Nitrogen Plasma Effect On The Physical Properties Of Tin Oxide Thin Film

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An enhancement of structural, optical and electrical properties of tin oxide thin films could be obtained by exposing these films to DC pseudo nitrogen plasma. The films were prepared by spray pyrolysis method, and then the properties are measured at different exposure times of plasma. It is found that the exposure time (~ 15 minutes) enhances the transmittance of the tin oxide while larger times decrease it. Also, it is found that; there is a dramatic change in thickness, optical band gap and the resistivity with changing the exposure time.

1. Introduction

Transparent conducting oxides (TCO) have many applications because of their high visible transmittance and low resistivity. These oxides have potential applications in many fields such as, gas sensors, liquid crystal display(LCDs), thermal mirrors, alcoholic detectors and solar energy windows [1-7].Among the various TCO films, tin oxide (SnO_2) is one of the promising transparent oxides because of its wide band gap, low toxicity and cost. Many studies tried to enhance optical properties (more transparent) and electrical properties (more conductive) by controlling the preparation conditions [8-10]. But these ways gave an enhancement of some physical properties on the account of other properties [8-10]. Spray pyrolysis is one of the simplest methods of depositing transparent conducting oxide films [3]. In this method the substrate temperature and flow rate control the most desirable structural, optical and electrical properties of tin oxide films. In present work, DC pseudo N_2 plasma is used to modify most of the properties of the prepared film.

2. Experimental

2.1. Sample preparation

Tin oxide thin film is prepared by spray pyrolysis method. A 5 *gm* of $SnCl_4$ (purity 99.9%) is dissolved in 5 *ml* of HCl acid, then the mixture is heated until the salt is completely dissolved in the acid, and 100 *ml* of ethyl-alcohol is added to the solution and heated again and stirred with a magnetic stirrer until the solution becomes completely clear. This solution is sprayed on the hot substrate (T= 400 ^oC) as shown in Fig. (1). The thickness of the sample could be controlled by changing the number of the spraying periods.

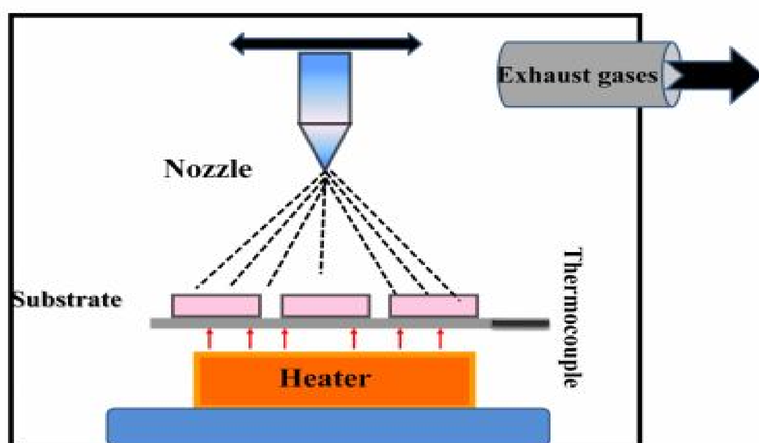

Fig. (1): Schemtic diagram of spray pyrolysis coating unit.

2.2. X-ray Diffraction

The XRD analysis of the tin oxide film has been obtained by Philips (CuK_α) X-ray diffractometer (λ=1.54056 *Å*).

2.3. Fourier Transformed Infrared Spectroscopy

The specific molecular components and structures of the prepared sample have been identified by Fourier Transform Infrared Spectroscopy (FTIR). The spectrometer used for achieving these analyses is Nicolet 6700; the wavenumber range is 400 - 4000 cm^{-1}.

2.4. Spectrophotometer Analysis

A double beam spectrophotometer (Shimadzu UV 160 spectrophotometer) is used for getting the transmission spectrum curve of the prepared sample. It has a wavelength rang of (300-1100 *nm*), double beam spectrophotometer.

2.5. Measurement of Resistivity

The resistivity of the thin film is measured by using four input probe method. It is an electrical impedance measuring technique that uses separate pairs of current-carrying and voltage-sensing electrodes to make more accurate measurements than traditional two-terminal (2T) sensing. 4T sensing is used in some ohmmeters and impedance analyzers, and in precision wiring configurations for strain gauges and resistance thermometers. 4-point probes are also used to measure resistivity of semiconductor thin films (e.g.SnO_2); the technique of the four probe is shown in Fig (2).

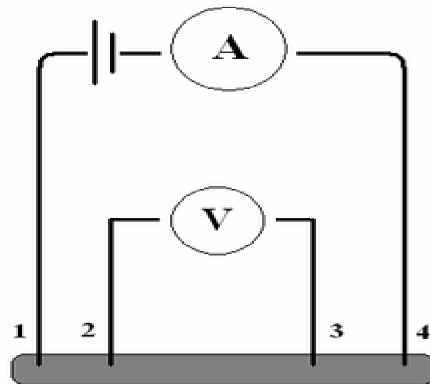

Fig. (2): Four-point measurement of resistance. The voltage connections are 2 and 3; Current connections are 1 and 4.

2.6. Exposing to Nitrogen Plasma

The schematic diagram of the experimental set-up of exposing the tin oxide (SnO_2) thin film to nitrogen plasma is shown in Fig (3). The two electrodes consisted of a cathode and a mesh anode to obtain DC pseudo-discharge .The discharge cell is evacuated to pressure 10^{-3} *torr* before filling in the nitrogen gas. The pressure is controlled by a needle valve. The anode is placed at 3 *mm* distance from the cathode. The tin oxide thin film sample is then exposed to pseudo plasma discharge. The sample is placed in front of the mesh anode at an axial distance $Z =$ [illegible] *cm* from the mesh anode. The pressure exerted on the sample is 0.4 *torr*, and the discharge current is 6 *mA*. The plasma power is 10 *watt*. The plasma density and temperature, measured by Langmuir probe, are 10^{12} cm^{-3} and 1.5 eV, respectively.

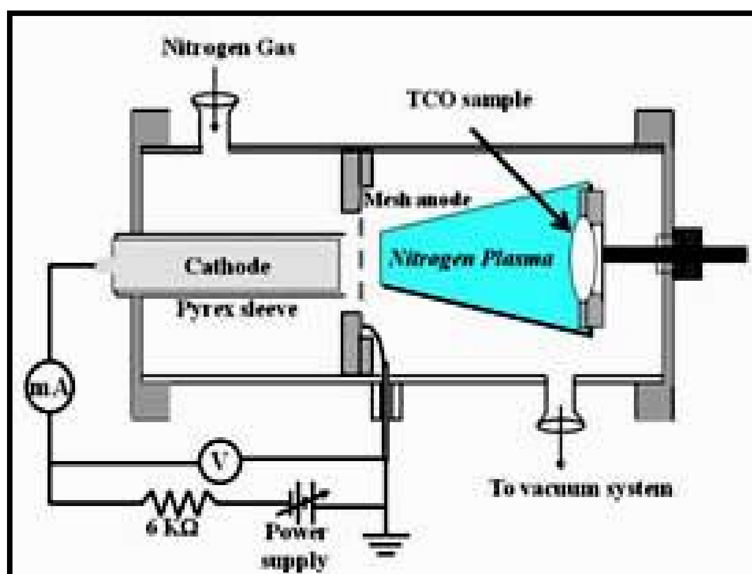

Fig. (3): Schematic diagram of a pseudo plasma discharge experiment used for exposing TCO samples.

3. Results and discussion

3.1. X-ray Diffraction Analysis

Figure (4) shows X-ray diffraction patterns for the prepared sample. It is found that the sample has a single phase tetragonal structure. The lattice parameters of the investigated film are found to be in good agreement with that reported by many authors [11,12] (a=b=4.73 *Å*, c=3.19 *Å*). Also, It is obvious that, the sample has a preferred orientation in (200) plane because of its highest peak in the XRD diffraction patterns. During plasma exposure, the plasma parameters, gas pressure and the current are fixed. Fig. (4) shows the X-ray diffraction pattern of the investigated sample after 180 minutes of plasma exposure. No extra peaks are observed i.e. the sample still has its tetragonal structure, so the structural properties of the film was not changed.

3.2. FTIR Analysis

FTIR absorbance spectrum gives information about how the way the oxygen ions are bounded to the tin ions (Sn-O structure). Fig. (5) shows IR absorbance spectra of the film are in the range of 400 – 2200 cm^{-1}. The absorption bands for the unexposed samples could be divided into three main regions:

1- Band between 1820 and 1320 cm^{-1} due to -OH vibrations [13,14].
2- Band between 1320 and 881 cm^{-1} due to chloride Cl^- retained ions in the film. Since the film under investigation is prepared from chloride salts [13].
3- Band at lower wavenumbers (500 and 700 cm^{-1}) due to the symmetric vibrations of Sn-O and O-Sn-O.[13,14].

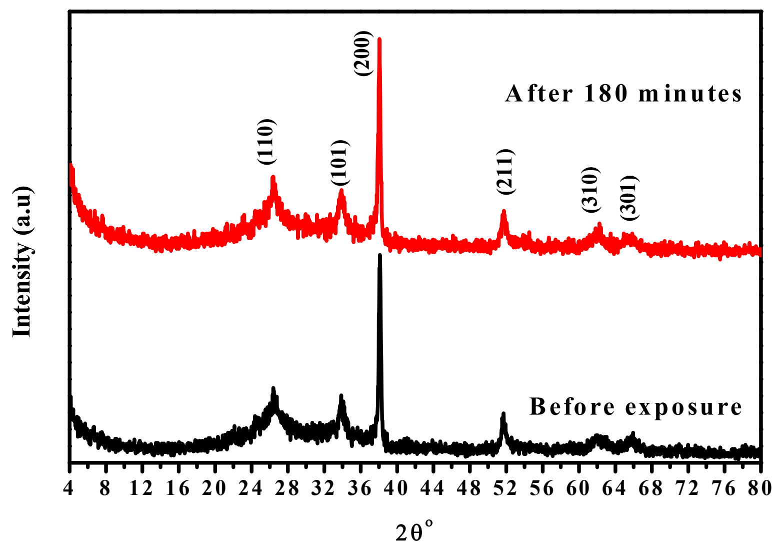

Fig. (4): Diffraction patterns of SnO_2 before and 180 minutes of exposure for sample of tin oxide thin film.

By observing Fig. (5), it is noticed that the exposing of the prepared sample to nitrogen plasma for a longer time, there is new bond appeared at 820 cm^{-1}.Morever, the absorption band of chloride ions retained in the film decrease with increasing the exposure time. Also, the O-Sn-O bond is appearing stronger. Table (1) shows ummery of the different bonds of FTIR with the exposure time. To confirm that the bond at 820 cm^{-1} is due to Sn-N bond, a theoretical value of wavenumber of Sn- N bond could be calculated by the relation

$$\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{k}{m^*}} \tag{1}$$

where k is the bond stength ($k = 5 \times 10^5$ dyne/cm) for single bond[15], is the speed of light ($c = 3 \times 10^{10}$ cm/sec), and m^* is the reduced mass for atomic masses of tin and nitrogen. The value of Sn-N wavenumber is found to be 822 cm^{-1} which is in agreement with the observed band FTIR absorbance spectrum.

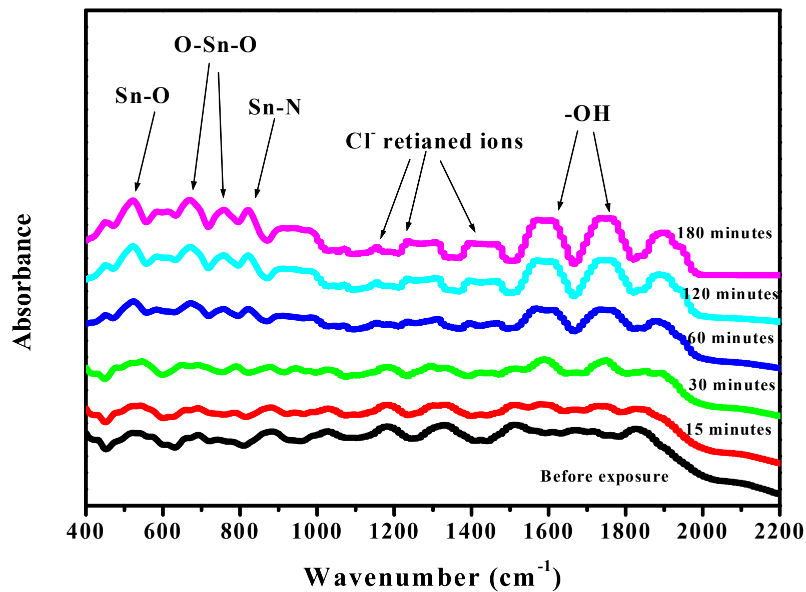

Fig. (5): FTIR analysis for the tin oxide thin film with different intervals of exposure time

Table (1): Wavenumber foundation of different bands

Fundamental vibrations	Exposure Time (minutes)					
	unexposed	15	30	60	120	180
	Wavenumber (cm^{-1})					
Sn-O	521	542	546	523;584	523;584	523
O-Sn-O	690	690	650;690	673	671	669
Cl^- retained ions	883;1030; 1330	879;1320	877;1290; 1330	910;1160; 1320	912;1240; 1310	1160;1240; 1310
Sn-N	not observed	not observed	not observed	822	820	820

3.3. Determination the thickness (d) and energy gap (E_g)

The transmission spectrum of the prepared sample at different exposure times in the range of 300-1100 *nm*, are shown in Fig. (6). It is clear that the transmission of the sample is relatively high in the visible and near infrared region while it dramatically decreases in the near UV region, this behavior is reported in

the literatures [16,17]. The thickness could be determined using the transmission spectrum curve (λ vs. T) and this is by using the relation.

$$d = \frac{\lambda_1 \lambda_2}{2|n_1 \lambda_2 - n_2 \lambda_1|} \tag{2}$$

where λ_1 *and* λ_2 are the wavelengths at the maxima or minima points on the transmission spectrum curve, n_1 and n_2 are refractive indices due to wavelengths λ_1 *and* λ_2, respectively, the refractive index of the thin film can be determined according to Tetsuka, et al. [18] .From this method the thickness of sample is found to be 302 nm. The transmission spectrum of the sample exposed to nitrogen plasma is shown in Fig (6), it is clear that the exposure to nitrogen plasma has great effect on the transmission spectra. Fig (7) shows the effect of exposure time on the transmission effect at wavelength 1100 *nm*. It is clear that there is an enhancement in the transmittance in IR region for the sample (d=302 *nm*). To explain these results, the effect of plasma exposure on the film's thickness should be taken into consideration. Fig (8) shows the time effect of plasma exposure on the thickness of the sample, it is obvious that in the first hour the thickness of the sample decreases by increasing the time of exposure and then the rate of decreasing is slowed. This observation could be explained in terms of plasma cleaning and etching [19], where the layers of SnO_2 that are on the surface of the thin film are sputtered due to the energy of the incoming plasma ions. Moreover, the Cl^- retained ions are removed due to exposure to plasma; these ions are decreasing with increasing the exposure time (as it was discussed before in FTIR). The decreasing in the thickness of the prepared tin oxide thin film gives chance to increase the transmission at higher wavelength as shown in Fig (7). For low wavelengths, a dramatic decreasing in transmittance is occurred although the reduction in thickness, and this due to injection of nitrogen plasma ions through the film and formation the bond generated between the tin and nitrogen ions (as shown in FTIR analysis). The linear absorption coefficient (α) is determined due to the relation.

$$\alpha = \left(\frac{1}{d}\right)\ln\left(\frac{1}{T}\right) \tag{3}$$

in which (d) is the thickness of the thin film and T is the transmittance. According to the solid state band theory, the relation between the absorption coefficient (α) and the photon energy ($h\nu$) [20,21]:

$$\alpha = \frac{A(E_g - h\nu)^n}{h\nu} \quad (4)$$

in which A is a constant and E_g is the band-gap energy. By using eq. (4) and for the direct allowed transition ($n = \frac{1}{2}$), then a relation between photon energy ($h\nu$) and $(\alpha h\nu)^2$ was plotted [20], as shown in Fig (9). It is found that, before exposure; the prepared sample has an energy gap (3.22 *eV*). The effect of the exposure time on the energy gap is shown in Fig (10). The energy gap E_g increases in the first 30 minutes, and then slightly decreases. This could be attributed due to the strong decreasing in the thickness of the thin film in the first 30 minutes of exposure time [21], then there is a slight decreasing in the energy gap with the exposure time, this is back to, as was confirmed before in IR spectrum , the formation of Sn-N bond in the thin film. The energy gap of tin nitride (1.5 eV) [22], the formation of Sn-N bond in the thin film tends to decrease the energy gap again by increasing of exposure time.

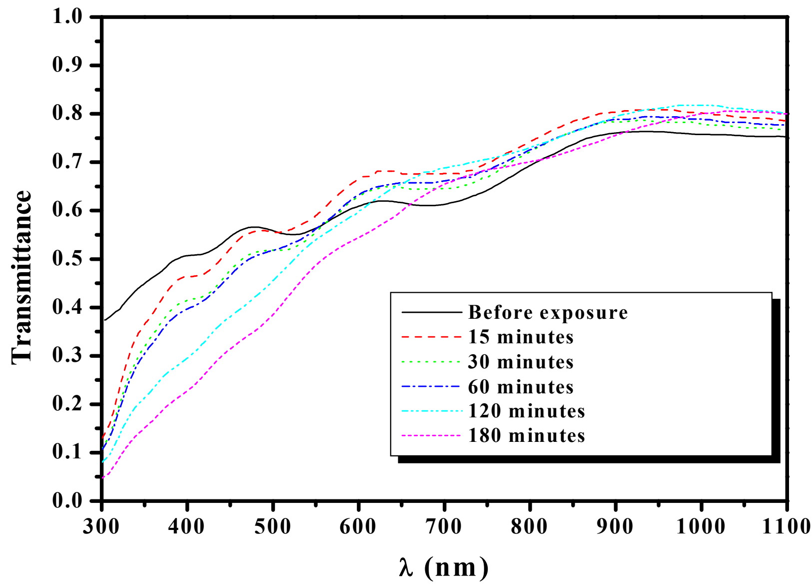

Fig. (6): The variation of the transmission with different time intervals of plasma exposure.

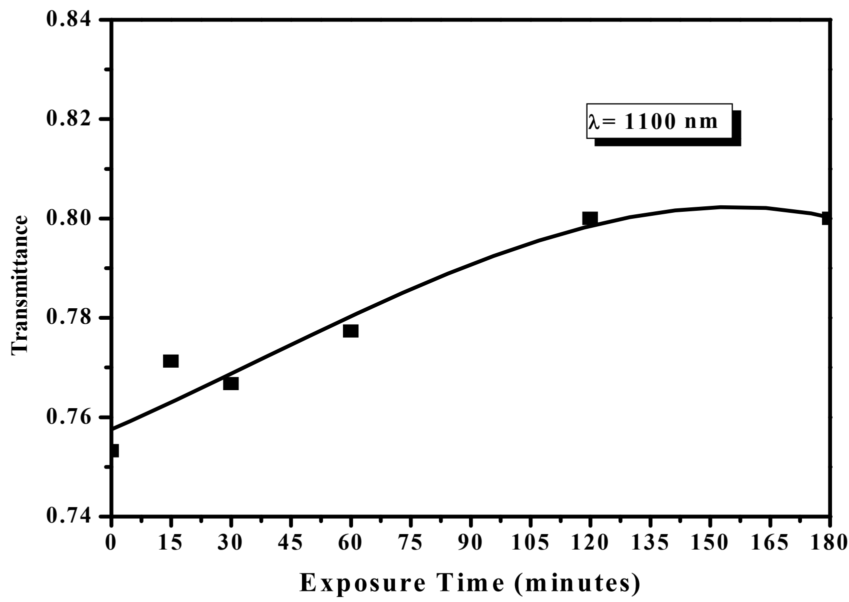

Fig. (7): Change of transmittance in the range of IR region with change in exposure time.

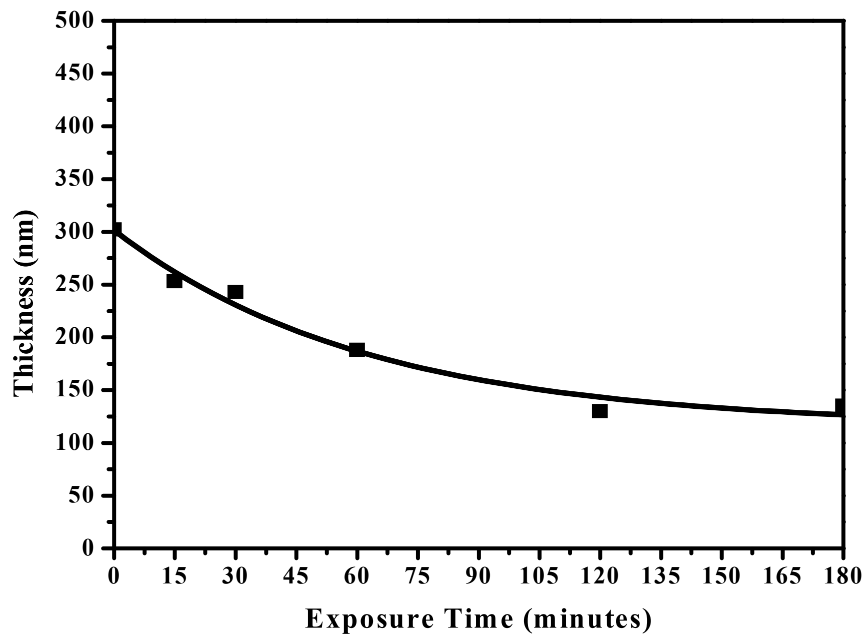

Fig. (8): Effect of nitrogen plasma on the thickness of the SnO_2 thin film.

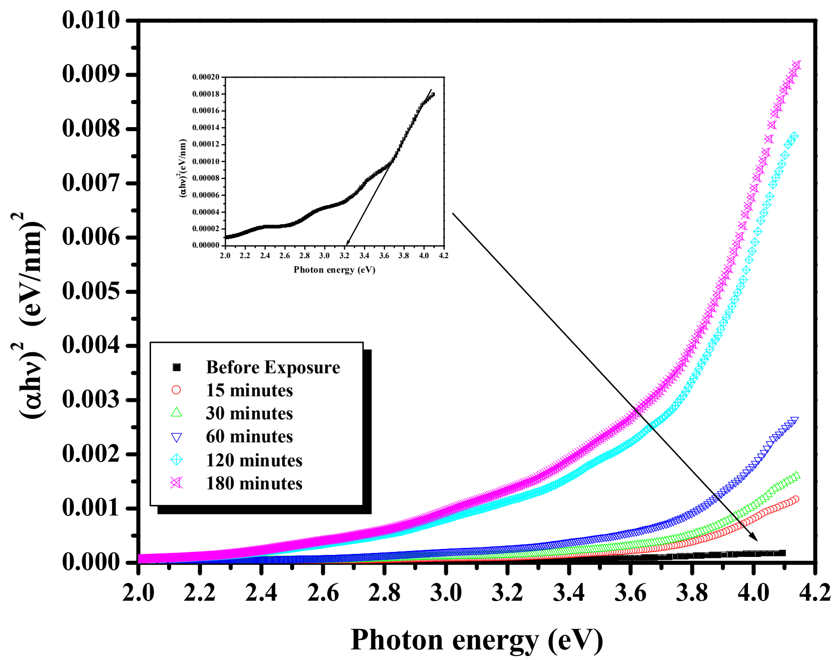

Fig. (9): The variation of the energy gap due to the change in exposure time

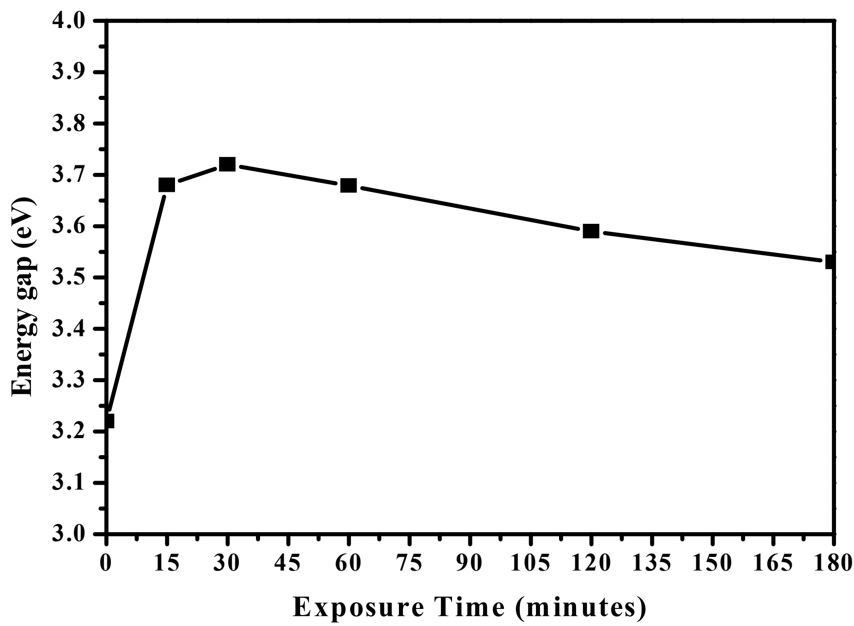

Fig. (10): Change of energy gap with change of plasma exposure time.

3.4. Effect of time of Exposure on Resistivity

The effect of time of exposure on the sheet resistance of the investigated sample is shown in the Fig (11). It is clear that as the time increases, the resistivity decreases, this could be attributed to two reasons; the first one is the cleaning process against the retained chloride ions from the preparation, and the second is reduction effect (oxygen deficient), due to plasma exposure which makes an increasing of the metallic phase in the sample, and so, increasing of the electrical conductivity of the film.

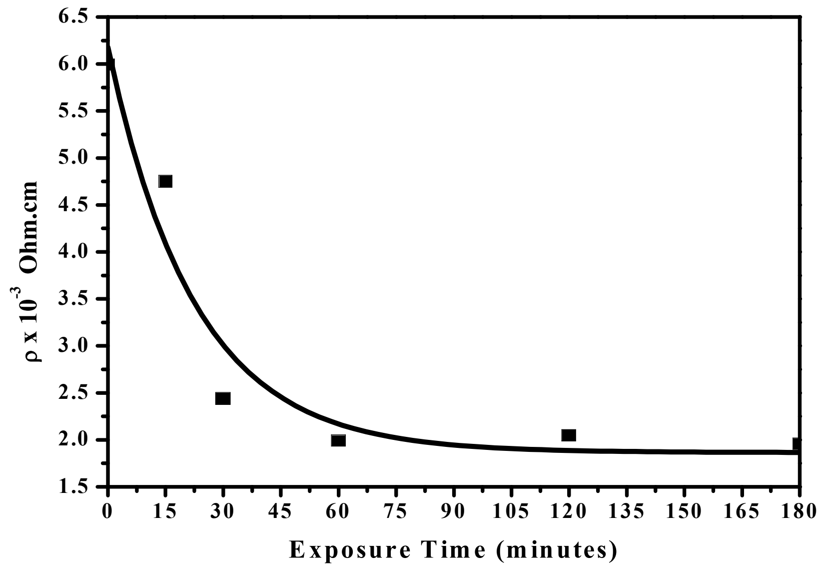

Fig (11): The variation of resistivity of SnO2 thin film with change of exposure time to plasma.

4. Conclusion:

The nitrogen plasma exposure has great effect on the optical and the electrical properties of SnO_2 thin films. The plasma exposure could enhance the transition in IR region and at the same time decreases the resistivity which makes the sample has promising application as solar cell window, and finally the exposing of the tin oxide to nitrogen plasma could make a passive cleaning of the film and sterilization from some impurities such as chlorides retained from the solution sprayed on the hot substrates, and this leads to make a good modification of the electrical properties of the SnO_2 thin films.

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