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Full Length Research Paper

Investigation of structural, morphological and optical properties of electrodeposited SnO_2 thin films

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In this study, we investigated the deposition time effects on structural, morphological and optical properties of electrodeposited SnO_2 thin films. Tin oxide thin films were deposited at 10, 15 and 20 min deposition times and characterized using X-ray diffraction (XRD), scanning electron microscope (SEM) and energy dispersive X-ray spectrometer (EDX) and UV-VIS spectrometer. XRD results showed that SnO_2 thin films were polycrystalline with tetragonal crystal structure and increasing the deposition time improved the crystallinity of SnO_2. From SEM images, there were particles on the surface of SnO_2 and particle size depended on deposition time. EDX analysis confirmed that the amount of Sn and O elements increased with increasing deposition time. From the optical studies, it was found that the transmittance values in visible region varied between 69.53 and 86.27%. These findings showed that SnO_2 films can be electrodeposited without oxygen rich environment at room temperature. Also, the films obtained can be used in many devices such as solar cells and gas sensors.

Key words: SnO_2, electrodeposition, deposition time.

INTRODUCTION

Transparent conducting oxides (TCOs) have attracted the attention of many researchers due to some of their properties (Elangovan and Ramamurthi, 2005). One of transparent conduction oxides, tin oxide is a insulator in stoichiometric form, but in non-stoichiometric form, oxygen deficiency makes it a semiconductor (Batzill and Diebold, 2005; Moholkar et al., 2007; Jadsadapattarakul et al., 2008). SnO_2 is widely used in solar cells, hybrid microelectronics (Ravichandran et al., 2009), touch-sensitive switches digital displays (Jain and Kumar, 2004), electro-chromic displays, gas sensors (Kasar et al., 2008), and architectural windows etc. due to theirs low electrical resistivity, high optical transmittance in visible region, high optical reflectance in infrared region, chemically inert and mechanically hard (Elangovan et al., 2005). Further, SnO_2 thin films are stable even at high temperatures, have excellent resistance to strong acids and they have very good adhesion to many substrates (Kim et al., 2001; Chacko et al., 2008; Elangovan et al., 2004).

In earlier works, tin oxide thin films were prepared by variety of methods such as chemical vapor deposition (CVD) (Kim et al., 2001), sputtering (Ma et al., 2002), sol-gel spin coating (Dua et al., 2008), spray pyrolysis (Jain and Kumar, 2004; Kasar et al., 2008), hydrothermal method (Zhang and Gao, 2004), pulsed laser deposition (Kim and Pique, 2004), and electrochemical deposition (Lai et al., 2009). One of these methods, electrodeposition is a desirable technique (Yang et al., 2010) due to its properties such as low-cost, simplicity and effectiveness in preparing large area thin films (Vequizo et al., 2010) and fast production (Yeh et al., 2012). Also, some properties of the thin films can be controlled by electrochemical parameters.

At the electrodeposition of metal oxides, it is necessary

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for the OH^- ions or O^- radicals to be present on the electrode surface. There are various oxygen sources for effective electrodeposition of oxides such as nitric acids, hydrogen peroxide and flow of oxygen gas into electrochemical solutions (Chang et al., 2004). If nitric acid is chosen as the oxygen source, the half-reaction on the cathode electrode surface is expressed as follows:

$$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^- \quad (1)$$

The OH^- ions formed on the electrode surface reacted with the stannic ions coming from the bulk solution to form nanocrystalline SnO_2 (Chang et al., 2005)

$$Sn^{4+} + 4OH^- \rightarrow SnO_2 + 2H_2O \quad (2)$$

Although electrodeposition of SnO_2 has been usually carried out at elevated temperatures or an oxygen-bubbled (Yang et al., 2010; Vequizo et al., 2010; Chang et al., 2004; Chang et al., 2005; Li et al., 2009), to our knowledge, a few studies (Lai et al., 2009; Chou et al., 2009; El-Etre and Reda, 2010) have been reported regarding electrodeposition of SnO_2 from solutions at room temperature. In this study, nanocrystalline SnO_2 thin films without any oxygen-bubble at room temperature were prepared by electrodeposition from solutions using nitric acid as the oxygen source.

EXPERIMENTAL

SnO_2 thin film has been electrodeposited from acidic solutions at room temperature. The solutions composed of 20 mM $SnO_2.2H_2O$, 0.1 M $NaNO_3$ and 75 mM HNO_3. The electrodeposition was performed in a conventional three-electrode electrochemical cell. A indium tin oxide (ITO) substrate with a sheet resistance of 100 Ω/cm^2, a platinum wire and Ag/AgCl in a saturated potassium chloride (KCl) solution were utilized as the working, counter, and reference electrodes, respectively. The deposition area was 1 cm^2. Prior to deposition, ITO substrate was ultrasonically cleansed using deionized water, methanol and acetone but the platinum wire was cleansed with solution of sulfuric acid and hydrogen peroxide. The film depositions were performed at times of 10, 15, 20 min and under constant potential of -0.6 V by using a potentiostat (SG 3000, Gamry Instruments). After the deposition, all the samples were washed softly in water and naturally dried in air and finally SnO_2 films electrodeposited were annealed in O_2 atmosphere at 500°C for 2 h.

The structural characterization of the films was carried out by X-ray diffraction (XRD) measurements using a Rigaku Miniflex II diffractometer with CuKα radiation (λ=1.5418 Å). The diffractometer reflections were taken at room temperature and the values of 2θ were altered between 20^o and 90^o. Morphological properties of the SnO_2 films were determined with Nova Nanosem 430. The optical transmittance of the samples was recorded in spectral region of 400 to 1000 nm at 300 K using a UV-VIS spectrophotometer (Perkin-Elmer, Lambda 40) which works in the range of 200 to 1100 nm.

RESULTS AND DISCUSSION

The structural properties of SnO_2 thin films electrodeposited at various deposition times were investigated by X-ray diffraction (XRD) studies. As seen from XRD spectra of the films were given in Figure 1, peaks marked with asterisk (*) belongs to indium oxide and its components, (110), (101), (211) and (301) peaks of tetragonal SnO_2 structure (JPDS card no: 41-1445). Similar XRD peaks were observed by Chang et al. (2005). From Figure 1, it was observed that the intensity of SnO_2 peaks increased with increasing deposition time.

The calculated inter planar distance 'd' values are presented in Table 1 and these values are compared with the standard ones from JPDS card no: 41-1445. The matching of the calculated and standard 'd' values confirmed that the deposited films were of SnO_2 with tetragonal structure. The lattice constants 'a' and 'c', for tetragonal phase structure were determined by the relation (Kasar et al., 2008)

$$\frac{1}{d^2} = \left(\frac{h^2+k^2}{a^2}\right) + \left(\frac{l^2}{c^2}\right) \quad (3)$$

where 'd' was the interplaner distance and (hkl) miller indices, respectively. The standard and calculated lattice constants are given in Table 1. The calculated 'a' and 'c' values agreed with standard values of a=4.738 Å and c=3.187 Å from JPCDS card no: 41-1445. As seen from Table 1, deposition time does not have too much effect on lattice constants of SnO_2. It was seen that the most striking peak of (101) and for this peak the average grain size was calculated using Scherrer formula (Chacko et al., 2008) given as

$$D = \frac{K\lambda}{(\beta\cos\theta)} \quad (4)$$

where D was mean grain size of nanoparticles, K = 0.9, β was the full width at half of the peak maximum (FWHM) in radians and 'θ' is Bragg's angle. For 10 min of deposition time, calculated D values of 29.74 nm increased to values of 37.31 and 42.23 nm for 15 and 20 min deposition times, respectively. Misfit stresses that one of the most important factors which adversely affected the structural properties resulted from geometric mismatch at interphase boundaries between crystalline lattices of films and substrate (Bedir et al., 2005). These stresses could cause microstrain in the films. The microstrain (ε) values of electrodeposited SnO_2 films were calculated by the relation (Dhanam et al., 2005)

$$\varepsilon = \left(\frac{1}{\sin\theta}\right)\left[\left(\frac{\lambda_x}{D}\right) - (\beta\cos\theta)\right] \quad (5)$$

where 'β' was full-width at half-maximum of the (101) peak and 'D' was the average grain size; the calculated values are given in Table 1. It was observed that the microstrain values exhibited a decreasing tendency with increasing deposition time. The dislocation density (δ), was defined as the length of dislocation lines per unit volume (lines /m^2). The dislocation density (δ) of the films

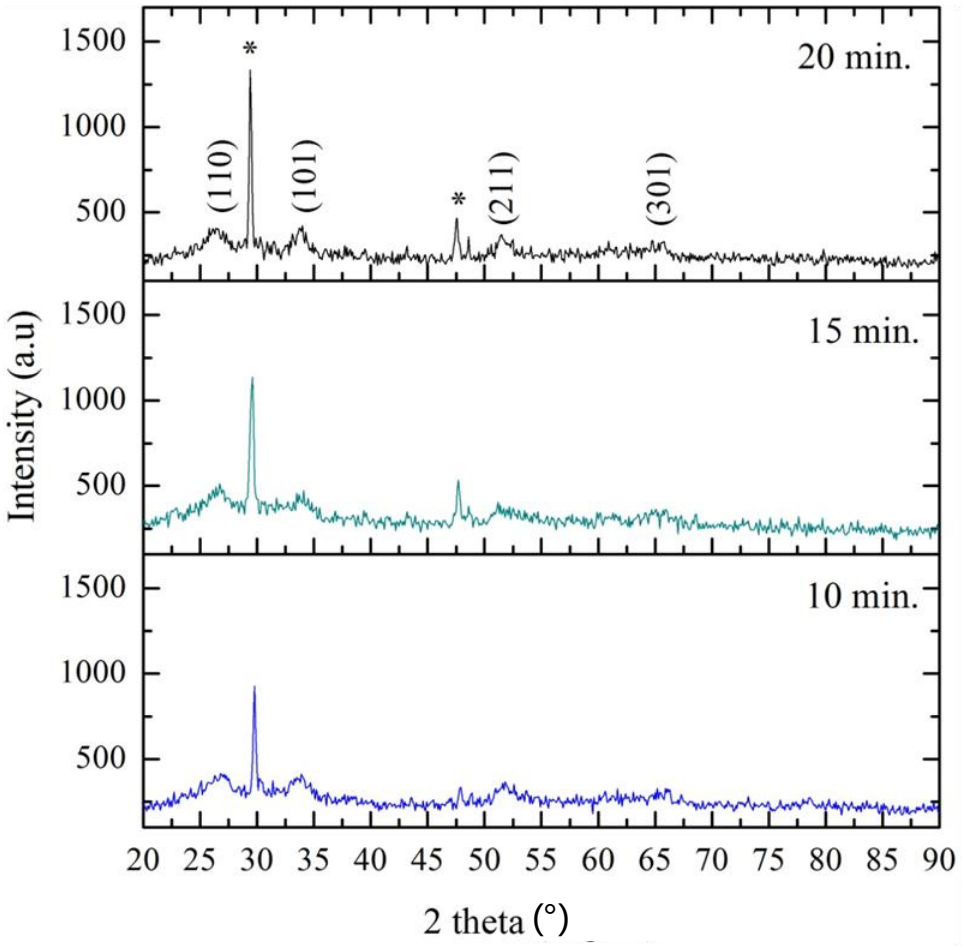

Figure 1. XRD patterns of SnO_2 films obtained at different deposition times.

was estimated using the equation (Ravichandran et al., 2009),

$$\delta = 1/D^2 \quad (6)$$

Since δ was the measure of the amount of the defects in a crystal, the small value of δ obtained for 20 min deposition time confirmed that increasing deposition time increased the crystallinity of SnO_2.

From SEM analysis shown in Figure 2 (a) to (c) it was quite clear that the surface nature of the films was affected by the deposition time. The grains at the films surface began to be big with increasing deposition time. This result collaborated with the results obtained from Scherrer Formula (Equation 4), that is XRD results. There were cracks and non-uniform particle distributions on the surface of SnO_2 films prepared at 10 min of deposition time. But, the samples prepared at 15 and 20 min exhibited uniform distribution over the surface. So, for the sample obtained at 10 min., deposition was not totally completed. Also, according to Figure 2d, the highest dislocation density was calculated for the films prepared at 10 min of deposition time. The particle structure of all samples was similar to that of Chang et al. (2005) and Li et al. (2009). Also, Vequizo et al. (2010) found that particle structure and size were affected by deposition time. The composition of the films was investigated using Energy dispersive X-ray spectrometer (EDX). EDX spectra of the films are given in Figure 3 and the atomic percentages of the elements in the films are given in Table 2. These spectra clearly confirmed that the amount of Sn and O elements increased with increasing deposition time. This suggested that increasing deposition time accumulated more SnO_2 on ITO. The In element and C, Si, Na, Mg, Ca elements in solid nanostructures resulted from ITO films and the glass substrates, respectively.

The optical properties of the films were investigated using UV-VIS spectrometer with respect to the ITO substrate as reference. Figure 3 shows the variation of transmittance (T) with deposition times. The visible transmittance at 550 nm has been found to be 86.27, 81.32, 69.53% for 10, 15, 20 deposition times, respectively. The values confirmed the surface morphology result and indicate that the deposited films were transparent under visible light. A change

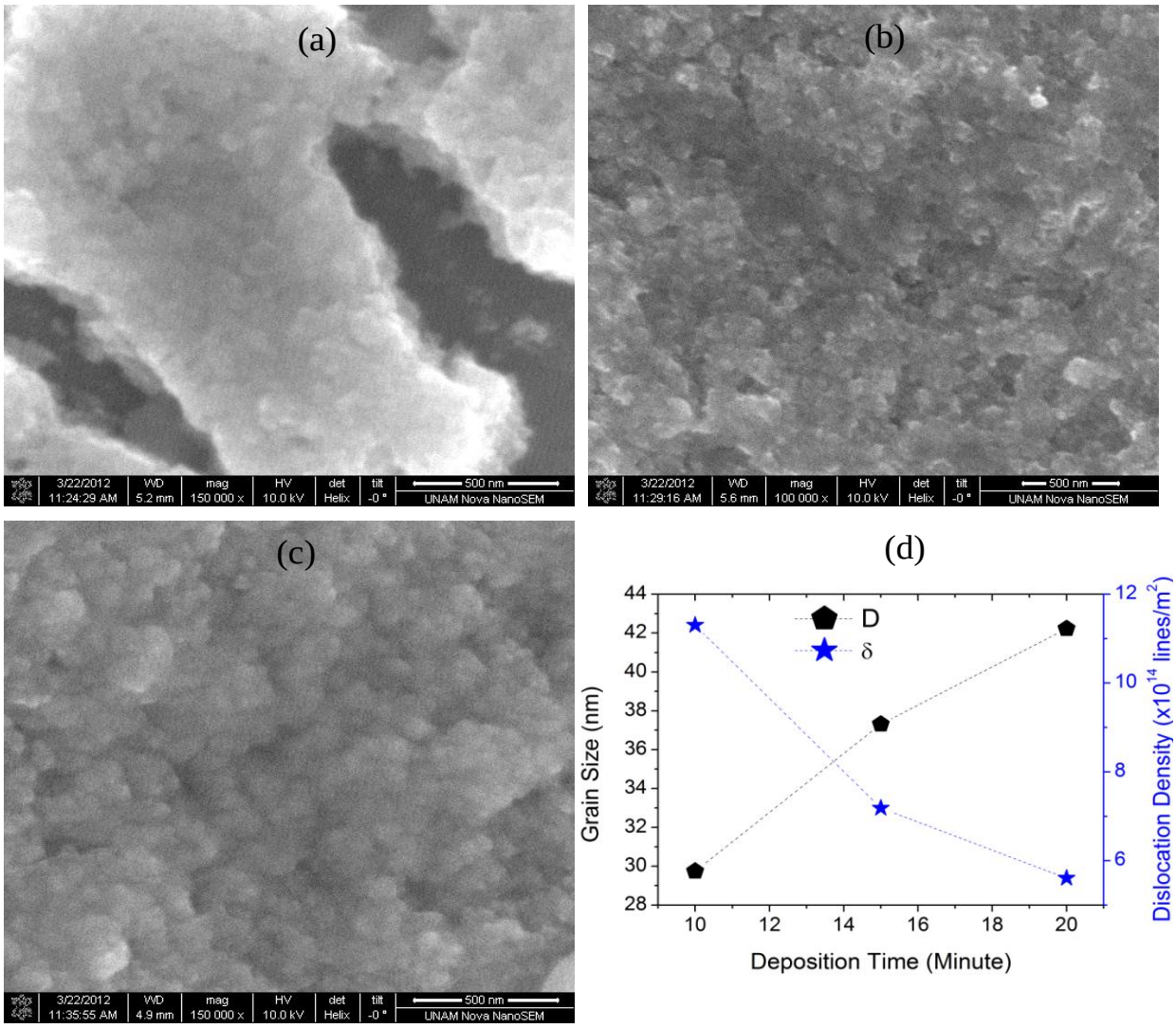

Figure 2. SEM images of SnO_2 films obtained at different deposition times; (a) 10 min (b) 15 min (c) 20 min time, (c) Variation of grain size and dislocation density with deposition time.

transmission was observed with increased deposition time. When deposition time increased, the values of transmittance decreased. However, we observed no clear absorption edge for the samples and the band gap of the films was not calculated. Similar results were observed by Vequizo et al. (2010). This suggested that the decrease in the transmittance of SnO_2 films with increase in deposition times might be due to the increasing amount of SnO_2 on surface of ITO which can cause increase in thickness. Elangovan and Ramamurthi (2005) found that decrease in transmittance of the films with increasing amount of SnO_2.

Conclusions

In the present study, we successfully prepared nanocrystalline SnO_2 thin films without an oxygen-bubble at room temperature by electrodeposition from solution using nitric acid as the oxygen source. Tin oxide thin films were deposited at 10, 15, 20 min deposition times and characterized by using XRD, SEM, EDX and UV-VIS spectrometer. XRD results showed that SnO_2 films were polycrystalline with tetragonal crystal structure and increasing deposition time improved the crystallinity of SnO_2. SEM images showed that there were nanoparticles on the surface of SnO_2 and particle size depended on deposition time. EDX analysis confirmed that the amount of Sn and O elements increased with increasing deposition time. From the optical studies, it was found that the transmittance values varied between 69.53 and 86.27%. These findings showed that SnO_2 films can be electrodeposited without oxygen bubbling at room temperature. Also, the obtained films can be used in

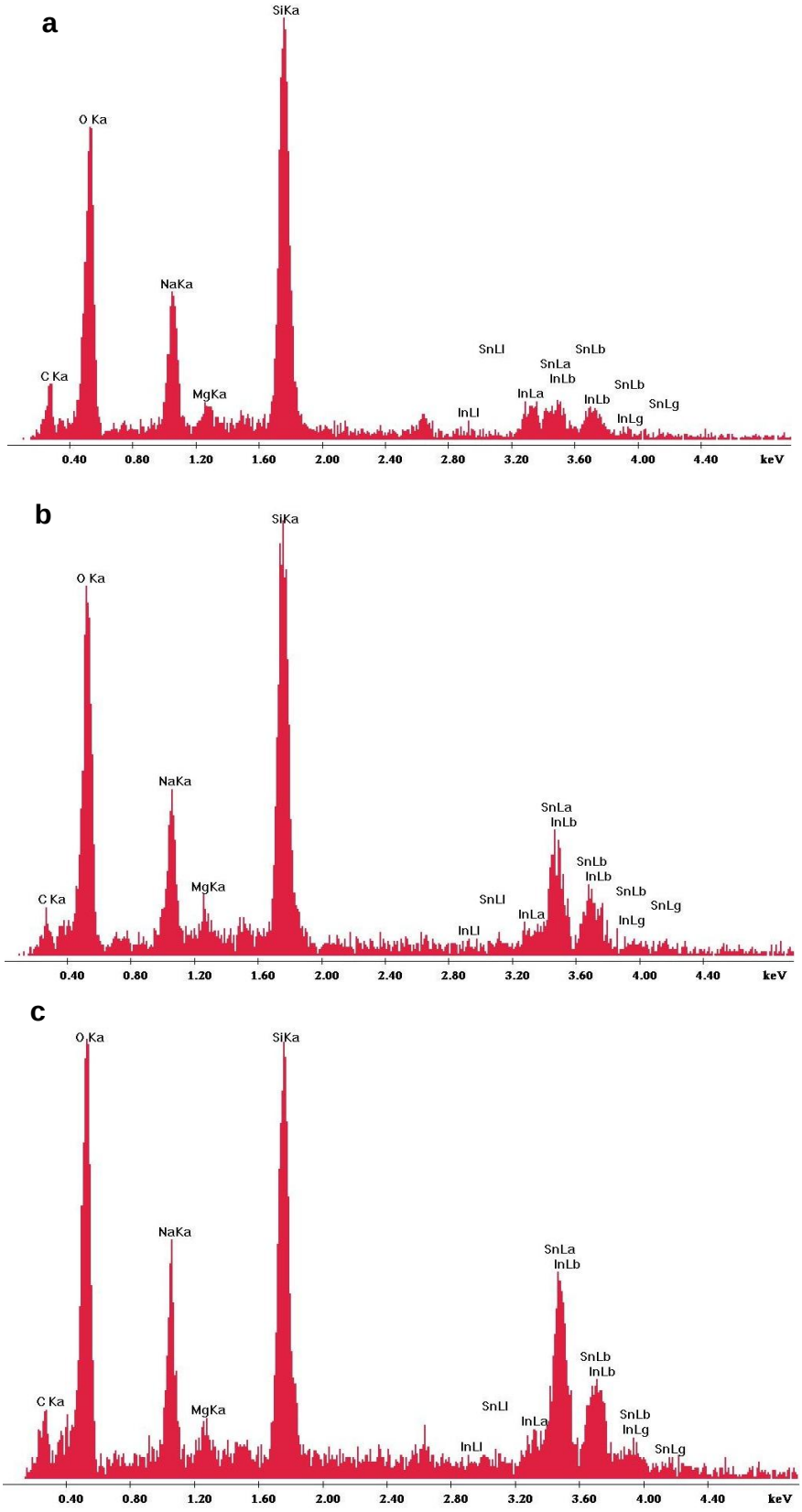

Figure 3. EDX spectra of SnO_2 films obtained at different deposition times; (a) 10 min (b) 15 min (c) 20 min times.

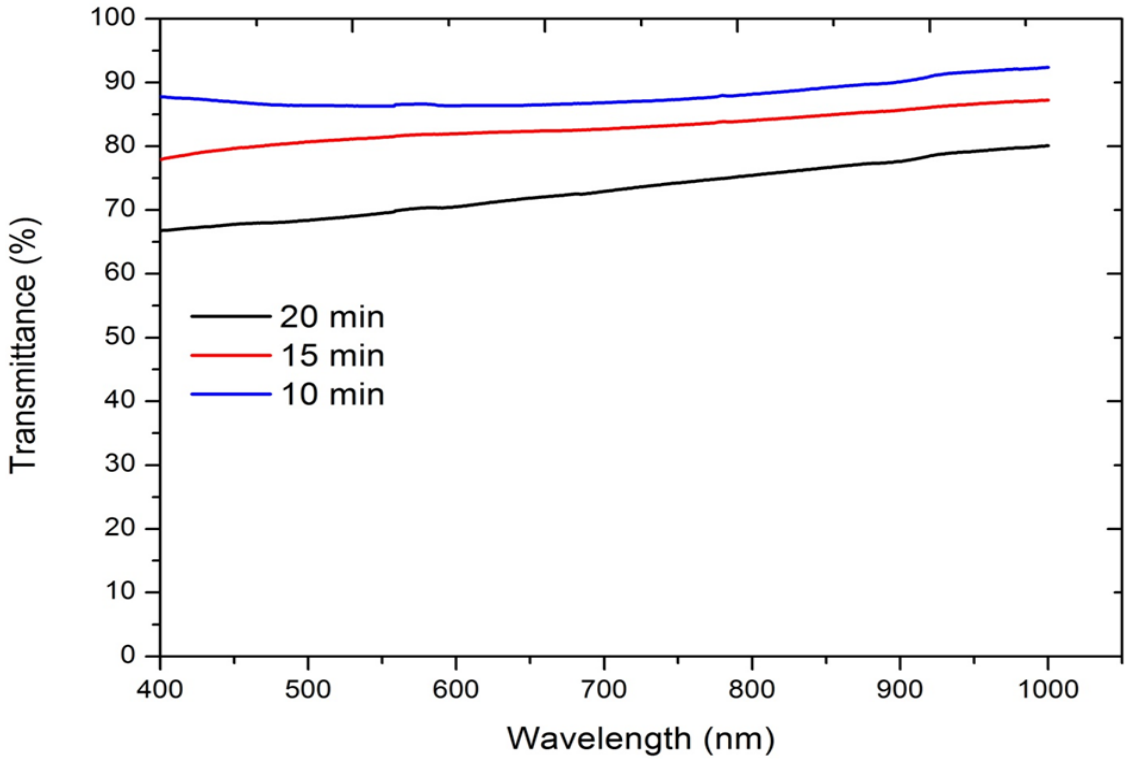

Figure 4. Optical transmittance spectra of SnO_2 films electro deposited at 10, 15, 20 min deposition times.

Table 1. Some properties of electrodeposited SnO_2.

Deposition time (min)	hkl	Calculated d (Å)	Standard d (Å)	D (nm)	δ ($\times10^{14}$ lines/m^2)	ε ($\times10^{-3}$)	Lattice constant (Å)	
							a	c
10	110	3.3321	3.3470	29.74	11.304	10.6	4.7123	3.1892
	101	2.6412	2.6427					
	211	1.7647	1.7641					
	301	1.4139	1.4155					
15	110	3.3487	3.3470	37.31	7.184	8.6	4.7358	3.2063
	101	2.6550	2.6427					
	211	1.7724	1.7641					
	301	1.4199	1.4155					
20	110	3.3275	3.3470	42.23	5.607	7.5	4.7058	3.2123
	101	2.6531	2.6427					
	211	1.7819	1.7641					
	301	1.4174	1.4155					

Table 2. Atomic percentages of the elements in SnO_2 thin films.

Deposition time (min)	Sn	O	In	Si	C	Na	Mg
10	2.33	46.01	1.88	19.93	19.61	8.96	1.29
15	6.38	51.38	1.17	19.26	11.13	9.05	1.64
20	8.24	51.76	1.31	14.86	12.96	9.44	1.43

many devices such as solar cells, gas sensors etc.

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