

Single-oscillator model and determination of optical constants of spray pyrolyzed amorphous SnO₂ thin films

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Abstract. Amorphous SnO₂ thin films have been deposited using different spraying times via the spray pyrolysis method. The structure of the films was analyzed by X-ray diffraction and the results obtained showed that the structure of the films was almost non-crystalline. The optical properties of these thin films have been investigated by means of optical transmittance and reflectance spectra. The dispersion of the refractive index is discussed in terms of the Wemple–DiDomenico single oscillator model. The optical band gap E_g , the width of band tails of localized states into the gap E_v ; the single oscillator energy E_o , the dispersion energy E_d and the optical constants such as refractive index, extinction coefficient, dielectric constant and optical conductivity were estimated.

PACS. 78.20.Ci Optical constants

1 Introduction

Transparent and conducting tin oxide (TCO) thin films are of considerable interest for solar-energy conversion, sensors and in various electrode applications. Tin oxide is an insulator in its bulk form, whereas it becomes semi-conducting when deposited in the form of thin films. This transition from insulator to semiconductor occurs as the result of deviation of stoichiometry when it is prepared in thin film form. The methods that are commonly used for depositing SnO₂ are sputtering [1], electron beam evaporation [2], chemical vapour deposition [3], sol–gel process [4] and pyrolysis of stannic compounds [5]. Of these methods, spray pyrolysis represents the least expensive alternative. It is interesting to note that this stoichiometry deviation is higher when the films are prepared by spray pyrolysis than the other deposition techniques. Tin oxide in thin film configurations are technologically important materials because of their application in photovoltaic cells [6], gas sensors [7], electrochromic devices and low-e windows [8], photocatalysis [9], etc.

Optical absorption measurements are used to obtain the band structure and the energy gap of amorphous thin films, because the analysis of the optical absorption spectra is one of the most productive tools for understanding and developing the energy band diagram of both crystalline and amorphous materials.

There have been extensive studies on the crystalline structure and optical transmittance of SnO₂ thin films prepared by spray pyrolysis methods [3, 4, 10]. However in

the available literature we found only a few data for optical parameters and the Wemple–DiDomenico single oscillator model of amorphous SnO₂ thin films. In this paper, we report on the optical properties of amorphous SnO₂ thin films deposited by the spray pyrolysis method.

2 Experimental

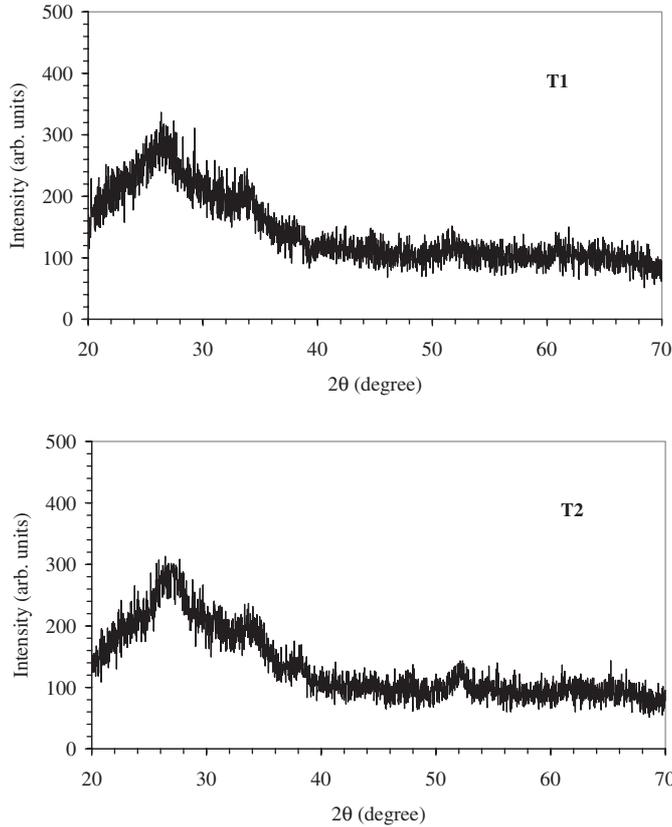
The SnO₂ thin films were deposited onto glass slices, chemically cleaned, using the spray pyrolysis method at a 300 °C substrate temperature. Tin tetrachloride pentahydrate (SnCl₄ · 5H₂O) was used as a cheap precursor for tin. 0.2 M solution of tin tetrachloride diluted in methanol and deionized water (3:1) was used for all the films. A few drops of acetic acid were added to improve the clarity of solution. Nitrogen was used as the carrier gas, at 0.2 bar pressure. The ultrasonic nozzle to substrate distance was 30 cm and during deposition, solution flow rate was held constant at 4 ml min⁻¹. The SnO₂ films deposited at the spraying times $t = 60$ s and $t = 240$ s were named as T1 and T2, respectively. The thicknesses of the films were determined with a Mettler Toledo MX5 microbalance using the weighing method. The thickness values of the T1 and T2 films were found to be 612 nm and 980 nm respectively.

X-ray diffraction (XRD) patterns were obtained with a RIGAKU RINT 2200 Series X-Ray Automatic Diffractometer using the CuK α radiations ($\lambda = 1.5405$ Å) in the range of 2θ between 20° and 70°. The diffractometer reflections were taken at room temperature. The optical measurements of all the films were carried out at room temperature using a Shimadzu UV-VIS-2450 spectrophotometer in the wavelength range from 190 to 900 nm.

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Table 1. The optical band gap, Urbach energy and refractive index dispersion parameters of the amorphous SnO₂ thin films.

Film name	E_g (eV)	E_u (eV)	E_o (eV)	E_d (eV)	M_{-1}	M_{-3} (eV) ⁻²	n_∞	β
T1	3.79 ± 0.02	1.61 ± 0.01	5.11	12.01	2.35	0.09	1.83	1.61×10^{-2}
T2	3.67 ± 0.02	1.94 ± 0.01	4.78	20.32	4.25	0.19	2.29	1.33×10^{-2}

**Fig. 1.** X-ray diffraction spectra of the amorphous SnO₂ thin films.

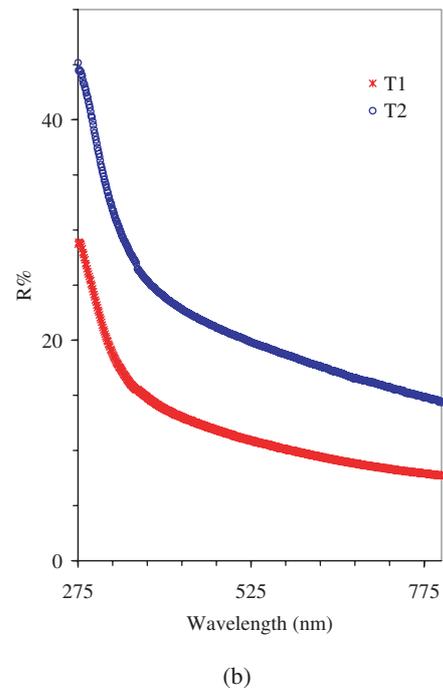
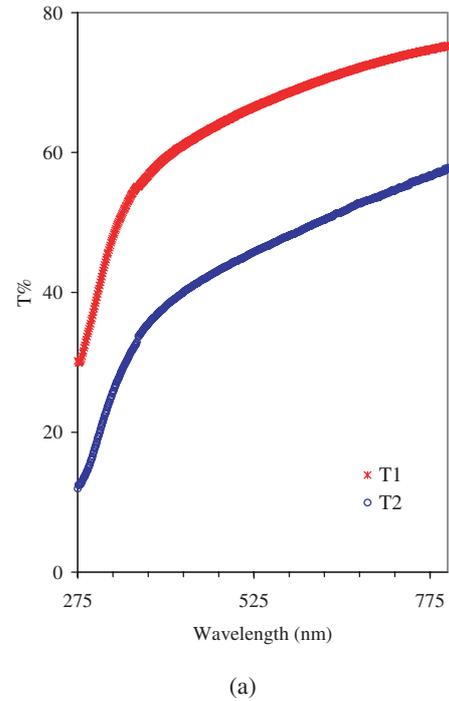
3 Results and discussion

3.1 Structural properties of the amorphous SnO₂ thin films

The crystal structure of the SnO₂ thin films were investigated by X-ray diffraction (XRD) patterns. Figure 1 shows the diffraction patterns of SnO₂ thin films. XRD patterns indicate that these films are almost entirely non-crystalline.

3.2 Optical band gap and Urbach energies of the amorphous SnO₂ thin films

Transmittance and reflectance of the films are shown in Figures 2a and 2b. The average transmittance in the 450–800 nm range is 70.18% and 50.33% for T1 and T2, respectively. The optical band gap can be calculated from

**Fig. 2.** Optical transmittance (a) and reflectance (b) spectra of amorphous SnO₂ thin films.

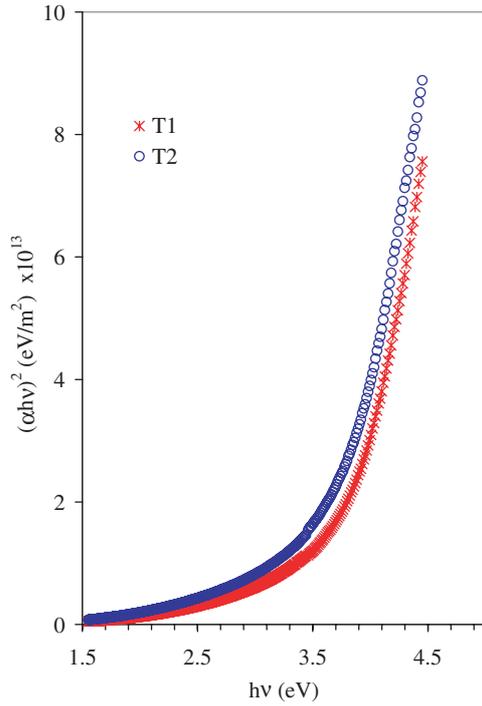


Fig. 3. Plots of $(\alpha h\nu)^2$ vs. photon energy of amorphous SnO_2 thin films.

the following relationship [11],

$$(\alpha h\nu) = A(h\nu - E_g)^m \quad (1)$$

where α is the absorption coefficient, h is Planck constant, ν is frequency, A is a constant, E_g is the optical band gap and m is a constant which determines the type of optical transition ($m = 1/2$ for allowed direct transitions and $m = 2$ for allowed indirect transitions). Here, the direct and indirect transitions are optical transitions that occur in the semiconductors. It is well-known that direct transition across the band gap is feasible between the valence and the conduction band edges in k -space. In the transition process, the total energy and momentum of the electron-photon system must be conserved. Figure 3 shows plots of $(\alpha h\nu)^2$ vs. photon energy. The values of the direct band gap E_g were determined, and are presented in Table 1. These are in good agreement with reported values [10,12].

The absorption coefficient near the fundamental absorption edge is exponentially dependent on the incident photon energy and obeys the empirical Urbach relation, where $\ln \alpha$ varies as a function of $h\nu$. The Urbach energy can be calculated by the following relation [13],

$$\alpha = \alpha_o \exp \left[\frac{h\nu - E_I}{E_U} \right] \quad (2)$$

where E_I and α_o are constants and E_U is the Urbach energy which refers the width of the exponential absorption edge. Figure 4 shows the variation of $\ln \alpha$ vs. photon energy for the films. The E_U value was calculated from the

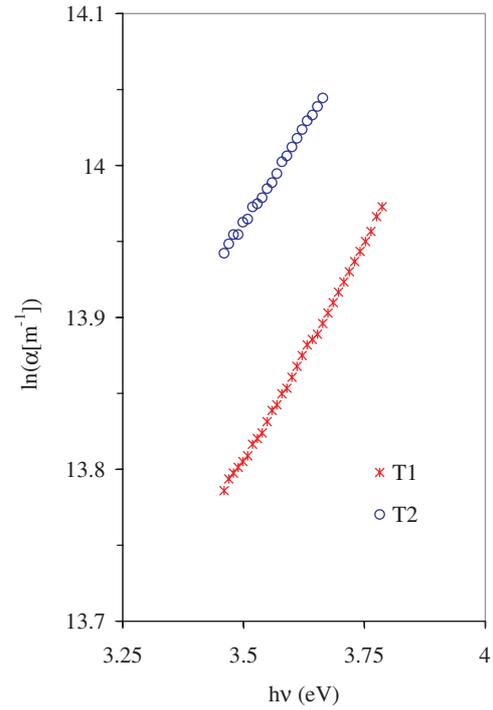


Fig. 4. Urbach plots of amorphous SnO_2 thin films.

slope of Figure 4 using the relationship,

$$E_U = \left(\frac{d(\ln \alpha)}{d(h\nu)} \right)^{-1} \quad (3)$$

and calculated values are given in Table 1. Urbach energy values of the films increase with spraying time, that is, the width of localized states in the optical band of the films increases. That is why the E_U values change inversely with optical band gaps of the films. In both crystalline and amorphous material there is no known origin of the exponential dependence of absorption coefficient with energy. This dependence may arise from random fluctuations of the internal fields associated with structural disorder in many amorphous materials. The dependence of the optical absorption coefficient with photon energy may arise from electronic transitions between localized states. The density of these states falls off exponentially with energy which is consistent with the theory of Tauc [14]. Equation (3) can be rewritten as,

$$\alpha = \alpha_o \exp \left[\frac{\beta}{kT} (E - E_I) \right] \quad (4)$$

where β is a called the steepness parameter, which characterizes the broadening of the absorption edge due to the electron-phonon interaction or exciton-phonon interaction [15]. If the width of the edge, E_U , is related to the slope of equation (3), the β parameter is found as $\beta = kT/E_U$. The β values were calculated using this relationship and taking $T = 300$ K and are given in Table 1. The β values suggest that the absorption edge changes with the spraying time.

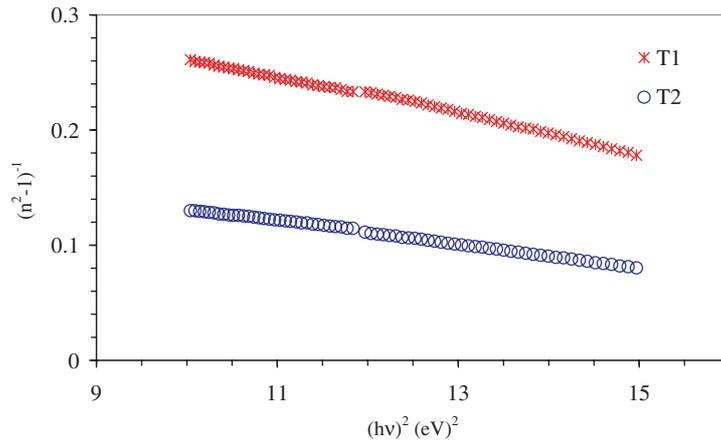


Fig. 5. Plots of $(n^2 - 1)^{-1}$ vs. $(h\nu)^2$ of amorphous SnO_2 thin films.

3.3 Refractive index dispersion of the amorphous SnO_2 thin films

The refractive index, n , is found to decrease with the increase in the wavelength of incident photon, and tends to be constant at higher wavelengths. The dispersion of refractive index below the inter-band absorption edge according to the Wemple-DiDomenico single oscillator model [16] is given as follows:

$$n^2 = 1 + \frac{E_d E_o}{E_o^2 - (h\nu)^2} \quad (5)$$

where E_o and E_d are the single-oscillator energy and dispersion energy parameter, respectively. By plotting $(n^2 - 1)^{-1}$ vs. $(h\nu)^2$ and fitting the data, a straight line is obtained as shown in Figure 5. E_o and E_d are determined directly from the gradient, $(n^2 - 1)^{-1}$ and the intercept (E_o/E_d), on the vertical axis [16]. The single-oscillator parameters for the amorphous SnO_2 thin films have been calculated and discussed in terms of the Wemple-DiDomenico model. Although E_d values increase with increasing spraying time, E_o values tend to decrease. The values of E_o and E_d for the amorphous SnO_2 thin films are given in Table 1. The dispersion parameters of various materials were investigated using this model in the literature [10, 17–20].

The single-oscillator energy is an average energy gap as pointed out in many references [21–24]. We found that the E_o value of the films is related empirically to the lowest direct band gap by $E_o \approx 1.3E_g$. This relation is in agreement with the obtained relation ($E_o \approx 1.4E_g$) obtained from the single oscillator model [21].

3.4 The refractive index and dielectric constants of the amorphous SnO_2 thin films

The complex refractive index ($n = n + ik$) and dielectric function ($\varepsilon = \varepsilon_1 + i\varepsilon_2$) characterize the optical properties of any solid material. Dispersion plays an important role in the research for optical materials, because it is a significant factor in optical communication and in designing devices

for spectral dispersion. The normal incidence reflectivity R can be given by [25],

$$R = \frac{(n - 1)^2 + k^2}{(n + 1)^2 + k^2} \quad (6)$$

where k ($k = \alpha\lambda/4\pi$) is the extinction coefficient. The refractive index values of the films were calculated using equation (6). The refractive index dependence of wavelength was plotted, as shown in Figure 6a. As can be seen in the plotted figure of refractive index, the refractive index decreases with photon energy. The extinction coefficient k dependence of wavelength is shown in Figure 6b. The k values of the films decrease up to a certain value of wavelength and then increase. The fundamental electron excitation spectrum of the films was described by means of a frequency dependence of the complex electronic dielectric constant. Real and imaginary parts of the dielectric constant are related to the n and k values. The ε_1 and ε_2 values were calculated using the formulae [25],

$$\varepsilon_1 = n^2 - k^2 \quad (7)$$

$$\varepsilon_2 = 2nk. \quad (8)$$

Figures 7a and 7b show ε_1 and ε_2 dependence on the wavelength.

The M_{-1} and M_{-3} moments of the optical spectra can be obtained from the following relations [20]

$$E_o^2 = \frac{M_{-1}}{M_{-3}}, \quad E_d^2 = \frac{M_{-1}^3}{M_{-3}}. \quad (9)$$

The obtained values are given in Table 1. It is seen that M_{-1} and M_{-3} moments increase with increasing spraying time.

3.5 Optical conductivity of the amorphous SnO_2 thin films

The real σ_1 and imaginary σ_2 components of optical conductivity are described as [26]

$$\sigma_1 = \omega\varepsilon_2\varepsilon_o \quad \text{and} \quad \sigma_2 = \omega\varepsilon_1\varepsilon_o \quad (10)$$

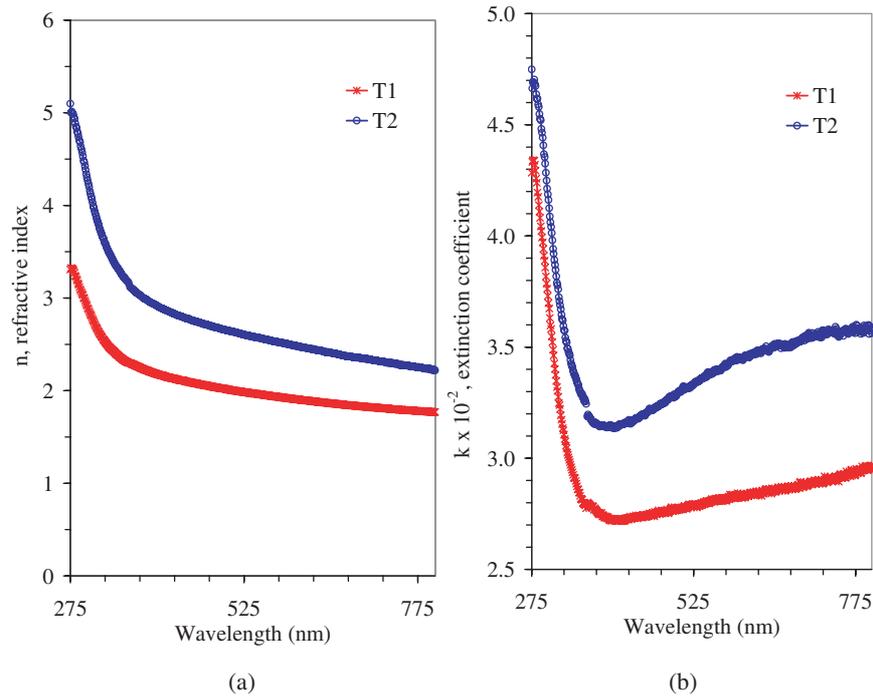


Fig. 6. Variation of refractive index (a) and extinction coefficient (b) of amorphous SnO₂ thin films.

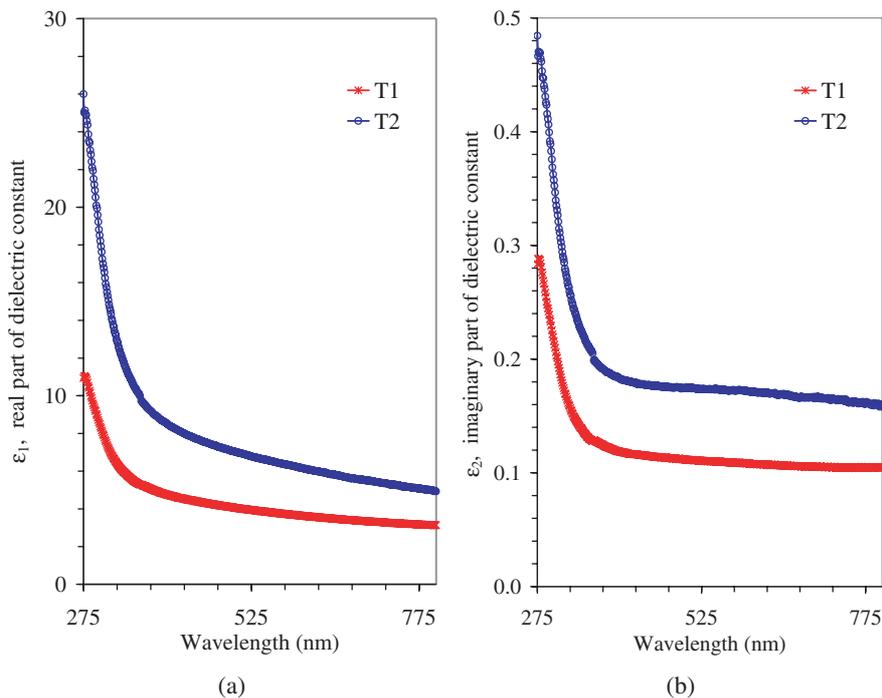


Fig. 7. Variation of real (a) and imaginary (b) parts of the dielectric constant of amorphous SnO₂ thin films.

where ω is the angular frequency, ϵ_o is the free space dielectric constant. The real and imaginary parts of the optical conductivity dependence of energy are shown in Figures 8a and 8b. It is seen in the figures that the optical conductivity increases with increasing energy. This suggests that the increase in optical conductivity is due to electrons excited by photon energy. The optical conductivity of the films changed with spraying time.

By increasing the spraying time, there is an effect on the variation of optical constants. This variation can be discussed in terms of defects present in the composition. During the film formation some defects may form, so, such defects produce localized states in the band gap of films. The presence of high concentration of localized states in the band structure is responsible for the variation of all optical parameters.

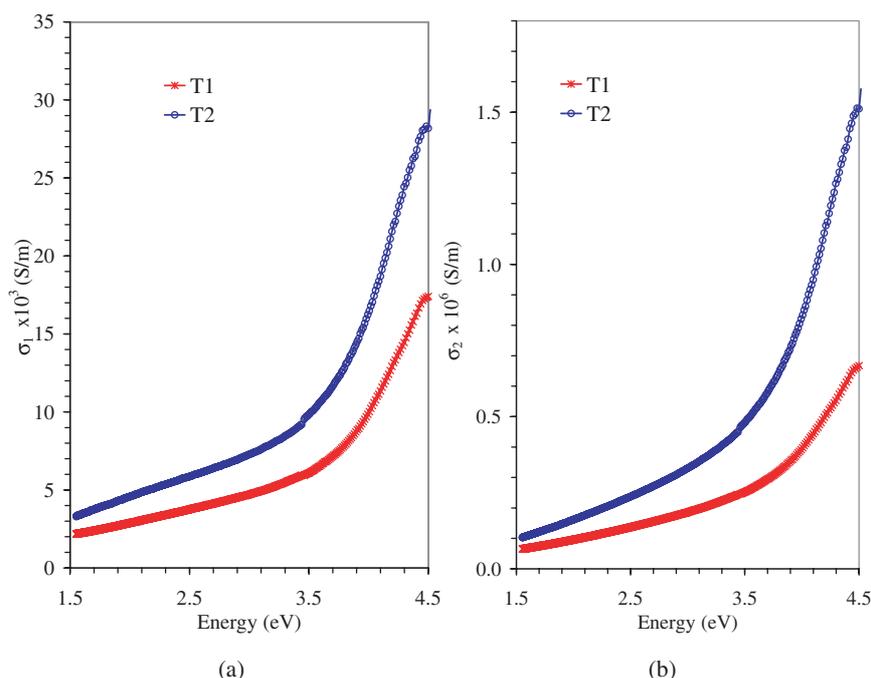


Fig. 8. Variation of real (a) and imaginary (b) parts of the optical conductivity with energy.

4 Conclusions

The optical properties of amorphous SnO_2 thin films have been investigated. The values of the optical band gap, E_g , and Urbach energy, E_U , were calculated using the optical method. The deposition time barely changes the direct optical band gap, whereas the deposition time changes the optical constants (refractive index, extinction coefficient, dielectric constants and optical conductivity), and Urbach energy values of the films. The dispersion curves of the refractive index of the amorphous SnO_2 thin films obey the single-oscillator model. The E_d dispersion energy of the amorphous films was determined and these values increase with increasing deposition time. The M_{-1} and M_{-3} optical moments of the amorphous SnO_2 thin films increase with increasing deposition time.

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