Eng. &Tech.Journal, Vol. 32,Part (B), No.3, 2014

The 4th International scientific Conference on Nanotechnology& Advanced Materials & Their Applications (ICNAMA 2013)3-4 Nov, 2013

Influence of Deposition Temperature on Structure and Morphology of Nanostructured Sno_2 Films Synthesized by Pulsed Laser Deposition (PLD)

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ABSTRACT

Nanostructured Tin oxide thin films were deposited on the Si (111) substrate using pulsed laser deposition technique at different substrate temperatures (200, 300,400 and 500 °C) in an oxygen pressure ($5*10^{-1}$ mbar). The structure and morphology of the as-deposited films indicate that the film crystallinity and surface topography are influenced by the deposition temperature by changing from an almost amorphous to crystalline nanostructure and rougher topography at a higher substrate temperature. Hall Effect has been studied to estimate the type of carriers, from the result we deduced that the SnO_2 thin films are **n**-type.

Keywords: Pulsed Laser Deposition (PLD), Sno_2 Thin Films, Nonstructural.

ثاثير درجه حرارة الترسيب على بنية ومورفولوجي التراكيب النانويه لأغشيه ثنائي اوكسيد القصدير المحضرة بطريقه الترسيب بلليزر النبضي

الخلاصه

التراكيب النانويه لثنائي اوكسيد القصدير المرسبة على قواعد من السليكون(111) باستعمال تقنيه الترسيب بالليزر النبضي وبمختلف درجه حرارة الترسيب (200°C,300°C,400°C,500°C) في ضغط أوكسجين ($5*10^{-1}$ mbar) .بينت التراكيب ومورفو لجيه الاغشيه المرسبة ان تبلور الغشاءو الطوبوغرافيا الأسطح قد تتاثر بدرجه حرارة الترسيب بواسطة التغير من عديم التبلور الى تراكيب نانويه متبلورة ومع أسطح خشنه عند درجه الحرارة العالية .وتم دراسة تاثير هول وبينت النتائج ان اغشيه ثنائي اوكسيد القصدير هي من النوع السالب .

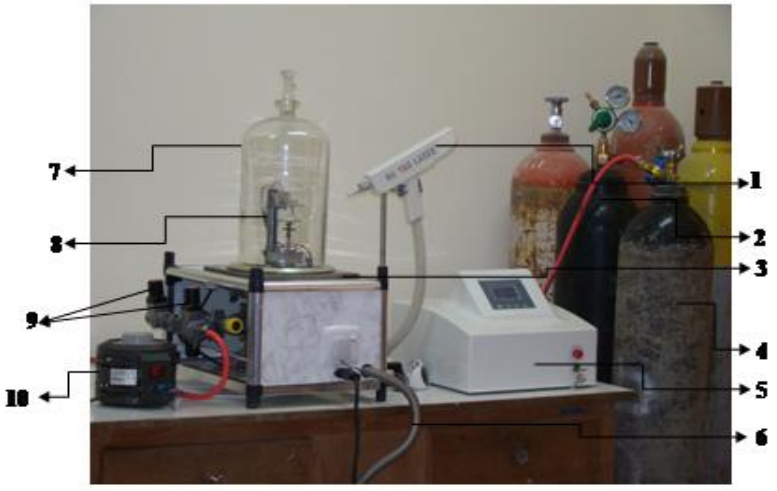
INTRODUCTION

The SnO_2 films are n-type semiconductors with a direct optical band gap of about 3.87–4.3 eV. The valence band is closed shell of oxygen $2S^2$, $2P^6$ state mixed with some Sn states. The structure of the material in its bulk form is tetragonal rutile with lattice parameters $a = b = 4.737$ ˚A and $c = 3.816$ ˚A. However in thin film form, depending on the deposition technique its structure can be polycrystalline or amorphous .The grain size is typically 200–400 ˚A, which is highly dependent on deposition technique, temperature, doping level etc. SnO_2 films close to stoichiometric condition have low free carrier concentration and high resistivity, but non-stoichiometric SnO_2 films have high carrier concentration, conductivity and transparency. This comes from an oxygen vacancy in the structure so that the formula for the thin film material is SnO_{2-x}, where x is the deviation from stoichiometry. [1]Tin dioxide (SnO_2) has many unique physical properties such as high electrical conductivity, high transmittance in the UV-visible region and unusual ferromagnetism, due to its n-type semiconductor behavior and wide band gap. As one of the most import transparent conductive oxide (TCO), SnO_2 and its alloys have been widely used in photovoltaic devices, solar cells, transparent electrodesand gas sensors[2]There are many different techniques used for depositing tin oxide films: r. f. sputtering, dc-magnetron sputtering ,thermal evaporation, ion beam deposition, rheotaxial growth and thermal oxidation (RGTO), chemical vapour deposition, spray pyrolysis, successive ionic layer deposition (SILD) and other chemical methods.Sberveglieri has presented a review of the techniques applied for tin oxide films deposition[3],[4] all methods discussed aquire high substrate temperature or post deposition annealing in order to fabricate good quality polycrystalline films. High temperature, however, damages the surface of the films and increases the interface thickness, which has negative effect on the optical properties, especially on the wave guiding. Pulsed laser deposition technique was successfully applied for growing of quality thin tin oxide films. They were produced by ablation of either Sn metal target or SnO_2 target the substrate use were Si, (001) SiO_2 [5]

We report were deposition of tin oxide layers on Si (111) substrate by laser ablation of SnO_2ceramic targets. The deposits were characterized by X-ray diffraction (XRD) to examine their crystallinity and scanning electron microscopy (SEM) and atomic force microscopy (AFM) to observe the surface structure. Hall Effect to examine type thin film.

EXPERIMENTAL PROCEDURE

The deposition was carried out using a Q switched Nd: YAG laser at 532nm (pulse width 7 nsec and laser fluence 1.2mJ/cm ^{2} . The studied films were prepared by from pure Sno_2 targets films which then were grown by pulsed laser deposition on glass substrates kept distance of 4cm from the SnO_2 target. The chamber shown in Figure (1). The SnO_2 disc was ablated from 10-100 pulses (10-20 min) to get single layered thin films.



1. Nd:YAG Laser Head.
2. O_2 cylinder gas
3. Stainless steel Flange.
4. N_2 cylinder gas.
5. Power supply Nd:YAG laser
6. Flexible tube KF16
7. Quartz Chamber.
8. Substrate holder
9. Vacuum system
10. Variac devices

Figure (1) System of Pulsed laser deposition (PLD).

RESULTS AND DISCUSSION

Figure (2) shows the XRD measurements results of different SnO_2 films formed at substrate temperatures of 200°C ,300° C,400 °C and 500° C on Silicon substrate at laser fluence 1.2J/cm^{2}and Oxygen pressure 5 *10^{-1} mbar and diffraction peaks located at 2θ=28° corresponding to Silicon substrates. It can be seen that the film is amorphous at T_s = 200 °C. When the temperature (T_s) increased to 300 °C, as shown in Figure(2,b) the films exhibit a dominant peak on 2θ =26.7993°, 2θ=34.0813.°,2θ =38.145°, 2θ =51.974°, 2θ=54.9861° corresponding to the (110) ,(101),(211) (200),(220) peaks respectively at T_s =400 °C as shown in figure(2,c) the films show dominant peaks on 2θ =26.652°, 2θ=33.9828.,2θ° =38.015°, 2θ =51.04°, 2θ=54.1161° corresponding to the (110) ,(101),(211), (200),(220) peaks and appeared at 2θ° = 53.75 corresponding to (002) the films show dominant with same peaks with very high intensity at T_s =500 °C by nanosecond ablation of SnO_2 thin film compound mainly consist of polycrystalline phases with the increase in temperature enhances the preferred orientation with an increase in grain size. It is led to decrease in Full Width at Half Maximums (FWHM) of peak .It is clear that the crystalline size at low temperature is lower compared to that at high T_s temperature and increases with increasing of T_s the FWHM of XRD depends on the crystalline quality of each grain and distribution of grain orientation. The FWHM is the reciprocal of the mean grain size as the mean grain size increases this can be confined by **Z.W**. Chen el at. [6] The increase in substrate temperature may cause decrease of the density of nucleation centers and, under these circumstances, a smaller number of centers start to grow, which results in large grains. [7] At a deposition temperature of 500 °C this is

possibly because the hybrid structure of films deposited at this temperature tends to be more homogeneous than that of the completely columnar films produced at higher temperature in which the voids separating then neighboring columns. [8]

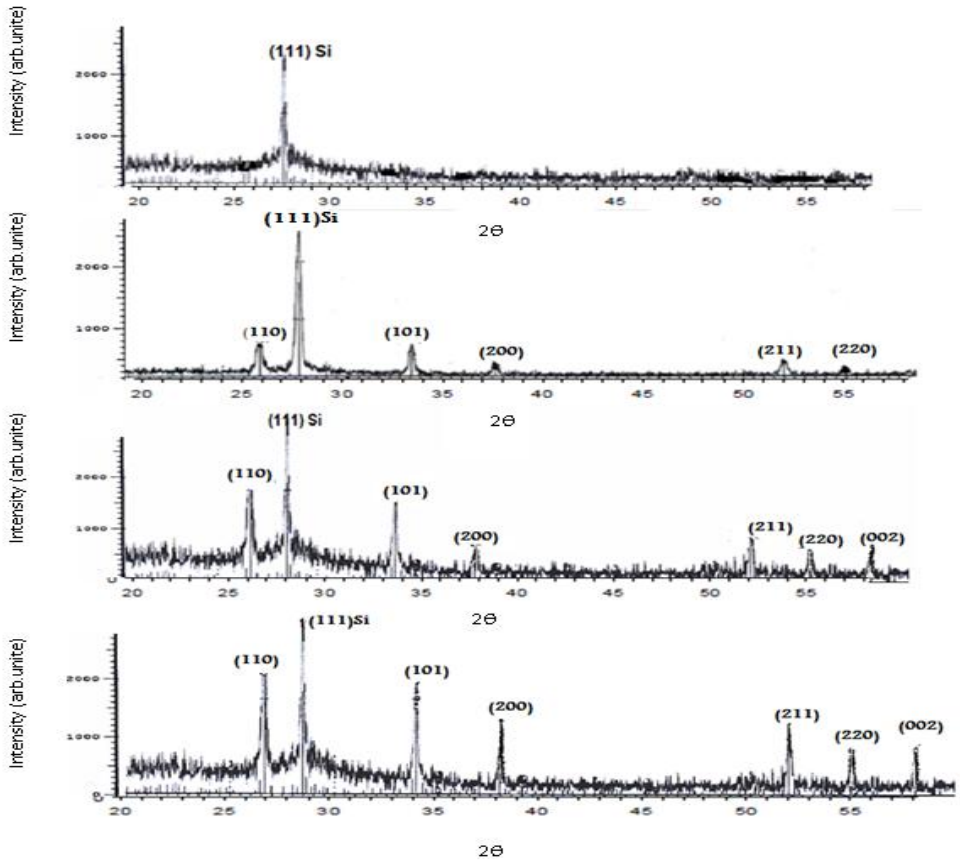
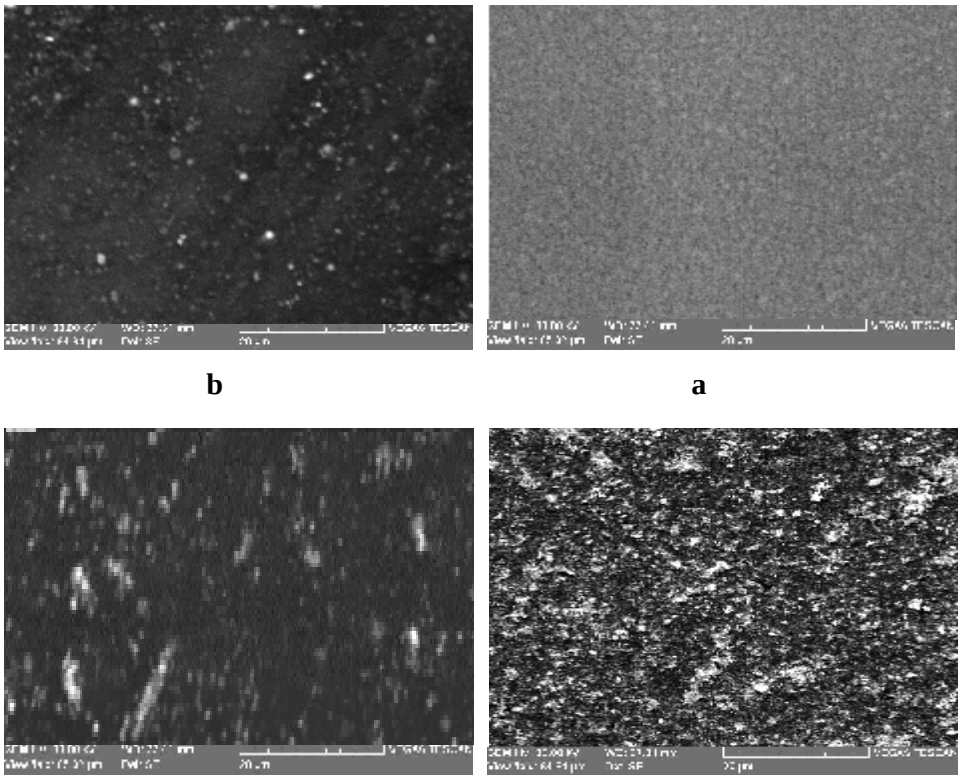


Figure (2) XRD spectra of SnO_2/Si at different substrate temperature a) 200 °C, b) 300 °C, c) 400°Cd) 500° C.

Figure (3) shows the SEM images of the SnO_2 thin films deposited at substrate temperatures of (200,300, 400 and 500) °C. In Figure (3a) the SEM image shows a smooth ,featureless surface in agreement with the amorphous structure observed by XRD a conformal flat film with no evidence of granularity as would be seen for a crystalline film. [9] At (300- 500) °C the film has homogeneous surface morphology, with a wide size distribution of the particles from about (12.75-24 nm) with increasing substrate temperature, the average size of aggregated particles increases when the substrate temperature reaches 500 °C the particle size increases obviously this this can be confined by K. Andan el al. [10] The grain size that calculated from SEM micrograph is given in Table (1).

Table (1)The grain size of the SnO_2 pure films deposited at different substrate temperature with 1.2 J/cm^2 laser fluence and 5*10^{-1} Mbar Oxygen pressure.

sample	*SEM of plane grain size (nm)*
SnO_2/Si 200°C	Unknown
SnO_2/Si 300°C	**12.75**
SnO_2/Si 400°C	**14**
SnO_2/Si 500°C	**24**



b **a**

c **d**

Figure (3) SEM image of the SnO_2/Si thin films deposited at various temperature of a) 200°C, b)300°C c) 400°C, d) 500°C, and laser Fluence 1.2 J/cm^2, O2 pressure=5*10^{-1} mbar.

Figure (4) shows the AFM images of the SnO_2 thin films deposited at substrate temperatures of (200, 300, 400) °C. It can be seen that the crystalline of the films improved and the crystallite size become larger with increasing substrate temperatures as be shown by XRD analysis, in addition ,to that the degree of surface roughness increases. [11] From the topographic images it can be seen that the films

deposited at 400 °C appears to be more uniform than the topography of the sample deposited at 200,300 and 500°C this can be agreed with Jin Jeongel at. [12] The RMS roughness decreased with increasing substrate temperatures to (T_s =500°C) probably because of particle or grain coalescence at a higher deposition temperature. [13] The surface roughness values at different deposition temperatures are shown in Table (2).

Table (2) Morphological characteristics of the SnO_2 Pure films Deposited at different substrate temperature at Oxygen Pressure 5×10^{-1} mbar and 1.2 J/cm^2 laser fluence.

sample	*RMS roughness(nm)*
SnO_2 Pure 200°C	**0.04**
SnO_2 Pure 300°C	**1.42**
SnO_2 Pure 400°C	**4.7**
SnO_2 Pure 500°C	**4.2**

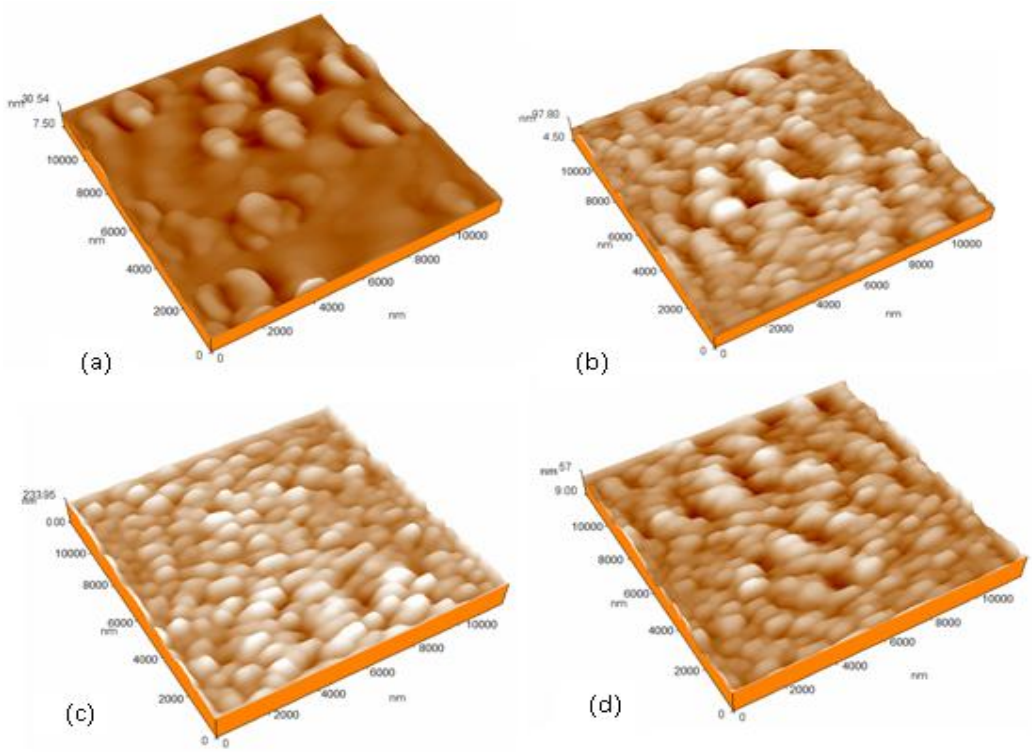


Figure (4) AFM image of the SnO_2/Si thin films deposited at various temperature of) 200°C,) b)300°C c) 400°C, d) 500°C, and laser fluence 1.2 J/cm^2 ,O_2 pressure=$5*10^{-1}$ mbar.

The results of measurements of undoped SnO_2 thin film and deposited at substrate temperature (200 and 300)are that the oxide(SnO_2) have a good conductivity and can be in terpted from the presence of atoms of SnO_2 in positions of compensatory within the lattice crystalline or due to Oxygen vacancy which

means that the atoms of SnO_2 are atoms of donor and this is can be confirmed by the results obtained from Hall effect which indicate that the pure SnO_2 films were n-type this goes in agreement with the previous work T.R. GIRALD and ZHAO Songqing [14],[15] It can be noted from these measurements that increasing the temperature has increased the value of conductivity especially at (400°C), without changing the quality of the semiconductor. This was noted through the negative Whole voltage. The increase in conductivity was accompanied by a little decrease in the value of Hall coefficient and increase in both the number of carriers and mobility charge. The latter is responsible for this increase and as clear in the Table (3). The phenomenon can be explained by the fact that, with the increase of the temperature, better crystallization and greater grain size in the films lead to the decrease of defects density and crystal-boundary. [16][17]

Table (3) The result of electrical measurement for SnO_2 at different substrate temperature.

T(sub)	R_H (cm^3/C)	Carrier type	n$(cm)^{-3}$	σ_{dc} (S/cm)	$_H$ cm^2 /Vs μ
200°C	-5.29	n	1.12×10^{18}	5.34	28
300°C	-5.12	n	1.32×10^{18}	6.8	33
400°C	-4.52	n	1.52×10^{18}	7.3	38

CONCLUSIONS

In this study, the structural and morphological properties of nanostructured SnO_2 films deposited on Si (111) substrates by pulsed laser deposition are directly influenced by the deposition temperature. The grain size and film thickness have been found to increase with increasing deposition temperature. SEM results showed that dense, homogeneous and fully crystalline film has been formed at higher deposition temperatures. XRD results indicate the structural changes induced with the variation of the deposition temperature of the substrate. AFM study reveals that the film surface becomes rougher at a higher deposition temperature (500 °C). The result of Hall Effect measurements, indicate that these films were n–type.

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