

# An economic CVD technique for pure SnO<sub>2</sub> thin films deposition: Temperature effects

M MALEKI and S M ROZATI\*

CVD Laboratory, Physics Department, University of Guilan, Rasht, Iran

MS received 21 January 2012; revised 9 April 2012

**Abstract.** A modified new method of CVD for formation of pure layers of tin oxide films was developed. This method is very simple and inexpensive and produces films with good electrical properties. The effect of substrate temperature on the sheet resistance, resistivity, mobility, carrier concentration and transparency of the films has been studied. The best sheet resistance obtained at substrate temperature of 500 °C was about 27 Ω/cm<sup>2</sup>. X-ray diffraction showed that the structure of deposited films was polycrystalline with a grain size between 150–300 Å. The preferred orientation was (211) for films deposited at substrate temperature of about 500 °C. FESEM micrographs revealed that substrate temperature is an important factor for increasing grain size and modifies electrical parameters. UV-visible measurement showed reduction of transparency and bandgap of the layers with increasing substrate temperature.

**Keywords.** SnO<sub>2</sub> thin films; substrate temperature; air pressure CVD.

## 1. Introduction

Transparent conducting oxides (TCO) are well known and have been widely used for a long time in opto-electronics industries as well as in research fields. Tin oxide films have, besides a high transparency and a low electrical resistivity, various other beneficial properties, such as high reflectivity for infrared light, high mechanical hardness and good environmental stability. This results in a variety of applications for tin oxide films, e.g. heating elements in aircraft windows, transparent electrodes in electroluminescent lamps and displays, gas sensors, solar cells, protective and wear-resistant coating of glass containers and infrared reflectors for glass windows (Chopra *et al* 1983; Takahashi *et al* 2000; Haga *et al* 2001; Salehi 2003; Medvedeva and Freeman 2004, 2005; Minami 2005; Poortmans and Arkhipov 2006).

While SnO<sub>2</sub> (TO) films have been produced by a variety of techniques including sputtering, evaporation, spray pyrolysis and others (Smith 2000; Sankapal *et al* 2000; Singha *et al* 2004; Horvath *et al* 2005; Fang and Chang 2005; Sahay and Nath 2007; Chako *et al* 2007; Pan *et al* 2007; Rozati and Akeste 2008; Ikhmayies and Ahmad-Bitar 2008; Paraguay-Delgado *et al* 2008). Little work appears to have been done with air pressure chemical vapour deposition (APCVD) technique (Advani *et al* 1979; Tarey and Raju 1985; Vlahovic and Persin 1990; Sheel *et al* 2009; Dagkaldiran *et al* 2009).

In the year 1978, transparent and conductive stannic oxide films were produced by Muranoi and Furukoshi (1978) at a relatively low temperature of 250 °C from the SnCl<sub>4</sub>–H<sub>2</sub>O and SnCl<sub>4</sub>–H<sub>2</sub>O<sub>2</sub> reaction systems by a chemical vapour

deposition method. The films were not doped with impurities. It has been found that the electrical properties depend on the absorption of hydrogen peroxide as well as on grain size, which depends on the deposition temperature and the reaction system (Muranoi and Furukoshi 1978). After a year, Advani *et al* (1979) by the use of thermodynamic analysis of the hydrolysis reaction between tin tetrachloride and water vapour showed that the rate of deposition of SnO<sub>2</sub> is a strong function of the temperature and the ratio of the reactants. Later, in the year 1990, undoped tin oxide films have been prepared by a chemical vapour deposition technique by Sanon *et al* (1990). He also used SnCl<sub>4</sub> as a precursor. The effect of different deposition parameters such as substrate temperature on the sheet resistance of films has been studied. In recent years, effect of substrate temperature on structural, optical and electrical properties of spray pyrolytically grown nanocrystalline SnO<sub>2</sub> thin films showed that the electrical conductivity, bandgap and optical transmittance of these samples depend on their crystallinity and so on the substrate temperature (Chako *et al* 2007). In the other work in the year 2011, the deposition of indium tin oxide (ITO) by atmospheric pressure chemical vapour deposition (APCVD) was reported by Gaskell and Sheel (2012). Although marginally faster growth rates were achieved by using higher substrate temperatures, increased substrate temperature had a detrimental effect on the conductivity of the ITO films. Also, Karslolu *et al* (2011) in the same year deposited tin oxide thin films by atmospheric pressure chemical vapour deposition (APCVD) on glass substrates at temperatures of 400, 500 and 600 °C with various deposition times from 15 to 60 min at 15 min time intervals. He used 5 CC/min oxygen flow rate as carrier gas and oxidizing

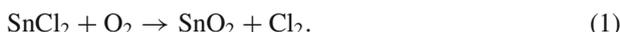
\*Author for correspondence (smrozati@guilan.ac.ir)

agent. He denoted in some results that the resistivity values were decreased by increasing substrate temperature and deposition time except for double oxide structures which exhibited SnO phase.

Based on the previous studies, till now we can conclude that substrate temperature is yet an important factor. So we have developed a new modified method of CVD for formation of thin films of SnO<sub>2</sub> on a glass substrate. This method is very simple and inexpensive, and produces films with good electrical properties that can be used for sensor applications. The effect of substrate temperature on electrical and optical parameters of thin pure SnO<sub>2</sub> films is evaluated in this work. X-ray diffraction and FESEM micrographs showed that grain size and orientation are severely dependent on substrate temperature.

## 2. Experimental

In the chemical vapour phase oxidation of SnCl<sub>2</sub> (2H<sub>2</sub>O), deposition takes place by the simple chemical reaction:



We have used oxygen gas with purification of 99.999 (contained: max 2 ppm argon, 5 ppm nitrogen, 0.5 ppm hydrogen, 0.5 ppm CO + CO<sub>2</sub>, 0.5 ppm methane + hydrocarbons and 1 ppm water). Deposition was carried out in a home-made air pressure chemical vapour deposition, schematically shown in figure 1. It contains a horizontal tubular furnace which has a diameter of 80 mm and almost 100 cm long.

The glass substrates were degreased for about 5 h in a solution of nitric acid and deionized water, then rinsed in deionized water. These glasses are cleaned ultrasonically in acetone and rinsed again in deionized water. The cleaned glass substrates are then placed in a tubular furnace. To avoid the oxidation of the glass substrate surface during heating the substrate, nitrogen flow is used to clean the tubular furnace before introducing the source materials. This flow was stopped during and after the deposition of tin oxide.

The properties of films depend on various parameters such as oxygen flow rate, deposition time and substrate temperature. The samples were grown at different substrate temperatures with oxygen flow rate of 100 cc/min and constant SnCl<sub>2</sub> mass for 1 h. The crystalline structure was obtained by means of a X-ray diffractometer with CuK $\alpha$  radiation (Philips-pw-1830). The electrical properties of thin films were measured by Hall effect and van der-Pauw setup

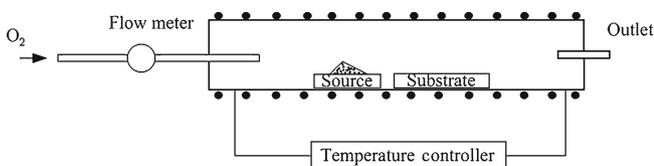


Figure 1. Air pressure chemical vapour deposition.

(RH 2010-PhysTech system). A UV-visible spectrophotometer (Cary 100 Scan Varian) was employed for obtaining the transmittance spectra. Morphology of the surface of films was examined by field emission scanning electron microscopy (S-4160 HITACHI).

## 3. Results and discussion

Figure 2 shows variation of sheet resistance of the samples vs substrate temperature. In the temperature range of 300–500 °C sheet resistance decreases as a result of increasing carrier concentration relevant to temperature. Also, improving crystallinity and increasing grain size are effective to reduce the sheet resistance. At low deposition temperatures, the sheet resistance of the grown layers is high, but it

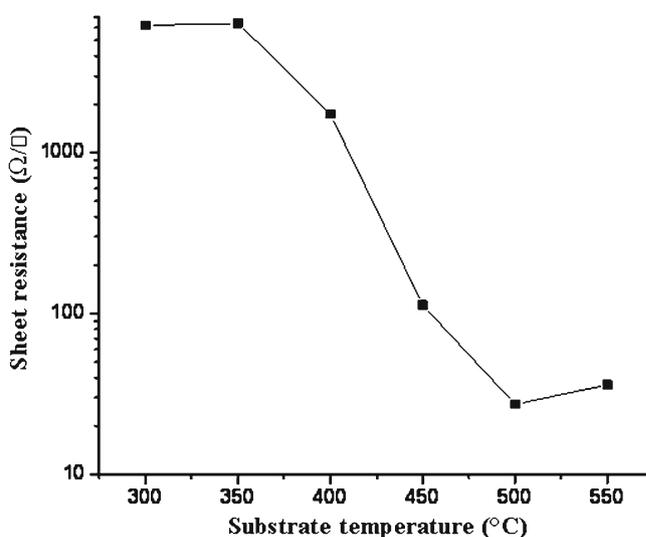


Figure 2. Variation of sheet resistance vs substrate temperature.

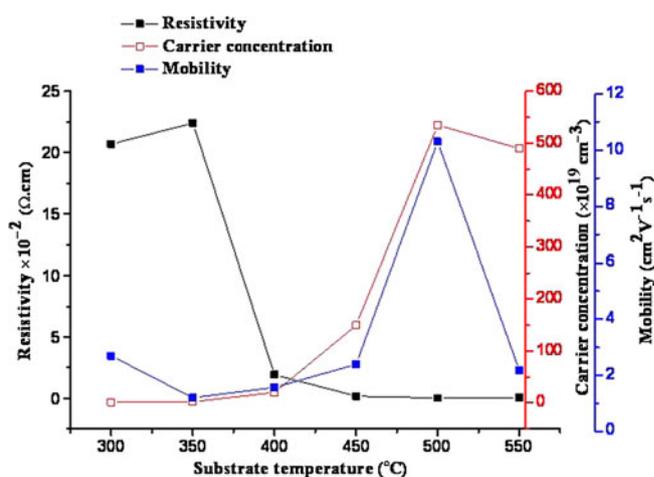
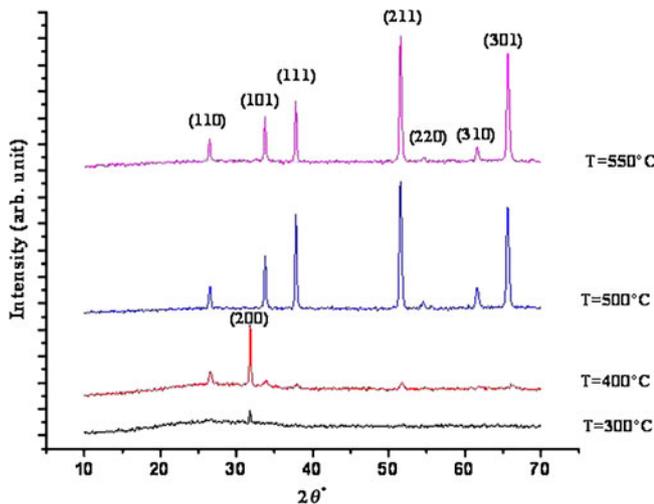


Figure 3. Electrical properties of pure tin oxide as a function of substrate temperature.

**Table 1.** Electrical parameters vs temperature.

Temperature (°C)	Sheet resistance ( $\Omega/\text{cm}^2$ )	Resistivity ( $\Omega\text{-cm}$ )	Hall Co. ( $\text{cm}^3/\text{As}$ )	Mobility ( $\text{cm}^2/\text{Vs}$ )	Carrier concentration ( $\text{cm}^{-3}$ )	Type
300	$6.19 \times 10^3$	$2.07 \times 10^{-1}$	$-5.50 \times 10^{-1}$	2.69	$1.12 \times 10^{19}$	<i>n</i>
350	$6.39 \times 10^3$	$2.24 \times 10^{-1}$	$-2.68 \times 10^{-1}$	1.20	$2.33 \times 10^{19}$	<i>n</i>
400	$1.74 \times 10^2$	$1.93 \times 10^{-2}$	$-3.03 \times 10^{-2}$	1.57	$2.06 \times 10^{20}$	<i>n</i>
450	113	$1.78 \times 10^{-3}$	$-4.25 \times 10^{-3}$	2.39	$1.47 \times 10^{21}$	<i>n</i>
500	27.3	$1.13 \times 10^{-4}$	$-1.16 \times 10^{-3}$	10.3	$5.35 \times 10^{21}$	<i>n</i>
550	36.1	$6.51 \times 10^{-4}$	$-1.41 \times 10^{-3}$	2.17	$4.41 \times 10^{21}$	<i>n</i>

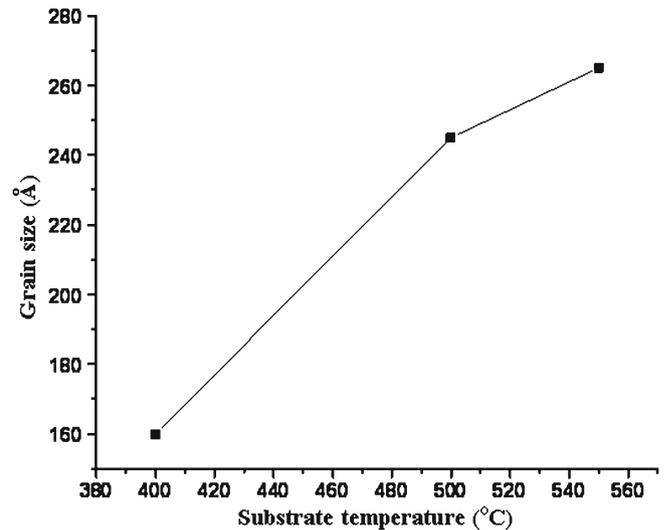
**Figure 4.** X-ray diffraction spectra of pure SnO<sub>2</sub> thin films at different substrate temperatures (300, 400, 500 and 550 °C) with oxygen flow rate of 100 cc/min for 1 h.

decreases with increasing deposition temperature to a minimum at about 400–500 °C and then increases again due to the elimination of oxygen vacancies.

Figure 3 shows dependence of the resistivity, mobility and carrier concentration with deposition temperature for an undoped tin oxide layer. The resistivity decreases initially with respect to temperature because of increasing grain size and the crystallinity of the layer. After a minimum value at about 500 °C, the resistivity of the layer increases which can be related to a decrease in carrier concentration and mobility. This is caused by the elimination of oxygen vacancies (more complete oxidation) or by a lower concentration of active chlorine ions at high temperatures (Antonius 2003). This treatment is also observed at FTO and ITO films investigated by Zhou *et al* (2001). Increasing the resistivity at temperatures higher than 500 °C was reported by Feng *et al* (2008) also.

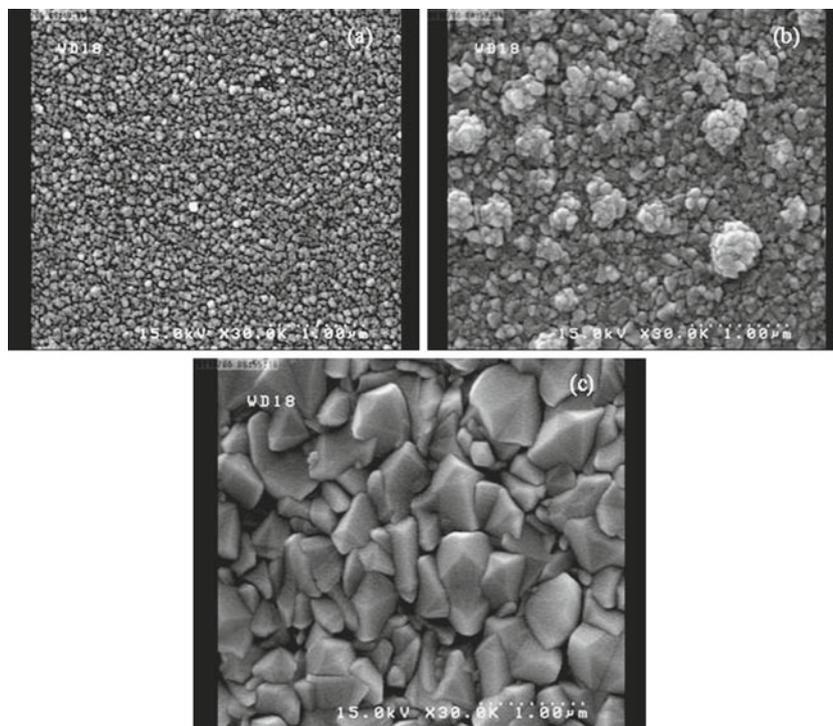
Table 1 shows values of sheet resistance, resistivity, mobility, Hall coefficient and carrier concentration of samples vs the substrate temperature which are presented in figure 3. Our data are in agreement with the results of Chako *et al* (2007).

Figure 4 shows XRD patterns of SnO<sub>2</sub> films grown at different substrate temperatures ranging from 300–550 °C. This

**Figure 5.** Grain size vs temperature.

analysis reveals that SnO<sub>2</sub> deposited at 300 °C is an amorphous structure whereas SnO<sub>2</sub> deposited at substrate temperatures above 400 °C, is exhibiting fine polycrystalline with a tetragonal rutile structure. All the SnO<sub>2</sub> polycrystalline films show peaks corresponding mainly to the (110), (101), (211), (200), (220), (301) and (310) planes of SnO<sub>2</sub>. Utilizing very simple and inexpensive air pressure CVD system and different precursor, the results are in good accordance with Kim and Chun (1986) results. Weak peaks in this diagram indicate that SnO<sub>2</sub> has very small crystalline size or SnO<sub>2</sub> particles are semicrystalline in nature (Chako *et al* 2007). The peak intensity of (110), (211), (200), (220), (301) and (310) planes increases when the substrate temperature is raised and at the substrate temperature of 500 °C, a change in the preferred orientation from (200) to (211) is noticed. It is found that the XRD peaks become gradually sharper with increase in temperature, indicating larger particle size, better crystallinity of the deposited films at higher temperature, in agreement with others (Kim and Chun 1986).

From figure 4, it is seen that with increasing the substrate temperature up to 550 °C, the peak intensities of the (211) and (301) planes increase when compared to the peak intensities in 500 °C, while peak intensities of (110), (101), (200), (220) and (310) are decreased. So we can expect that



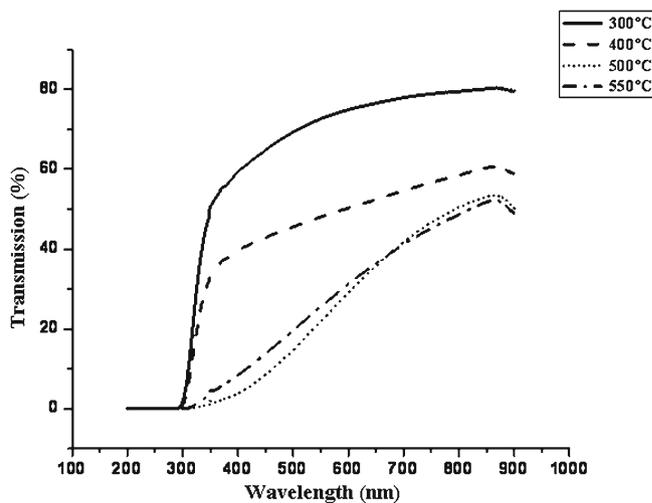
**Figure 6.** Scanning electron micrographs of deposited films at oxygen flow rate of 100 cc/min with substrate temperature of (a) 300 °C, (b) 400 °C and (c) 500 °C.

with increasing temperature, preferred orientation overcomes other peaks which need more investigation in higher temperatures. Because of our substrate type we can not choose the higher temperatures.

The mean crystallite size,  $D$  was calculated for the diffraction peaks using Scherer's formula (Cullity 1978). With increasing temperature, grain size increases. Grain size was calculated for (211) orientation. Figure 5 shows grain size vs temperature.

Figure 6 shows field emission scanning electron microscopy micrographs of pure tin oxide films deposited at different substrate temperatures of 300, 400 and 500 °C with oxygen flow rate of 100 cc/min for 1 h. In general, the films produced showed a smooth and highly uniform structure. It is clear from the FESEM images of the coatings that with increasing the substrate temperature, uniformity and grain size of the films are increased. A noticeable increase in grain size with deposition temperature is observed. At 500 °C, small flakes are observed which grew into well-faceted tiny crystals. This is in accordance with the results of Karshoglu *et al* (2010).

Optical transmittance measurements of SnO<sub>2</sub> films with different substrate temperatures in the range of 300–550 °C are depicted in figure 7. It is observed that the cut-off wavelength (intercept of the transmittance curve with the  $\lambda$  axis) is shifted towards greater values of  $\lambda$  when the substrate temperature increases, indicating that the energy gap,  $E_g$  of the SnO<sub>2</sub> films decreases when their substrate temperature



**Figure 7.** Optical transmittance of SnO<sub>2</sub> thin films with different substrate temperatures (300, 400, 500 and 550 °C).

increases. The obtained cut-off wavelength values for the studied SnO<sub>2</sub> films varies among 350, 360 and 790 nm, indicating that the energy gap of the SnO<sub>2</sub> films varies among 3.54, 3.35 and 1.8 eV. It is also observed that the transmittance decreases by increasing the synthesis temperature, this behaviour seems to be associated with an increase in the film thickness. This result gives basis to suggest that the growth

rate of the SnO<sub>2</sub> films increases by increasing the synthesis temperature. On the other hand, it was found that the increase in film thickness leads to a strong reduction of the transmittance, which could be attributed to the absorption via states within the gap (Quinonez *et al* 2010).

It has also been reported that the concentration of oxygen vacancies increases with increasing the substrate temperature. These oxygen vacancies were created as the donor level below the conduction band are the origin of the *n*-type SnO<sub>2</sub> thin films (Jeong *et al* 2003). So, we can conclude that with increasing oxygen nonstoichiometry due to increasing substrate temperature, energy gap of SnO<sub>2</sub> decreases.

#### 4. Conclusions

Based on the studies which have been done for about thirty years ago, until now we can conclude that the substrate temperature is an effective parameter on the properties of thin layers. In this paper, thin films of pure tin oxide prepared on glass substrates by a novel and simple technique of APCVD. The variation of sheet resistance, resistivity, carrier concentration and mobility with temperature were investigated. The results indicate that the best resistivity can be achieved at substrate temperature of 500 °C. XRD analysis revealed that SnO<sub>2</sub> deposited at 300 °C has an amorphous structure whereas films deposited at the substrate temperature of above 400 °C have fine polycrystalline with the tetragonal rutile structure. The effect of increasing temperature on grain size was investigated as well. FESEM images showed that with increasing substrate temperature, grain size of the sample will be increased. Investigation of temperature effects on optical transmittance also revealed a reduction of transmittance and bandgap with increasing temperature.

#### Acknowledgement

The authors gratefully acknowledge the research department of University of Guilan.

#### References

- Advani G N, Jordan A G, Lupis C H P and Longini R L 1979 *Thin Solid Films* **62** 361  
 Antonius Maria Bernardus van 2003 *Mol, PhD Thesis*  
 Chako S, Philip N S and Vaidyan V K 2007 *Phys. Stat. Sol. (a)* **204** 3305  
 Chopra K L, Major S and Pandya D K 1983 *Thin Solid Films* **102** 1  
 Cullity B D 1978 *Elements of X-ray diffraction* (Addison-Wesley publishing company: INC)  
 Dagkaldiran U, Gordijn A, Finger F, Yates H M, Sheel D W, Remes Z, Vanecek M and Evans P 2009 *Mater. Sci. Eng.* **B159** 6  
 Fang T H and Chang W J 2005 *Appl. Surf. Sci.* **252** 1863  
 Feng X, Ma J, Yang F, Ji F and Luan C 2008 *Mater. Lett.* **62** 1809  
 Gaskell J M and Sheel D W 2012 *Thin Solid Films* **520** 4110  
 Haga K, Wijesena P S and Watanabe H 2001 *Appl. Surf. Sci.* **169** 504  
 Horvath E, Kristof J, Nasser H, Frost R L, De Battisti A and Redey A 2005 *Appl. Surf. Sci.* **242** 13  
 Ikhmayies S J and Ahmad-Bitar R N 2008 *Am. J. Appl. Sci.* **5** 1141  
 Jeong J, Choi S P, Chang C I, Shin D C, Park J S, Lee B T, Park Y J and Song H J 2003 *Solid State Commun.* **127** 595  
 Karshoglu R, Uysal M and Akbulut H 2010 *J. Coat. Technol. Res.* **7** 503  
 Karslolu R, Uysal M and Akbulut H 2011 *J. Crystal Growth* **327** 22  
 Kim K H and Chun J S 1986 *Thin Solid Films* **141** 287  
 Medvedeva J E and Freeman A J 2004 *Appl. Phys. Lett.* **85** 955  
 Medvedeva J E and Freeman A J 2005 *Europhys. Lett.* **69** 583  
 Minami T 2005 *Semicond. Sci. Technol.* **20** 35  
 Muranoi T and Furukoshi M 1978 *Thin Solid Films* **48** 309  
 Pan S S, Ye C, Teng X M and Li G H 2007 *J. Phys. D: Appl. Phys.* **40** 4771  
 Paraguay-Delgado F, Miki-Yoshida M, Antunez W, Gonzalez-Hernandez J, Vorobiev Y V and Prokhorov E 2008 *Thin Solid Films* **516** 1104  
 Poortmans J and Arkhipov V (eds) 2006 *Thin film solar cells: fabrication, characterization and applications* (John Wiley & Sons Ltd)  
 Quinonez C, Vallejo W and Gordillo G 2010 *Appl. Surf. Sci.* **256** 4065  
 Rozati S M and Akeste Sh 2008 *Cryst. Res. Technol.* **43** 273  
 Sahay P P and Nath R K 2007 *Cryst. Res. Technol.* **42** 275  
 Salehi A 2003 *Sens. Actuator.* **B96** 88  
 Sankapal B R, Mane R S and Lokhande C D 2000 *Mater. Res. Bull.* **35** 177  
 Sanon G, Rup R and Mansingh A 1990 *Thin Solid Films* **190** 287  
 Sheel D W, Yates H M, Evans P, Dagkaldiran U, Gordijn A, Finger F, Remes Z and Vanecek M 2009 *Thin Solid Films* **517** 3061  
 Singha V P, Singha R S and Thompson G W 2004 *Solar Energy Mater. Solar Cells* **81** 293  
 Smith A 2000 *Thin Solid Films* **376** 47  
 Takahashi N, Kaiya K, Omichi K, Nakamura T, Okamoto S and Yamamoto H 2000 *J. Crystal Growth* **209** 822  
 Tarey R D and Raju T A 1985 *Thin Solid Films* **128** 181  
 Vlahovic B and Persin M 1990 *J. Phys. D: Appl. Phys.* **23** 1324  
 Zhou Z B, Cui R Q, Pang Q J, Wang Y D, Meng F Y, Sun T T, Ding Z M and Yu X B 2001 *Appl. Surf. Sci.* **172** 245