

Preparation and properties of SnO₂:F thin films

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High quality fluorine doped tin oxide films have been prepared by an improved spray process in which the droplets are produced using an ultrasonic atomiser. Films with thickness about 0.1 and 1.5 μm were deposited on soda lime glass substrates. The microstructure of these thin films is analysed by XRD and SEM. The transmittance and reflectance spectra in the 260-2600nm spectral region are presented. The minimum of the electrical resistivity is 800 μΩcm.

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1. Introduction

The growing interest in materials supplied as thin films form has led to considerable diversification of deposition processes [1, 2]. Each process has its advantages and drawbacks in terms of complexity of implementation and quality of deposit. The pyrosol method would seem to be an excellent compromise for obtaining simply and economically thin films with excellent physical properties. The pyrosol technique is based on the transport and subsequent pyrolysis of a spray generated by an ultrasonic atomiser.

Fluorine doped tin oxides thin films have been successfully demonstrated their applications as transparent conductors, optical windows for solar spectrum, light emitting diodes and many more.

The aim of our investigation was to improve the quality of sprayed F doped tin oxide thin films and to reduce their preparation cost by increasing the efficiency of the spraying method. We have been able to determine the experimental conditions necessary to obtain layers with high conductivity and transparency and in this work we present some of the structural, optical and electrical properties of investigated SnO₂:F thin films.

2. Experimental details

The pyrosol system consists essentially of two independent zones linked by a transport nozzle: the atomisation chamber and the pyrolysis reactor. The spray generated in the first zone is conveyed by a supporting gas through the nozzle inside the second zone where it is pyrolysed on heated substrate. Since the carrier gas is used only to direct the aerosol into the reaction zone a lower flow can be used, which reduces the effect of substrate cooling.

The ultrasonic vibrator produces very fine liquid drops, which form a dense stream. The droplets size is very small and does not exhibit a wide distribution. The mean diameter, *d*, of the resulting droplets is a function of

the excitation frequency and the liquid characteristics. Following Lang [3] it can be expressed as:

$$d = 0.34\lambda \quad (1)$$

where λ is the wavelength of the resulting vibration, given by Kelvin's formula [4]:

$$\lambda = \left(\frac{8\pi\eta}{\rho\nu^2} \right)^{\frac{1}{3}} \quad (2)$$

where η and ρ respectively are the surface tension and the density of the liquid, while ν is the frequency of the ultrasonic vibration. In order to protect the crystal oscillator from erosion and to avoid contamination we used another container for the spraying solution. These two containers are separated by a glass membrane.

The carrier gas was nitrogen and for all experiments we maintained a gas flow rate of about 0.8 l/min, that optimises the quality of the films. The resulted waste gases are removed by an extraction pump and passed through a scrubber.

The precursor solution was prepared using 0.2M SnCl₄ and 0.14M NH₄F in CH₃OH (98%). The metallic salt solution, when sprayed onto a hot substrate pyrolytically decomposes to oxide films.

Films were deposited onto microscope cover glass substrates at temperature ranges between 350 and 500 °C and the deposition duration was varied between 3 and 25 min. The substrate temperature was measured with a thermocouple and controlled electronically. The deposition rate varied with the deposition temperature and for a substrate temperature of 480 °C was about 1nm/s.

The thickness, *d*, of thin films was determined using an interferential microscope MII 4.

The structure of the films was determined by X-ray diffraction measurements with Mo K α radiation from a Philips X-ray generator, operating at 30 mA and 35 kV. The film morphology was examined using a (JOEL-JEM-820) scanning electron microscope (SEM).

The transmittance and reflectance of thin films were measured using a Hitachi UV-4001 spectrophotometer in the 260-2600 nm spectral range.

The electrical resistivity, ρ , was measured using surface-type cells. Thin silver electrodes with thickness of 1.1-1.3 μm were deposited onto substrates by thermal evaporation under vacuum. The interelectrode distance was about 2.5 mm. For measurement of ρ , static electric fields with intensity lower than 10^2V/cm were used.

3. Results and discussion

In agreement with [5,6] the deposition rate is function of reaction temperature. Fig. 1 shows the variation of deposition rate as function of substrate temperature for the investigated samples.

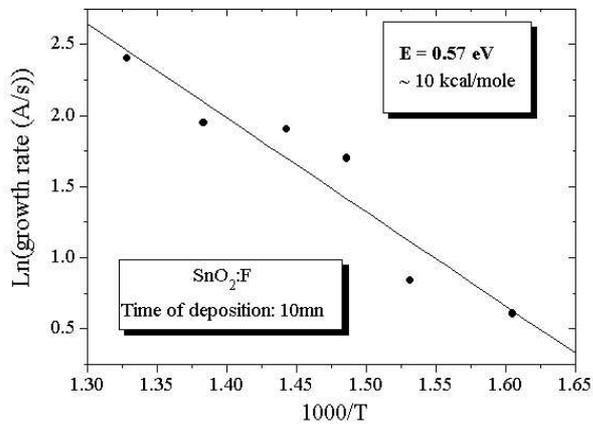


Fig. 1. Deposition rate versus reaction temperature for F doped SnO_2 thin films.

X-ray diffraction measurements (Fig. 2) showed that films deposited at high temperature ($>400^\circ\text{C}$) and thicker than about 3000 \AA , are polycrystalline in nature.

SEM observation shows that films are very homogenous, the grain size increases on one hand with deposition temperature from about 100 to 400 nm, when the temperature increases from 380 to 480°C and on an other hand with film thickness from 70 to 600nm when film thickness increase from 0.2 μm to 1.3 μm .

The improvement of films quality produced by ultrasonic spraying process is due to the fineness of drops, which promotes regular crystal orientations and grain dimensions.

Films have a good transparency in the visible and a high reflectivity in the IR spectral range. The plasma frequency, ω_p , could be obtained with satisfied approximation from the intercept of transmission and reflection spectra. At frequencies $\omega < \omega_p$, high reflection occurs and for $\omega > \omega_p$ the reflectance decreases sharply ($\omega_p \sim 1/\lambda_p$). The threshold of the plasma edge has been found to shift to a shorter wavelength for F - doped tin oxide films deposited at temperatures ranged between

350 and 450°C and to longer wavelength for films deposited at temperatures ranged between 450 and 500°C (Fig. 3).

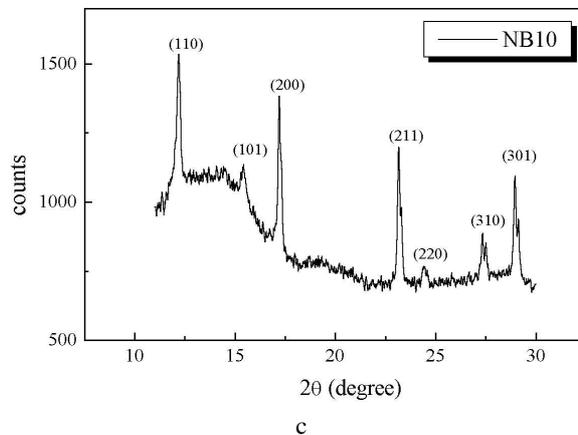
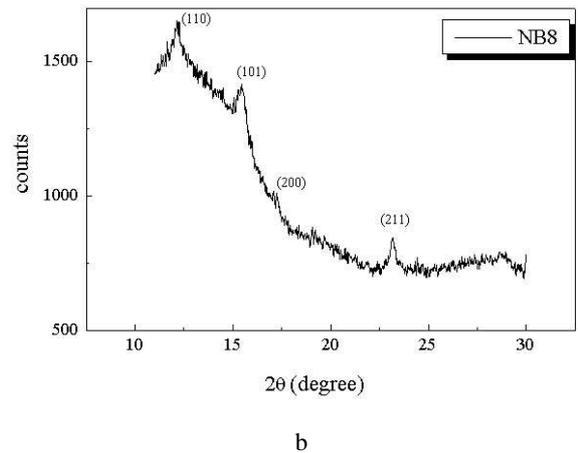
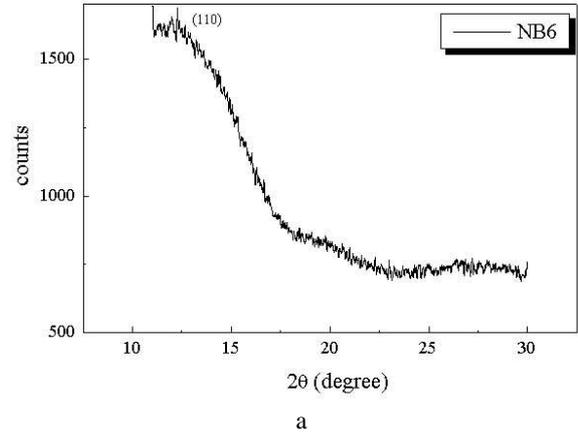


Fig. 2. XRD spectra of SnO_2 :F thin films deposited at different temperatures: (a) $T_s=380^\circ\text{C}$ and film thickness is 1390 \AA ; (b) $T_s=420^\circ\text{C}$, 4020 \AA ; (c) $T_s=480^\circ\text{C}$, 6650 \AA .

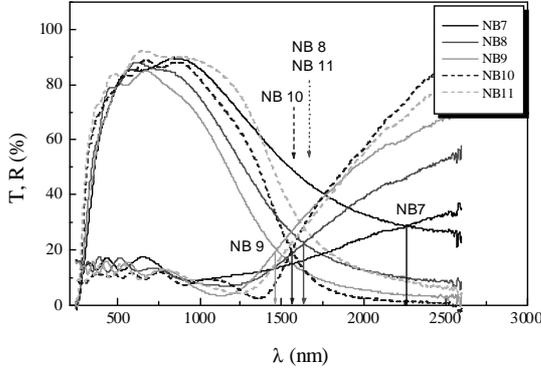


Fig. 3. Transmission and reflection spectra for SnO₂: F films deposited at different substrate temperatures: NB7: 400 °C; NB8: 420 °C; NB9: 450 °C; NB10: 480 °C; NB11: 500 °C. The spraying duration was 10 min.

The plasma resonance frequency ω_p is first determined by carrier concentration n:

$$\omega_p = \sqrt{\frac{4\pi n e^2}{\epsilon_0 \epsilon_\infty m_e^*}} \quad (3)$$

where n is the carrier concentration, e is electronic charge, ϵ_∞ represents the high frequency dielectric constant of the tin oxide film, ϵ_0 represents the dielectric constant of free space m_e^* denotes the mass of charge carriers in the conduction band. In accordance with relation (3) the higher the carrier concentration the lower will be the plasma wavelength.

From the transmission T (λ) and reflection R (λ) data, the absorption coefficient was calculated using the formula [7]:

$$\alpha(\lambda) = \frac{1}{t} \ln \left[\frac{(1-R(\lambda))^2}{T(\lambda)} \right] \quad (4)$$

where t – is the film thickness.

For direct allowed transition the values of α follow the formula [8]:

$$\alpha \sim A(h\nu - E_g)^{1/2}, \quad (5)$$

where E_g is the optical band gap and $h\nu$ is the photon energy.

The dependences $(\alpha)^2$ vs. $h\nu$ are represented in Fig. 4, for films grown at different temperatures. As the plots show a linear dependence, the optical band gap values were determined from the intercept with x-axis and listed in Table 1.

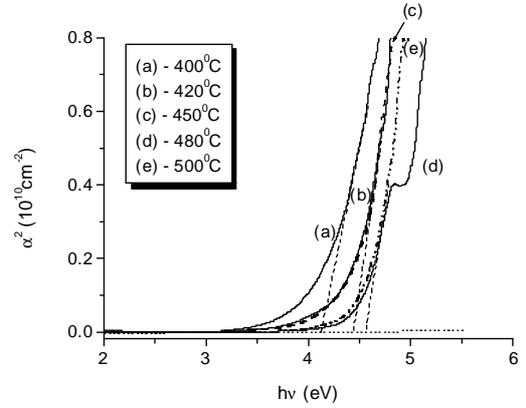


Fig. 4. Photon energy dependence on α^2 for F - doped SnO₂ grown at different temperatures.

Table 1. Optical band gap calculated from $(\alpha)^2 = f(h\nu)$ dependencies for F - doped SnO₂ thin films deposited at different temperatures.

Sample	Deposition temperature (°C)	Thickness (nm)	Optical band gap (eV)
NB7	400	328	4.08
NB8	420	402	4.43
NB9	450	422	4.43
NB10	480	665	4.51
NB11	500	393	4.55

The shift in the absorption edge from 4.08 to 4.55eV is a result of Burstein-Moss effect [9, 10].

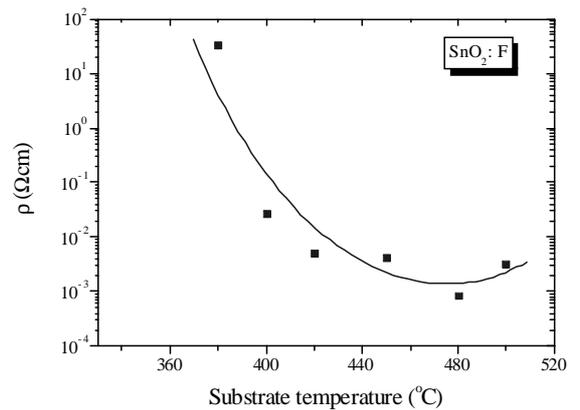


Fig. 5. Electrical resistivity versus reaction temperature for fluorine doped SnO₂ films.

According to previous results presented here (Fig. 3) the electrical resistivity decreases with the increase of substrate temperature (Fig. 5). The minimum value of electrical resistivity was about 800 $\mu\Omega\text{cm}$ for films deposited at 480 °C.

4. Conclusions

Highly conductive ($800 \mu\Omega\text{cm}$) and transparent ($T > 85\%$ in visible domain) films were deposited by pyrosol with a relative high rate of deposition (about 1nm/s). The deposition parameters are in good agreement with the structural, optical and electrical properties.

The crystallinity and grain size of the films increase when the deposition temperature increases in the range $380\text{--}480\text{ }^\circ\text{C}$. The value of optical band gap for investigated F - doped SnO_2 films are in relation to the deposition temperature and increases from 4.08 to 4.55 eV for an increase of temperature from 400 to $500\text{ }^\circ\text{C}$. The electrical resistivity decreases with the deposition temperature and reaches a minimum at $480\text{ }^\circ\text{C}$.

References

- [1] K. L. Chopra, S. Major, D. K. Pandya, *Thin Solid Films* **102**, 1 (1983).
- [2] H. L. Hartnagel, A. L. Dawar, A. K. Jain, C. Jagadish, "Semiconducting Transparent Thin Films", Institute of Publishing, Bristol and Philadelphia, 1995
- [3] R. T. Lang, *J. Acoust. Soc. AM.* **34**, 6 (1962).
- [4] J. W. S. Rayleigh, *The theory of sound*2. Dover Publications, New York, p.344 (1945).
- [5] G. N. Advani, A. G. Jordon , C. Lupis, R. Longini, *Thin Solid Films* **62**, 361 (1979).
- [6] T. Muranoi, M. Furukoshi, *Thin Solid Films* **48**, 309 (1978).
- [7] R. H. Bube "Electronic Properties of Crystalline Solids", Academic Press, London, 1974.
- [8] P. S. Kireev, *Semiconductor Physics* (roum.), Scientific and Encyclopedic Publ. House, Bucharest, 1977, p.706.
- [9] F. Burstein, *Phys. Rev.* **93**, 632 (1954).
- [10] T. S. Moss, *Proc. Phys. Soc.* **B67**, 775 (1964).

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