studied are (1) dark conductivity, (2) thermoelectric power, (3) Hall effect, and (4) optical transmission and band gap. The structure of the films has been studied by the x-ray diffraction method. The effects of annealing in air as well as in a vacuum have also been studied.

II. EXPERIMENT

The rf sputtering was carried out with a commercial instrument (CVC Inc.) employing a planar magnetron configuration. The sputtering target of size 8 in. diameter by 0.25 in. thick was a disc of hot pressed powder with the composition 90% In_2O_3 -10% SnO_2 (by weight) supplied by CERAC Inc. USA. The target was silver-epoxy bonded to a water cooled copper backing plate and housed in an 18-in.-diam Pyrex glass belljar which served as the sputtering chamber. Depositions were made on Corning 7059 glass substrates fitted on a stainless steel disc held parallel to the target and grounded for both rf and dc. The large area of the target allowed at least four samples to be deposited in a single run which could be used for different characterization measurements. The substrate holder was heated by radiant heaters using quartz halogen lamps and the temperature was monitored by a thermocouple. High purity Ar (99.999%, IOLAR grade, Indian Oxygen Ltd.) was used as the sputtering gas and could be introduced at any desired rate through a Mass Flow Controller (Matheson). The gas pressure was monitored by a precision Pirani Gauge using a calibration for Ar supplied by the manufacturer. The rf power (13.56 MHz) was introduced through a matching network which was tuned for minimum reflected power.

TABLE I. Transport and optical properties of ITO films prepared at different substrate temperatures.

Sample No.	Substrate temperature (°C)	Thickness (Å)	Resistivity (Ω cm)	Hall mobility ($\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$)	Carrier concentration (cm^{-3})	Thermoelectric power ($\mu\text{V}/\text{deg}$)	Optical band gap	
							Direct	Indirect
							(eV)	
S1	50	1400	4.9×10^{-4}	29	4.4×10^{20}	29	3.56	2.95
S2	190	1200	2.1×10^{-4}	30	1.0×10^{21}	22	3.80	3.26
S3	250	900	1.3×10^{-4}	30	1.8×10^{21}	20	4.08	3.64
S4	330	1200	7.8×10^{-5}	35	2.3×10^{21}	17	4.34	3.70
S5	370	1500	6.8×10^{-5}	36	2.7×10^{21}	17	4.40	3.78

The whole system was first evacuated to a vacuum $\sim 10^{-7}$ Torr at a baking temperature of 400 °C using a conventional oil-diffusion pump system with liquid nitrogen trap, and then back filled with Ar gas at the desired pressure. A presputter etching of the target was carried out with the shutters closed for at least 15 min to obtain an identical surface condition in each run. Depositions were then carried out with rf power, gas pressure, substrate temperature, and target substrate spacing as the variables. The thickness of the film was measured by a stylus type thickness measuring apparatus (Planer Products, U.K.).

The dark conductivity of the films was measured by using van der Pauw's technique. The Hall effect was also studied by the four probe method with an electromagnet having a maximum field strength of 7.6 kG. The thermoelectric power of the films were measured at room temperature. The transmission, absorption, and reflectance data of the films were obtained with a Cary 17 D Double beam spectrophotometer. From these data the optical band gaps of the ITO films were calculated.

III. RESULTS AND DISCUSSION

A. Electronic properties

The resistivities at room temperature (300 K) of the ITO films deposited at substrate temperatures from 50 to 370 °C

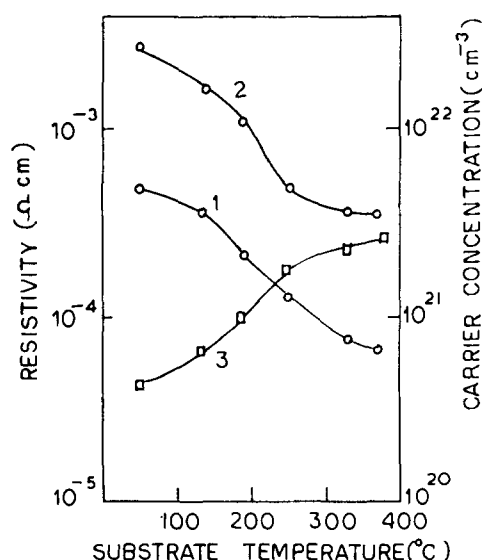


FIG. 1. Variation of the resistivity and carrier concentration of ITO films with substrate temperature. Curve 1—resistivity as deposited; 2: resistivity after annealing in air; 3: carrier concentration of as deposited films.

have been shown in Table I and plotted in Fig. 1. The films have been prepared at Ar pressure of 4.5 mTorr with a rf power of 200 W supplied to the target (area $\sim 320 \text{ cm}^2$). It is seen that as the substrate temperature increases from 50 to 370 °C the resistivity decreases from 4.9×10^{-4} to $6.8 \times 10^{-5} \Omega \text{ cm}$. The resistivity did not show significant temperature dependence, thus proving that the ITO films are degenerate semiconductors. The Hall mobility of these films at room temperature did not vary appreciably ($28\text{--}35 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$). However, the carrier concentration increased from 4×10^{20} to $2.7 \times 10^{21} \text{ cm}^{-3}$ with the increase of substrate temperature as shown in Table I and Fig. 1. The increase in the carrier concentration is probably due to the increase in the number of oxygen vacancies with the rise in substrate temperature. The direction of the Hall voltage shows that electrons are the majority carriers in the ITO films.

The rf power to the target was varied from 100–500 W. However, the resistivity of the ITO films did not show significant change within this power range. The change in the resistivity with the thickness of the film was also studied and the results are given in Table II. The resistivity shows slight decrease with the increase of film thickness.

The variation of the resistivity of ITO films with Ar pressure inside the sputtering chamber was studied. The pressure was varied from 4.5 to 12.5 mTorr and the results are shown in Table II. It is seen that the resistivity of the film deposited at 12.5 mTorr is comparatively high ($\sim 10^{-3} \Omega \text{ cm}$). The mobility is $4.2 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ which is significantly lower than that for the films deposited at 4.5 mTorr. The decrease in mobility may be due to the increased grain boundary scattering¹³ as the size of the crystallites are likely to be smaller at a high background pressure during deposition. This would happen because the sputtered neutrals arrive at the substrate with less kinetic energy due to increased

TABLE II. Variation of resistivity of ITO films with thickness and argon pressure.

Sample No.	Substrate temperature (°C)	Thickness (Å)	Ar pressure (mTorr)	Resistivity (Ω cm)
S1	50	1400	4.5	4.9×10^{-4}
S6	50	7500	4.5	3.1×10^{-4}
S3	250	900	4.5	1.3×10^{-4}
S7	250	4200	4.5	8×10^{-5}
S8	250	900	12.5	1.4×10^{-3}

scattering and hence have less energy for migration along the substrate surface.

The effect of the variation of the spacing between the substrate and target was studied at a constant Ar pressure of 4.5 mTorr. With the variation from 5 to 15.5 cm the resistivity did not show significant change.

From the results reported above it is seen that the ITO films prepared by us have resistivity lower than the values reported so far for the films of comparable thickness. Vossen¹ rf sputtered ITO target in an Ar atmosphere and obtained resistivity of $6 \times 10^{-4} \Omega \text{ cm}$ for films thicker than 2000 Å. For films of thickness ~ 1000 Å the resistivity was much higher. To obtain resistivity of $4.3 \times 10^{-4} \Omega \text{ cm}$ Haines and Bube¹¹ had to heat treat the sample in hydrogen. Recently, planar magnetron sputtering has been used by Buchanan *et al.*¹² who obtained resistivity of $4 \times 10^{-4} \Omega \text{ cm}$ by depositing the film in the presence of oxygen. They observed the films to be partly amorphous and partly crystalline, the degree of crystallinity increasing with the partial pressure of the added oxygen. In our case, however, x-ray diffraction studies showed that the ITO films prepared under different conditions were polycrystalline without introduction of oxygen. Prem Nath *et al.*⁵ have reported a resistivity of $7 \times 10^{-5} \Omega \text{ cm}$ for $\text{In}_2\text{O}_3:\text{Sn}$ film prepared by reactive evaporation technique. They obtained this resistivity at a substrate temperature of 370 °C. The resistivities at lower substrate temperatures were much higher. In our case, even for a substrate temperature of 50 °C the resistivity is of the order of $10^{-4} \Omega \text{ cm}$, which is an advantage for the fabrication of devices. The variation of conductivity and carrier concentration with different deposition parameters is not sharp in our deposition system; we consider this a distinct advantage of the magnetron sputtering technique.

We have measured the thermoelectric power of some of the ITO samples at room temperature, the values of which are shown in Table I. The direction of thermoelectric power also showed that all the films are *n* type. The thermoelectric power *S* can be expressed in case of degenerate semiconductors by¹⁴

$$S = - \left(\frac{p}{6} + \frac{1}{2} \right) \frac{\pi^2 k^2 T}{e E_F}, \quad (1)$$

where E_F is the Fermi energy, e the electronic charge, T the temperature, and p the scattering index. The Fermi energy is given by

$$E_F = \frac{h^2}{8m^*} \left(\frac{3N}{\pi} \right)^{2/3}, \quad (2)$$

where m^* is the effective mass of the carrier and N the carrier concentration. Combining Eqs. (1) and (2) we get

$$S = - \left(\frac{p}{6} + \frac{1}{2} \right) \frac{\pi^2 k^2 T}{eh^2} 8m^* \left(\frac{\pi}{3} \right)^{2/3} N^{-2/3}. \quad (3)$$

As can be seen from this expression, at a particular temperature *S* should decrease with the increase of carrier concentration. We have obtained similar dependence of *S* as shown in Table I.

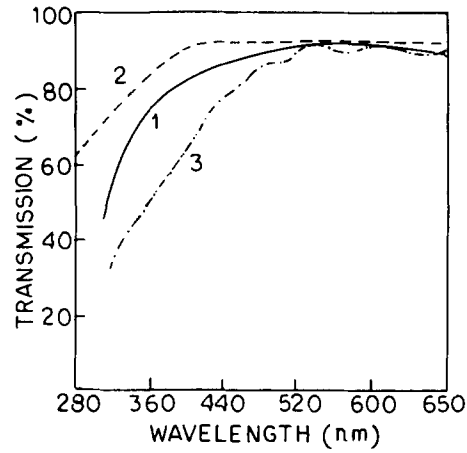


FIG. 2. Transmission spectra of ITO films. Curve 1, deposited at 50 °C, thickness—1400 Å; 2—deposited at 370 °C thickness—1000 Å; 3—deposited at 250 °C, thickness—4200 Å.

B. Optical properties

The transmission of the ITO films of thickness ~ 1000 Å deposited at 50 and 370 °C in the wavelength range 280–680 nm is given in Fig. 2. In the longer wavelength region the transmission of both the films are more or less the same. For the film deposited at 50 °C the transmission decreases below 400 nm, whereas for the other film the transmission remains high in this range. Transmission for the 4200-Å-thick film deposited at 250 °C is also shown in Fig. 2. It is seen from the figure that within this range of thickness the transmission does not vary significantly with thickness in the visible range.

Absorption coefficients of the films at different wavelengths were calculated from transmission and reflection data. The absorption coefficient for the direct allowed transition can be written as¹⁵

$$\alpha \approx (h\nu - E_g)^{1/2}, \quad (4)$$

where $h\nu$ is the photon energy and E_g the transition energy gap. Figure 3 shows the photon energy dependence of α^2 for

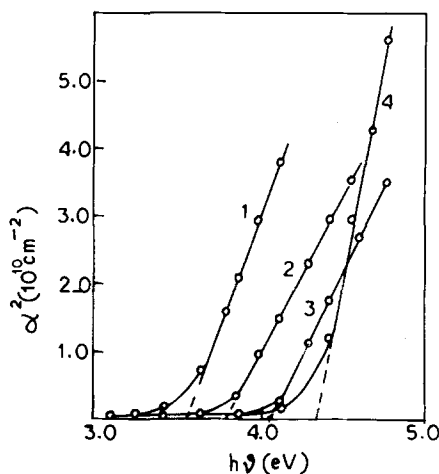


FIG. 3. Square of the absorption coefficient (α) plotted as a function of photon energy ($h\nu$). Substrate temperatures: Curve 1—50 °C; 2—180 °C; 3—250 °C; 4—330 °C.

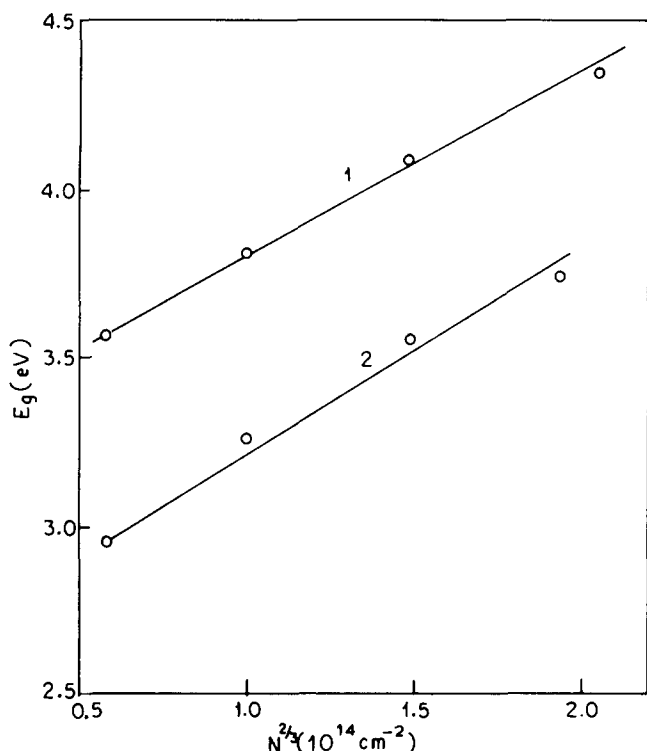


FIG. 4. Direct (curve 1) and indirect (curve 2) band gaps of ITO films as functions of $N^{2/3}$ (N being the carrier concentration).

four ITO films deposited at different substrate temperatures. Extrapolations of the straight regions of the plots to $\alpha = 0$ give E_g . The values of E_g are given in Table I. It can be seen from the Fig. 3 that as substrate temperature and hence the carrier concentration increases the absorption edge shifts towards higher energy. This shift is known as Burstein-Moss shift and this shift energy can be written as

$$E_g - E_{g_0} = \frac{\pi^2 \hbar^2}{2m_r^*} \left(\frac{3N}{\pi} \right)^{2/3}, \quad (5)$$

where E_{g_0} is the intrinsic band gap and m_r^* the reduced effective mass. Figure 4 shows the linear dependence of E_g on $N^{2/3}$. Extrapolation of this straight line to $N = 0$ yields the value of intrinsic absorption edge of 3.52 eV. Ohhata *et al.*¹⁵ obtained $E_g = 3.67$ eV and Haines and Bube¹² obtained this as 2.98 eV for their ITO films. The slope of the line yields $m_r^* = 0.65 m_0$. This value is also in good agreement with that obtained by Ohhata *et al.*¹⁵

For indirect transitions, the absorption coefficient near the edge is given by

$$\alpha \approx (h\nu - E_g')^2. \quad (6)$$

From $\alpha^{1/2}$ vs $h\nu$ plots we obtained indirect band gaps, which are given in Table I. The plot of the indirect band gap against $N^{2/3}$ yield a straight line as shown in Fig. 4. Similar results were obtained by Ohhata *et al.*¹⁵ In Fig. 5 the variation of direct band gap with substrate temperature has been shown. As the carrier concentration increases with the increase of substrate temperature, the band gap increases, which is in agreement with the variation indicated in Eq. (5).

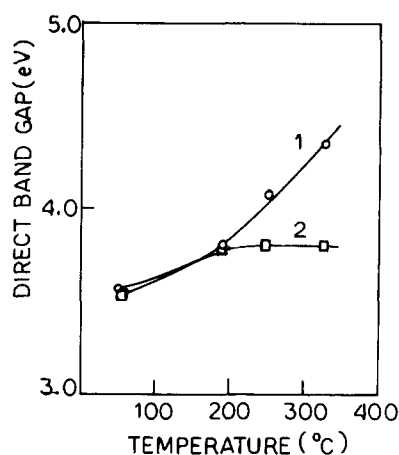


FIG. 5. Variation of direct band gap of ITO films with substrate temperature. Curve 1—as deposited; 2—after annealing in air at 400 °C.

C. Effect of annealing

The effects of annealing in air and vacuum on the properties of ITO films have been studied. The films were annealed in vacuum at 300 °C for one hour and no significant change in resistivity or transmittance was observed. The films were then annealed in air at 400 °C for one hour. This resulted in an increase of the resistivity of the film, as shown in Fig. 1. Heat treatment in air or oxygen causes diffusion of oxygen into the ITO film, thus reducing oxygen vacancies. Therefore, the number of charge carriers of nonstoichiometric origin decreases and the resistivity increases. The band gap, as shown in Fig. 5, also decreases simultaneously with the decrease of the number of charge carriers. It is seen from Fig. 5 that the direct band gap of all the ITO films deposited above 100 °C reduces to a fixed value of 3.8 eV. The film deposited at 50 °C has a band gap less than 3.8 eV and this did not change significantly by annealing. These results show that there is a limit in the number of oxygen vacancies which can be filled up by oxygen introduced during annealing.

D. Figure of merit

The sheet resistivity of a film is defined as

$$R_{sh} = \frac{\rho}{t}, \quad (7)$$

where ρ is the resistivity in ohm centimeter and t the thickness of the film in centimeters. As the substrate temperature increases from 50 to 370 °C the sheet resistivity decreases from 35 to 4.5 Ω/\square for the same order of thickness. As can be seen from the definition, a thicker film with almost the same resistivity will have a lower sheet resistance.

However, for a thicker film the transmittance decreases. Therefore, there should be an optimum value of resistance and transmittance to obtain best performance of the film. To judge the performance of transparent conducting films several authors have defined “figure of merit” in different ways.^{16,17} Haacke defined it as¹⁷

TABLE III. Comparison of the performance of ITO films prepared by different workers.

Reference	Sheet resistance Ω/\square	Transmission percent at different wavelengths (μm)						Figure of merit ($10^{-3} \Omega^{-1}$) at different wavelengths (μm)					
		0.40	0.45	0.50	0.55	0.60	0.65	0.40	0.45	0.50	0.55	0.60	0.65
Present work (S5)	4.5	0.82	0.89	0.91	0.90	0.91	0.93	30.5	69.3	86.5	77.5	86.5	107.6
Present work (S7)	1.9	0.64	0.79	0.86	0.91	0.92	0.91	6.1	49.8	116.5	205.0	228.6	205.0
Fraser and Cook ¹⁰	3.1				0.83						52		
Nath and Bunshah ¹⁸	2.2	0.79				0.91		43				177	

$$\varphi_{TC} = T^{10}/R_{sh}, \quad (8)$$

where T is the transmittance. We have evaluated values of "figure of merit" for some of our films which are shown in Table III along with some of the values obtained by other workers. It will be seen that the "figure of merit" of films obtained by us are higher.

E. Conclusions

The ITO films prepared by us via the magnetron sputtering method have very low resistivity and high transmittance. In fact, the resistivity of $6.8 \times 10^{-5} \Omega \text{ cm}$ obtained by us (deposited at 370°C) is the lowest so far reported for ITO films. The "figure of merit" of our films is also higher than those reported earlier by other workers.

The electrical and optical properties of the ITO films are not found to be very sensitive to deposition parameters in the magnetron sputtering method. Therefore, the properties of the films are easily reproducible.

ACKNOWLEDGMENT

The work has been done under a project funded by the Commission for Additional Sources of Energy, Government

of India.

- ¹J. L. Vossen, in *Physics of Thin Films*, edited by G. Hass, M. H. Francombe, and R. W. Hoffman (Academic, New York, 1976), Vol. 9, p. 1.
- ²H. Okamoto, Y. Nitta, T. Yamaguchi, and Y. Hamakawa, *Solar Energy Mater.* **2**, 313 (1980).
- ³H. Okamoto, Y. Nitta, T. Adachi, and Y. Hamakawa, *Surf. Sci.* **86**, 486 (1979).
- ⁴J. C. Manifacier, L. Szepersy, J. F. Bresse, M. Perotin, and R. Stuck, *Mater. Res. Bull.* **13**, 109 (1978).
- ⁵P. Nath, R. F. Bunshah, B. M. Basol, and O. M. Staffsud, *Thin Solid Films* **72**, 463 (1980).
- ⁶A. Hjortsberg, I. Hamberg, and C. G. Granqvist, *Thin Solid Films* **90**, 323 (1982).
- ⁷R. R. Mehta, and S. F. Vogel, *J. Electrochem. Soc.* **119**, 752 (1972).
- ⁸H. W. Lehmann and R. Widmer, *Thin Solid Films* **27**, 359 (1975).
- ⁹J. L. Vossen and E. S. Poloniak, *Thin Solid Films* **13**, 281 (1972).
- ¹⁰D. B. Fraser and H. D. Cook, *J. Electrochem. Soc.* **119**, 1368 (1972).
- ¹¹W. G. Haines and R. H. Bube, *J. Appl. Phys.* **49**, 304 (1978).
- ¹²M. Buchanan, J. B. Webb, and D. F. Williams, *Appl. Phys. Lett.* **37**, 213 (1980).
- ¹³E. Shanti, A. Banerjee, V. Dutta, and K. L. Chopra, *J. Appl. Phys.* **53**, 1615 (1982).
- ¹⁴K. Ishiguro, T. Sasaki, T. Arai, and I. Imai, *J. Phys. Soc. Jpn.* **13**, 296 (1958).
- ¹⁵Y. Ohhata, F. Shinoki, and S. Yoshida, *Thin Solid Films*, **59**, 255 (1979).
- ¹⁶G. Haacke, *J. Appl. Phys.* **47**, 4086 (1976).
- ¹⁷V. K. Jain and A. P. Kulshreshtha, *Solar Energy Mater.* **4**, 151 (1981).
- ¹⁸P. Nath and R. F. Bunshah, *Thin Solid Films* **69**, 63 (1980).