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Effect of annealing conditions on physical properties of tin oxide thin films

Sanaa M. Al-Delaimy[1,*] , Akram R. Al-Khaerow[2]

[1] *Physics Department, College of Education, Mosul University, Iraq*
[2] *Research & Development Department, Ministry of Industry & Minerals, Baghdad, Iraq*

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Abstract

Thin films of SnO_2 were deposited by chemical vapor deposition method. Group of these films was annealed for 60 minutes at temperature (100, 200, 300, 400) ºC in air and another group was annealed in vacuum for the same period and the same temperatures. Structural properties have been studied for all films using XRD technique. It was found that the intensity of the preferred orientation plain was increased in both types of annealing. Current-voltage measurements was carried out using four point probe unit for all films and sheet resistance (R_S) was calculated. The effect of annealing temperature on R_S was studied. It was found that its value increases with annealing temperature increment for films annealed in air, while it decreases for films annealed in vacuum within the studied range. Transmission percent for some films was measured in the visible region. It was found that it increases with annealing temperature for films annealed in air while it slightly decreases for samples annealed in vacuum. Figure of merit (Q) was calculated for all annealed films. Its value increases with the increasing of annealing temperature for films annealed in vacuum while it decreases for films annealed in air within the studied range.

Keywords: Optical properties; Electrical properties: X-ray; Annealing.
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1. Introduction

Transparent, electrically conductive films have been prepared from a wide variety of materials. These include metals (such as silver, gold and titanium nitride) and semiconducting oxides (of tin, indium, zinc and cadmium etc). They have been used for many years as electrodes or resistive elements and applied to semiconductor devices as transparent gates on charge injection devices and charge coupled devices and as transparent barrier layers on solar cells [1].

The coexistence of electrical conductivity and optical transparency in these materials depends on the nature, number, and atomic arrangements of metal cations in crystalline or amorphous oxide structures, also on the resident morphology, and on the presence of intrinsic or intentionally introduced defects [2]. The combination of conductivity and transparency is usually impossible in intrinsic stoichiometric oxides. However, it could be achieved by producing oxide either with a non-stoichiometric composition or by introducing appropriate dopants [3, 4, 5].

[*]) For correspondence: E-mail: sadelaimy@yahoo.com.

Tin oxide film is the most common material used for this purpose because of its cheap raw materials and highly existing in nature, beside of it's good transparency anti-reflecting properties. It is characterized by a wide band gap and high electrical conductivity through the existing of O_2 vacancies and interestial tin atoms in the crystal structure of the films and that is depend on the method of deposition [6]. An effective transparent conductor should have high electrical conductivity combined with low absorption of visible light. Thus an appropriate quantitative measure of the performance of transparent conductors is the ratio of the electrical conductivity (σ) to the visible absorption coefficient (α) which called figure of merit (Q) [7].

Temperature stability and reproducibility of films properties are important for devices reliability. Films are exposed to heat during the preparation and operation of any device. This may cause structural changes which tend to either influence or degradation in most of the physical properties of the films. The effects of annealing are complex because of the variety of phenomenon that may observe. Many studies have been done on different transparent conducting oxides to find the effect of annealing on certain property of the films such as resistivety and factor of merit [8], grain size, porosity and conductivity [9] and many others [10,11,12,13]. In this study annealing in air and in vacuum at different temperatures have been done on tin oxide films. The effect of annealing on structural, electrical and optical properties has been studied. Also the figure of merit for some samples was calculated.

2. Experimental Work

Thin films of SnO_2 used in this work were deposited by atmospheric pressure chemical vapor deposition (APCVD) technique on glass substrate type (Gloim 1003/Italy) at 450°C substrate temperature and 2.5 L/min gas flow rate. The average film thickness is about 1500A. Material used was $SnCl_2.2H_2O$ (purity 99.99%) supplied by Fluka company. Schematic diagram of the experimental set-up used for film deposition is shown in figure (1).

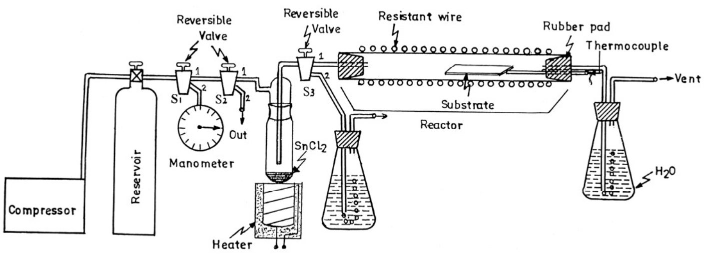

Fig. 1: Schematic Diagram of CVD System for SnO_2 Films deposition.

One group of SnO_2 films was annealed in air for 60 minute at (100, 200, 300, 400) ºC using controllable electric oven type Heraeus. Another group was annealed, at the same temperatures and for the same periods, in vacuum, using the setting shown in photo (1). Structural properties for all films were studied by X-ray diffraction (XRD) technique using Philips X-ray diffractometer model (PW 1130). Source of radiation was Cukα (λ=1.5405 A) and the scanning range of 2θ was restricted to range (10-60) °.

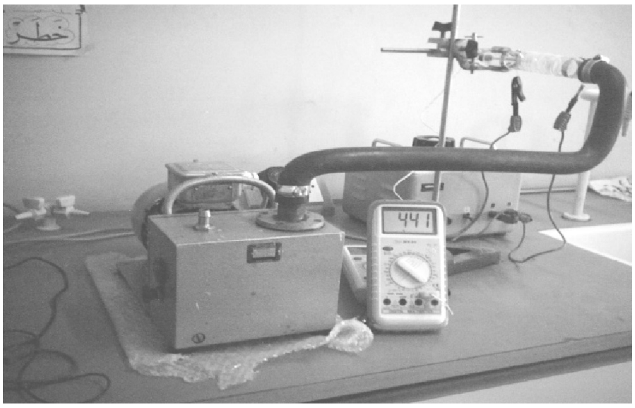

Photo 1: Setting used for annealing in vacuum.

Current-voltage characteristics for all films were measured using four-point probe unit, and sheet resistance was calculated. A comparison between the effects of the two types of annealing on the electrical properties of the films was discussed. Transmission spectrum for films annealed in air and in vacuum at (200, 300, and 400) ºC was studied at wave-length range of (300-800) nm using Shimadzu UV-visible spectrophotometer model (1650 PC). The absorption-coefficient for all films in visible range was calculated. Figure of merit for each film was calculated by using the electrical conductivity and absorption coefficient values and applying the following equation [7]:

$$Q = \frac{\sigma}{\alpha} = \{R_s \ln (T+R)\}^{-1} \tag{1}$$

Where R_s is the sheet resistance in ohm per square (Ω/☐), T is the total visible transmission percent, R is the total visible reflectance which is very small compare to the transmission percent in transparent films.

3. Results and Discussions

X-ray diffraction pattern for SnO_2 films annealed in air at (200, 300, 400) ºC is displays in Fig. 2, 3, and 4 respectively. It is clear that the intensity of (221) plane and the preferred orientation (110) plane [14] increases gradually with annealing temperature. That is because of the crystal growth due to crystallization that increases by annealing temperature specially in the preferred orientation growth. The figure also shows that the intensity of (101) plane and (200) plane decreases with annealing temperature.

This can be explained as follows: The intensity of (110) plain and (200) plain are due to the present of tin atoms inserted in the interstitial site and the present of oxygen vacancies in crystal structure of the film respectively. This result has been concluded by a group of researchers [15] using a computer program to calculate the structural factor $|F(hkl)|^2$. Annealing the film in air reduces the number of tin atoms through the oxidation process and, the oxygen from air has been absorbed gradually to fill the oxygen vacancies.

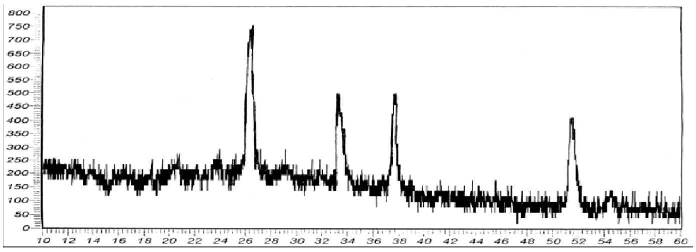

Fig. 2: XRD pattern for SnO_2 thin film annealed in air at 200 ºC.

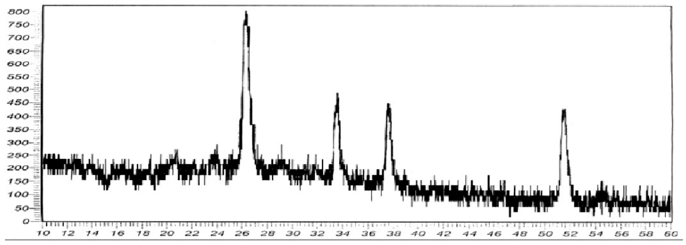

Fig. 3: XRD pattern for SnO_2 thin film annealed in air at 300 ºC.

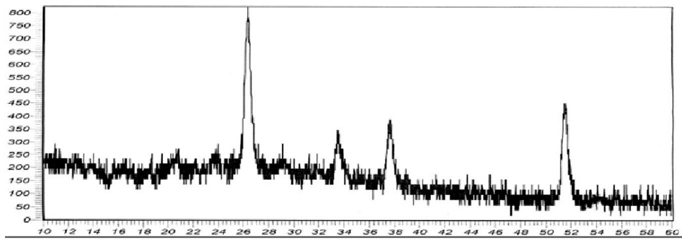

Fig. 4: XRD pattern for SnO_2 thin film annealed in air at 400 ºC.

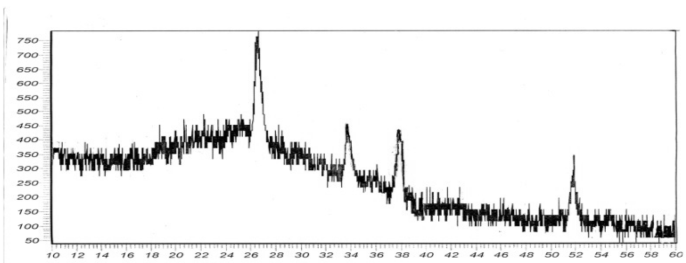

Fig. 5: XRD pattern for SnO_2 thin film annealed in vacuum at 200 ºC.

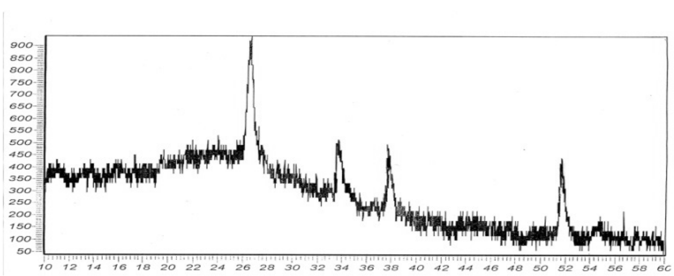

Fig. 6: XRD pattern for SnO_2 thin film annealed in vacuum at 300 ºC.

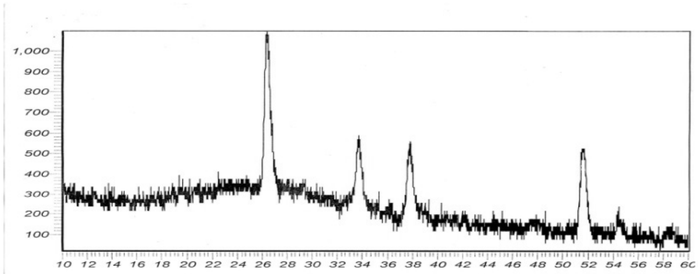

Fig. 7: XRD pattern for SnO_2 thin film annealed in vacuum at 400 ºC.

X-ray diffraction pattern for SnO_2 thin films annealed in vacuum at (200, 300, 400) ºC is displays in Fig. 5, 6, and 7 respectively. One can notice that the intensity of all the planes increased by annealing temperature. But the increment of (110) plane is larger than that of (101), (200), and (211). That's because annealing in vacuum does not affect the chemical structure of the film but it will help the small grains to coalescence and form larger once. The intensity increment in (110) plain is more than any other plains because it is the preferred growth orientation for SnO_2 film so it becomes the dominate [14].

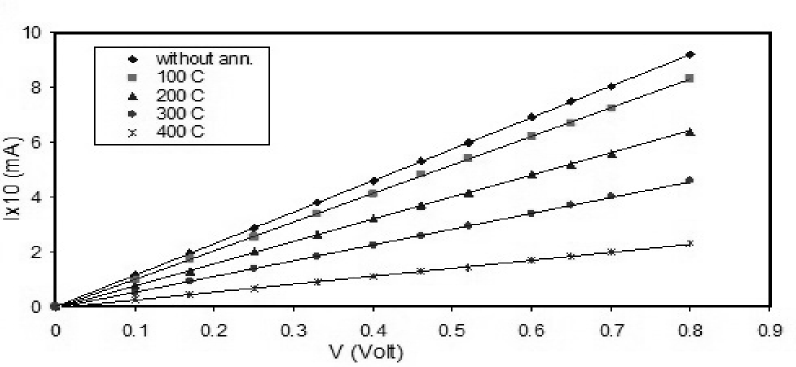

Fig. 8: I-V characteristics for SnO_2 films annealed in air.

Current-voltage characteristics for annealed and unannealed SnO_2 films deposited on glass substrate were shown in Fig. (8). Annealing was done in air at (100, 200, 300, 400) ºC for 60 minutes. The figure shows that the current is proportional to the voltage within the applied voltage range for all films. The current values at certain voltage decrease with annealing temperature increment. Sheet resistance of SnO_2 films versus annealing temperature is displayed in Fig. (9).

Figure shows that the sheet resistance increases with annealing temperature increment. SnO_2 film is considered as a semiconductor material. Its conductivity is attributed to the combination of chloride ions and oxygen vacancies and the interestial tin ions result from incomplete decomposition of $SnCl_2$ and incomplete oxidation of the non-stoichiometric SnO_2 film [3, 4, 5]. Annealing SnO_2 film in air decreases its conductivity. This is probably due to the presence of oxygen. The oxygen fills many of the oxygen vacancies and oxidized tin ions in the film which will tend to increase the sheet resistance. Increasing the temperature of annealing will tend to increase the oxidation reactions, therefore conductivity will decrease and sheet resistance will increase.

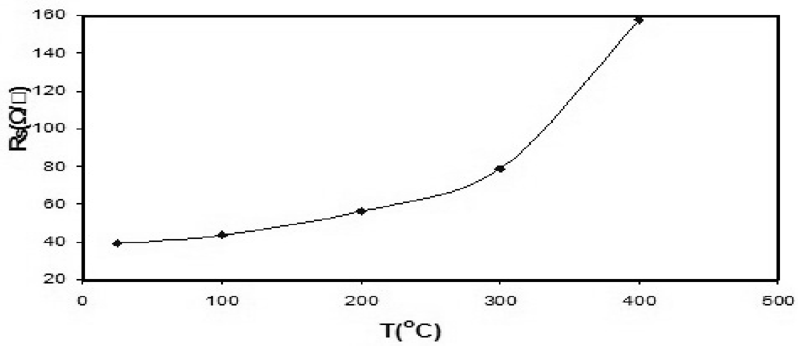

Fig. 9: Sheet resistance of SnO_2 films annealed in air versus annealing temperature.

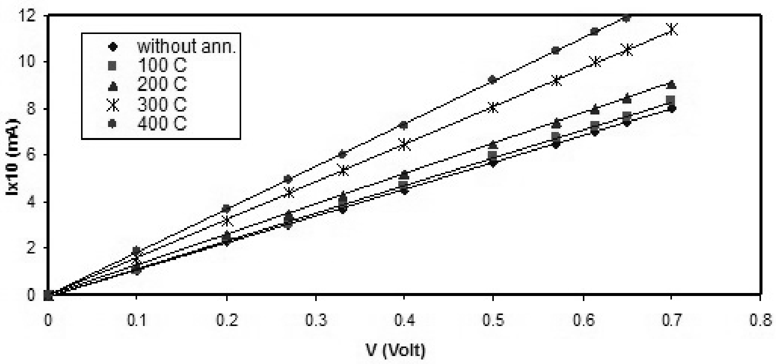

Fig. 10: I-V characteristic of SnO_2 films annealed in vacuum.

Figure (10) shows current-voltage characteristics of SnO_2 films deposited on glass substrate unannealed and annealed in vacuum at (100, 200, 300, 400) ºC for 60 minutes. It is clear that the current increases with applied voltage within the applied range for all films but current values at certain voltage increase by annealing temperature increment.

Figure (11) displays sheet resistance of SnO_2 films, annealed in vacuum, as a function of annealing temperature. It is clear that the sheet resistance decreases gradually with annealing temperature increment within the studied range. This is attributed to the increase in the mobility of charge carriers which can be explained as follows:

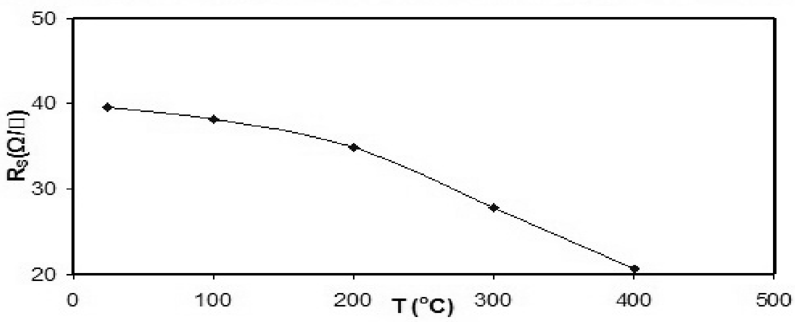

Fig. 11: Sheet resistance of SnO_2 films annealed in vacuum versus annealing temperature.

Tin oxide thin films deposited by (CVD) method have polycrystalline structure. It is well known that the grain boundaries considered as charge carriers scattering centers. Annealing a polycrystalline film in vacuum will enhance the film structure by increasing the grain size and reduce the grain boundaries and potential barriers then reduce the charge carrier scattering in grain boundary regions. This will tend to mobility and electrical conductivity increment and sheet resistance decrement.

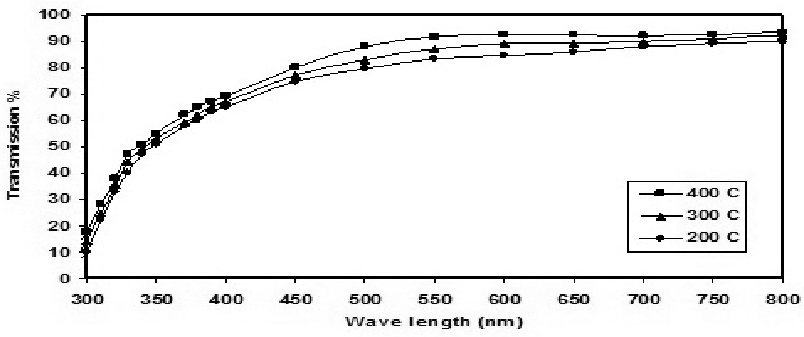

Fig. 12: Transmission spectrum of SnO_2 film annealed in air.

Figure (12) shows transmission percent (T%) as a function of wavelength at visible region for SnO_2 films annealed in air at (200, 300, 400) ºC for 60 minutes. It is clear that T% increases with annealing temperature within the studied range. The increment in transmission percent was reported by several researchers (16, 17, 18). We thought that this increment attributed to the decrease in free charges in SnO_2 films, by annealing, through oxidation and removing oxygen vacancies.

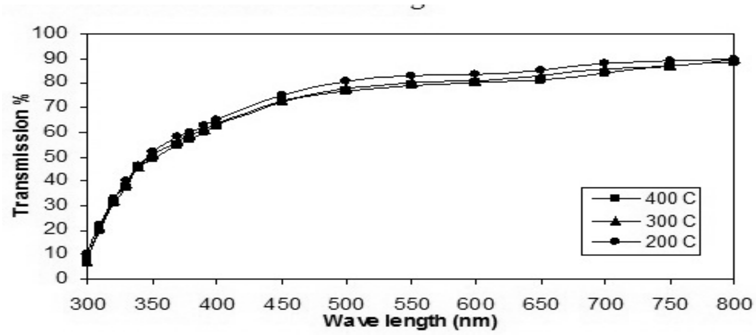

Fig. 13: Transmission spectrum of SnO_2 film annealed in vacuum.

Figure (13) shows transmission percent (T %) as a function of wavelength at visible region for SnO_2 films annealed in vacuum at (200, 300, 400) ºC for 60 minutes. Transmission percent for films slightly decreases within the studied range. This depends on the structure of the films after annealing.

Figure of merit (Q) for all annealed films is calculated using equation (1). Its values for all film are listed in table (1). One can notice that Q factor increases for films annealed in vacuum, while it slightly decreases for films annealed in air compared with the unannealed one. It was reported by several researchers (1, 16, 18) that figure of merit for Transparent Conducting Oxides films (TCO) are depend on the method of preparation and its value is changed in the range of (0.2-7) approximately.

Table 1: Figure of merit for annealed films.

Ann. temp.(ºC)	Ann. in air	Ann. in vac.
200	0.114	1.22
300	0.069	1.44
400	0.043	1.51

4. Conclusions

1-Sheet resistance for SnO_2 films annealed in air increases from about (40 to 157) Ω/☐ as annealing-temperature increased, while it decreases from about (40 to 20) Ω/☐ for SnO_2 films annealed in vacuum, within the studied annealing temperature range.

2-Transmission percent (T%) in visible region for SnO_2 films annealed in air increases with annealing temperature, while it decreases, slightly, for films annealed in vacuum.

3-Figuer of merit (Q) for SnO_2 film increases as annealing temperature increased for films annealed in vacuum, while it decreases for films annealed in air.

4- SnO_2 films annealed in air suffer from degradation, while annealing in vacuum enhance film properties.

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