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Effect of Post-Oxidation on SnO_2 Thin Films

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ABSTRACT

An investigation which include synthesis of SnO_2 thin film by depositing onto glass substrates at room temperature using thermal evaporation technique. The films were post-annealing in furnace tube at 250 ^oC temperature for different time (10, 20, 30 and 40 minutes). The films were characterized by AFM microscopy, FTIR and optical absorption spectrophotometer. The grain size was observed to increase with increase the annealing duration. Absorbance spectra were taken to examine the optical properties and band gap energy was observed to decrease with increase the annealing duration. The effect of annealing time on the optical and morphological properties of films were studied and discussed.

Keywords: SnO_2 thin film, oxidation of tin, annealing of thin film.

دراسة تاثير الاكسدة على الغشاء الرقيق SnO_2

الخلاصة

هذا البحث يتضمن تحضير غشاء رقيق من مادة ثاني اوكسيد القصديرعلى قاعدة من الزجاج بدرجة حرارة الغرفة باستخدام تقنية التبخير الحراري. ثم تم تلدين العينات داخل فرن انبوبي بدرجة حرارة تصل الى 250 ^oC ولاوقات مختلفة (10، 20، 30 و40) دقيقة. بعدها تم دراسة خصائص الفلم بواسطة مجهر (AFM) ، قياسات (FTIR) و الخصائص البصرية المتضمنة الامتصاصية. وجد ان حجم الحبيبات يزداد بزيادة زمن التلدين. ايضا تم دراسة مخطط الامتصاصية لفحص الخصائص البصرية حيث لوحظ ان قيمة فجوة الطاقة تقل بزيادة زمن التلدين. هكذا تم دراسة ومنافشة تأثير زمن التلدين على الخصائص البصرية والتركيبية للفلم المحضر.

INTRODUCTION

Since the last decade there has been a great interest in the properties of inexpensive thin films of SnO_2 [1]. This is due to the thin film with large band gap (Eg >3 eV)[1,2]. Tin oxide (TO) films are attractive from the scientific and technological point of view since tin oxide are a transparent conductive oxide in the visible region of the electromagnetic spectrum as a consequence of the large band gap[1,3] as well as high infrared reflectivity[4]. Also SnO_2 film are stable, strongly adherent to the substrate, mechanically hard and resistant to moister and acids and thermal stability [2,5]. Several potential

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applications have been reported due to their unique physical and chemical properties such as ; a transparent conductive electrodes [6], solar cells and gas sensing material and devices, etc [1-7]. The most common phases of tin oxide are tin (II) or SnO_2 and tin (IV) or SnO_2 which are more stable [6,7]. In spite of many studies on the oxidation of SnO_x thin films prepared from Sn or SnO_2 precursors, there is little amount of work on the oxidation process of SnO2 nano-particles found in the literature[7]. The best known crystallographic structures of SnO_2 are Orthorhombic and tetragonal which are thermodynamically more stable [8,10]. A variety of techniques have been used to deposit TO films on different substrates. These includes; thermal evaporation [8], spray pyrolusis, chemical vapor deposition, sputtering and pulsed laser deposition methods [1,6]. Band gap range of (1.4-3.2) eV has been reported using this techniques [3]. Among these techniques, thermal evaporation has classified as a simple, reproducible and inexpensive as well as simple experimental arrangement [1]. It is reported that the crystallite sizes in the film could be controlled over a nm range by varying the film thickness, deposition method and post deposition annealing [1,9]. It is known that annealing treatments influence the normalized conductance of SnO_2 thin film. However, this can be due to changes in crystallites size as well as in the crystal phase [10]. There are two distinct techniques used for annealing; thermal furnace annealing (TFA) and rapid thermal annealing (RTA) [8].

Therefore, our objective in this work was to prepare SnO_2 thin films by thermal evaporation method, extensive characterization is also performed in order to explore the relationship of the morphology, crystallinity and nano-size with post annealing of the TO films.

EXPERIMENTAL METHODOLOGY

Preparation of the thin films

Thin films of tin oxide are prepared by using thermal evaporation technique (Edwards system) at room temperature under low vacuum of 10^{-6} torr. Spectrosopically pure (about 99.9%) tin oxide powder is used as the source material. Glass slides have been used as the substrates after cleaned by alcohol with ultrasonic waves to improve the adhesion of the coating to the glass substrate. The thicknesses of the films are monitored by interferometric method.

The resulting films then passed through an tube furnace for a fixed temperature of 250 ^{o}C and for a different annealing duration (10, 20, 30 and 40) minutes. The procedure allowed fabricating almost equal sized nano- particles with a very good crystallinity, in which the size could be selected independently from the synthesis conditions. See figure (1).

CHARACTERIZATION

The structural, morphological and optical properties have been studied. The surface morphology and roughness of the film was examined by atomic force microscopy (AFM). The structure was analyzed by fourier transform infrared reflection (FTIR). Also spectrophotometer (dual double beam) was used to study the bang gap energy of the prepared films.

RESULT AND DISCUSSION

Fourier Transformation Infrared results give information about phase composition and the way in which oxygen is bound to metal ions. Figure (2) shows that the absorption peak is around (447-2854)cm^{-1} spectra which is related to the tin oxide annealed for 40 minutes with a constant temperature of 250 ^{o}C. the peaks shown in the figure are (694, 725, 879, 975, 1743,and1780) cm^{-1}. The peaks can be assigned to O-Sn-O , Sn-O-Sn stretching vibrations, and to lattice vibrations. Peaks at 665, 770 and 960 cm^{-1}, respectively; their peaks were comparatively narrower in comparison with the FTIR spectra. This may be due to amorphous and nano-crystalline nature of these films. The shape of FTIR spectra and positions of the peaks have been shown to vary with the synthesis routes and particle size. Also the mean kinetic energy of the Sn atoms decreases through the annealing time. So, chemical bonding like (Sn-0) vibrational and (O-Sn-O) stretching modes are formed respectively.

The surface morphology of 150 nm thick SnO2 films was analyzed using an Atomic Force Microscope (AFM).The AFM images of the SnO_2 thin films after annealing are shown in Fig.(3). We can see that with oxidation, the distribution of particles become more consistent and the size is larger. During the annealing process, the atoms of the film get enough energy, so that the position of the atoms changes and re-crystallization occurs. The density and homogeneity of the film improve after annealing. Images of microstructure for various annealing times are shown in Fig.(3a). The average particle size measured for lower annealing duration (annealed for 10 minutes at 250 ^{o}C) was found to be 101 nm and for more time (40 minutes) it was found to be 109 nm see figure (3b). This clearly indicates that the annealing time inhibits grain growth. The microstructural images taken for all samples revealed that the grain sizes in general were smaller than those for further annealed samples. The higher points in Fig. 4 correspond to the lightest parts of the photo, and dark parts reflect the deepest regions. As it may be seen, the film under investigation is enough uniform and consists of approximately equalize Nano-grains.

The optical transmittances spectra of the SnO_2 deposited thin film then annealed at different oxidation durations were recorded. The variation of optical transmittance (%T) with wavelength λ of tin oxide film at glass substrate, It was found that the average transmittance of the film is 70% see fig (4). The absorption coefficient can be calculated from the Lambert's formula.

$$\alpha = (1/t) \log (1/T)$$

Where, t = is a thickness of the film T= is a transmittance of the film. The value of absorption coefficient (α) is of the order of 10^4 cm−1. Absorption coefficient decreases with increase in annealing time.

The different transmittance behavior of the film consists with the crystal difference of them, in order to estimate the size of the band gap of the films at low annealing time.

Fig. (5)shows the variation of $(\alpha h\nu)^2$ & ($h\nu$) for the determining of the band gap Eg of SnO_2 film by extrapolation of curve (the optimum condition of 30 min) . The band gap is determined by extrapolating the straight line portion of the plot to the

energy axis. The intercept on energy axis gives the value of band gap energy for all the samples. The incident photon energy is related to the direct band gap Eg and it increased from 3·5–3·8 eV by increasing the annealing time. The direct optical band gap increases to give a blue shift. This shift is due to increase in carrier concentration which results in filling the bottom of the conduction band and this filling prevents the transition of the photogenerated carriers into the filled levels according to quantum rules and hence leads to far transition with larger photon energy. Any variation in transmittance caused by annealing may be related with non-stoichiometry, improvement in the structural order, removal of residual stresses and defects formed during film deposition.

CONCLUSIONS

We have concluded that Tin oxide (SnO_2) thin films were deposited successfully by thermal evaporation deposition technique using Sn metal. Post deposition annealing of the film at temperature of 250^oC and different annealing duration of (10, 20, 30 and 40 minutes) sharpened the properties of the films. The shape of FTIR spectra and positions of the peaks vary with the synthesis routes and particle size. Also the mean kinetic energy of the Sn atoms decreases through the duration of the annealing. So, chemical bonding like (Sn-0) vibrational and (O-Sn-O) stretching modes are formed respectively. Increasing the annealing time increases the grain size and the surface roughness. SnO_2 film is a transparent oxide film. It has a very high transmittance in all the regions of the electromagnetic spectrum. The transmittance increased from UV-NIR regions up to 75%. Band gap of 3.5-3.8 eV were obtained for the oxide film under various annealing times.

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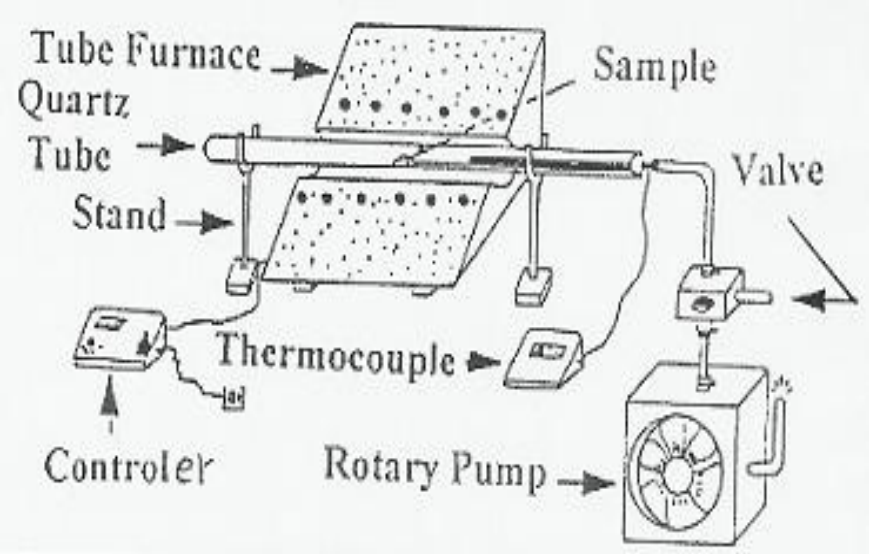


Figure (1) Set up of thermal oxidation

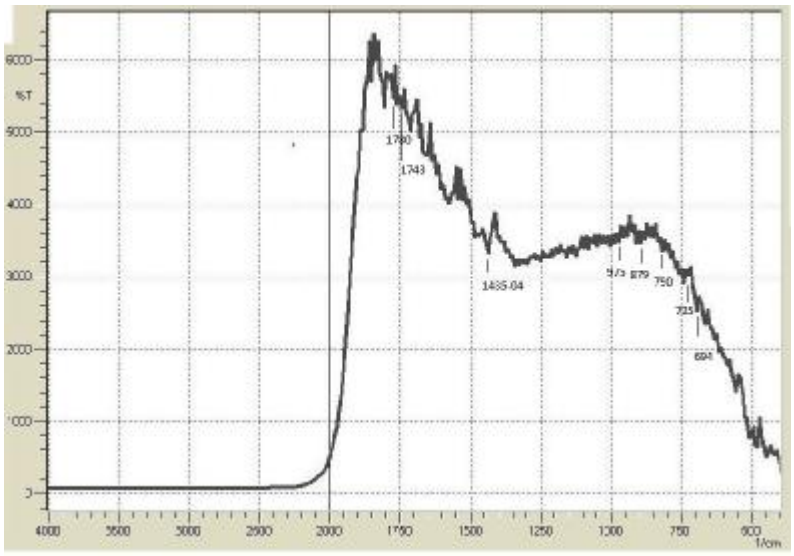
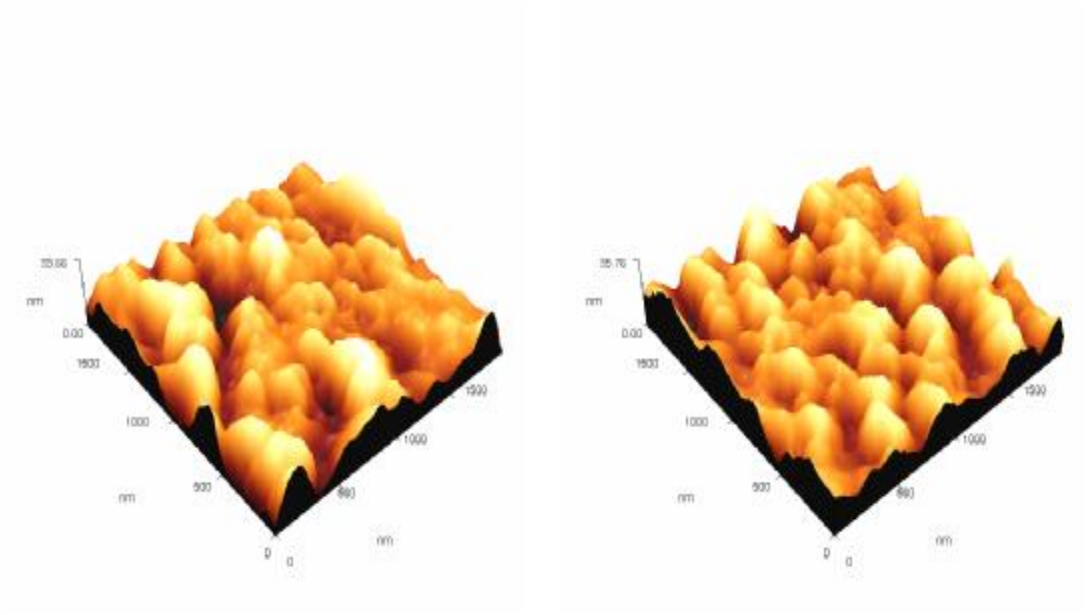


Figure (2): FTIR peaks of oxidized SnO_2 films at 40 minutes.



(a) **(b)**

Figure (3) AFM images of Tin oxide annealed for a)10 minutes, b)40 minutes.

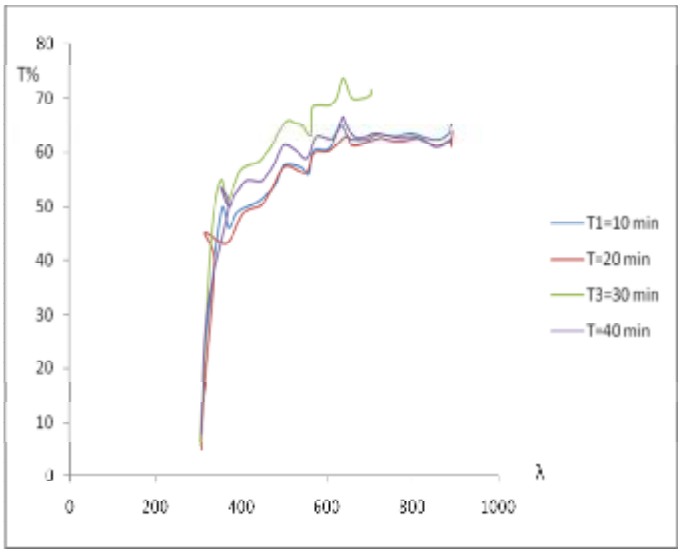


Figure (4) Transmittance of tin thin film oxidized for different time

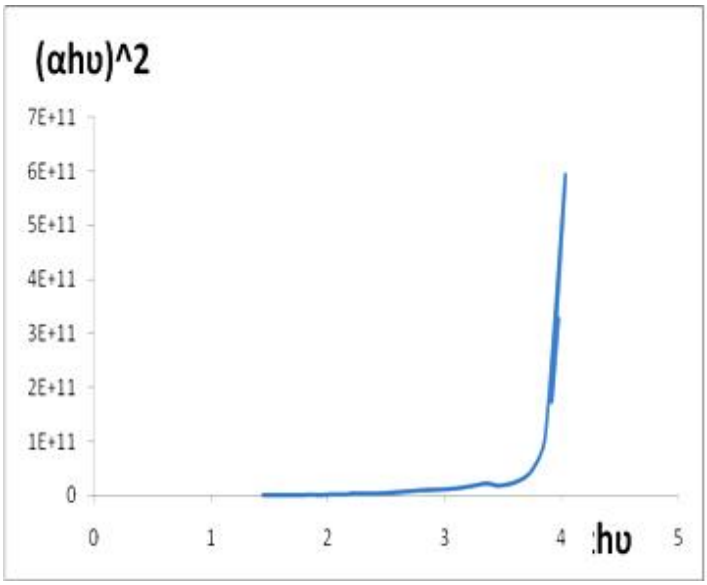


Figure (5) $(\alpha h\upsilon)^2$-hυ variation of SnO_2 film