Oxygen Effect on Nanostructure SnO_2 Films and Morphology by Pulsed Laser Deposition

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ABSTRACT

This work includes the deposition of SnO_2 as a thin film on Si (111) by using the pulsed laser deposition method. The influences of oxygen pressure on the structural properties of Tin dioxide films were investigated. The X-ray diffraction results show that the structure of the films change from high polycrystalline to worse polycrystalline at an oxygen pressure of 10mbar. The surface morphology of the deposits materials was also studied by using a scanning electron microscope (SEM) and atomic force microscope (AFM). The results show that, the grain sizes of the nano particles observed at the surface depends on the oxygen pressure. As the pressure of the O_2 gas increases the densities of the particles increases too. An oxygen pressure of 5×10^{-1} mbar was found the best pressure for the growth process. While the RMS roughness was seen to increase with increasing oxygen pressure. It was equal to (11.3 nm) for thin films deposited at (300)°C.

Keywords: Pulsed Laser Deposition (PLD), SnO_2 thin films, nonstructural.

تاثيرضغط الاوكسجين على التراكيب النانويه والمورفوليجيه لاغشيه ثنائي اوكسيد القصدير بطريقه الترسيب بالليزرالنبضي

الخلاصه

يتضمن هذا البحث ترسيب ثاني اوكسيد القصدير كأغشيه رقيقه على السليكون باستخدام طريقه الترسيب بالليزر النبضي. وقد تم منا قشة تاثيرضغط الاوكسجين على الخصائص التركيبيه لاغشيه ثنائي اوكسيد القصدير . و بينت نتائج حيود الاشعه السينيه ان تركيب الاغشية قد تغير من تبلور عالي الى تبلور قليل عند ضغط الاوكسيجين ١٠ملي بار . اما مورفولوجا السطح للماده المترسبه فقد تم دراسته ايضا باستخدام المجهر الماسح الالكتروني ومجهر القوى الذريه. وقد بينت النتائج ان الحجم الحبيبي للجسيمات النانويه عند السطح يعتمد على ضغط الاوكسجين. عند زياده ضغط الاوكسجين فان كثافه الجسيمات تزداد ايضا. حيث وجد ان ضغط اوكسجين (٥× ١٠$^{-١}$)

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ملي بار كان افضل ضغط خلال عمليه النمو. بينما لوحظ بان الخشونه انها تزداد مع زياده ضغط الاوكسجين. و كانت تساوي (١١,٣)نانو للاغشيه المرسبه عند درجه حراره ٣٠٠ سيليزي.

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 about 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 electrodes and 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 require 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) SiO2.[5]

We report on deposition of tin oxide layers on si (111) substrate by laser ablation of SnO_2ceramic targets. Silicon oxide is used as a substrate, because of its transparency and low refractive.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.

EXPERIMENTAL PROCEDURE

The deposition was carried out using a Q switched Nd:YAG laser at 532nm (pulse width 7nsec and laser fluence 1.2mJ/cm^2 . The studied films were prepared by from pure Sno_2 targets films were grown by pulsed laser deposition on glass substrates kept distance of 4cm from the Sno_2 target. . During the deposition the substrate temperatures (Ts) were kept at 300 ˚C. 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.

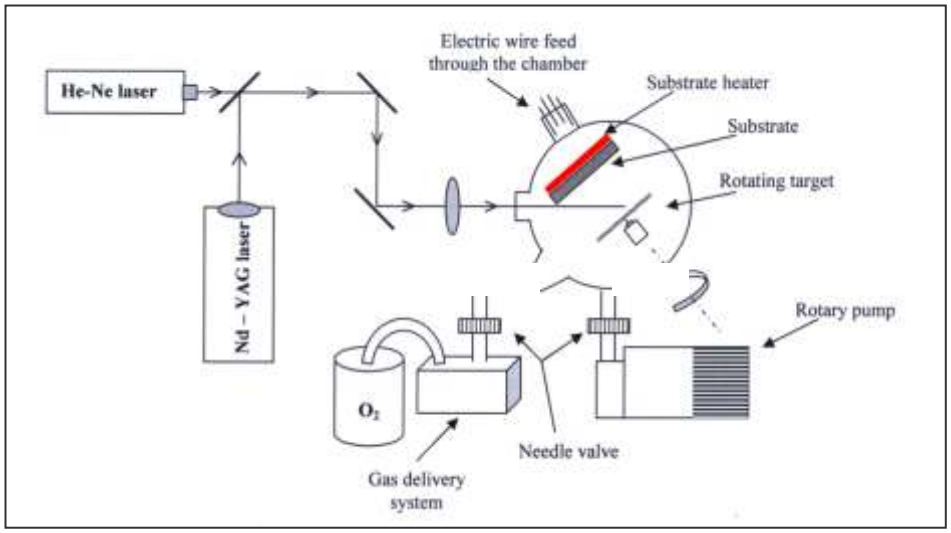


Figure (l) Schematic diagram of the PLD system of this work

Film characterization

The crystalline structure of the films was determined by X-Ray Diffraction (XRD) measurements **(Philips PW** 1050, λ=1.54 A^0) using Cu kα . The surface morphology was examined by **Scanning Electron Microscopy** (SEM–JEOL 7000) and by atomic force microscopy (AFM) (Digital Instruments Nanoscope II) **Scanning Probe Microscope (AA3000)** was used.)

RESULT AND DISCUSSION

Figure (2) shows the XRD patterns of the SnO_2 films grown on Si (111) at T_s =300 ˚C diffraction peaks located at 2θ=28˚ at laser fluence 1.2 J/cm^2 under oxygen pressures of ($5*10^{-2}$, $5*10^{-1}$ and 10 mbar). We can see that, under the oxygen pressure of $5*10^{-2}$ mbar appearances of peak with low intensity The films exhibit a dominant peak on 2θ =27˚, 2θ=34˚, 2θ =52˚ corresponding to the (110) ,(101),(211) peaks respectively as shown in Figure (2-a)where as , at the pressure $5*10^{-1}$ mbar as shown in Figure (2-b) , The films exhibit a dominant peak on 2θ =27˚, 2θ=34˚, 2θ =52˚ corresponding to the (110) ,(101),(211) peaks respectively with high intensity and a appearances of peak on 2θ =38˚, 2θ=54.3 ˚ corresponding to the (200),(220) peaks respectively The increase in peak intensity indicates an improvement in the crystallinity of the films. This leads to decrease in

Full Width at Half Maximums (FWHM) of peak and increase in grain size [6] where as , at the pressure 10 mbar as shown in Figure (2-c) , The films became amorphous and just has a single line of Si(111) substrate.

However, in the case of low oxygen pressure $5*10^{-2}$ mbar the interaction between the ablated species and oxygen molecules was very weak in connection , which resulted in ablated species with sufficiently high kinetic energy to form polycrystalline..When oxygen partial pressure increased, the kinetic energy of the ablated species was presumably reduced and the crystalline of it becomes high polycrystalline. When the oxygen pressure further increased to 10mbar, the SnO_2 films became amorphous, indicating that the pressure was so high that the plasma form the target was prevented from reaching the surface of the substrates and the kinetic energy was so low that the film of a poor crystalline formed[7]

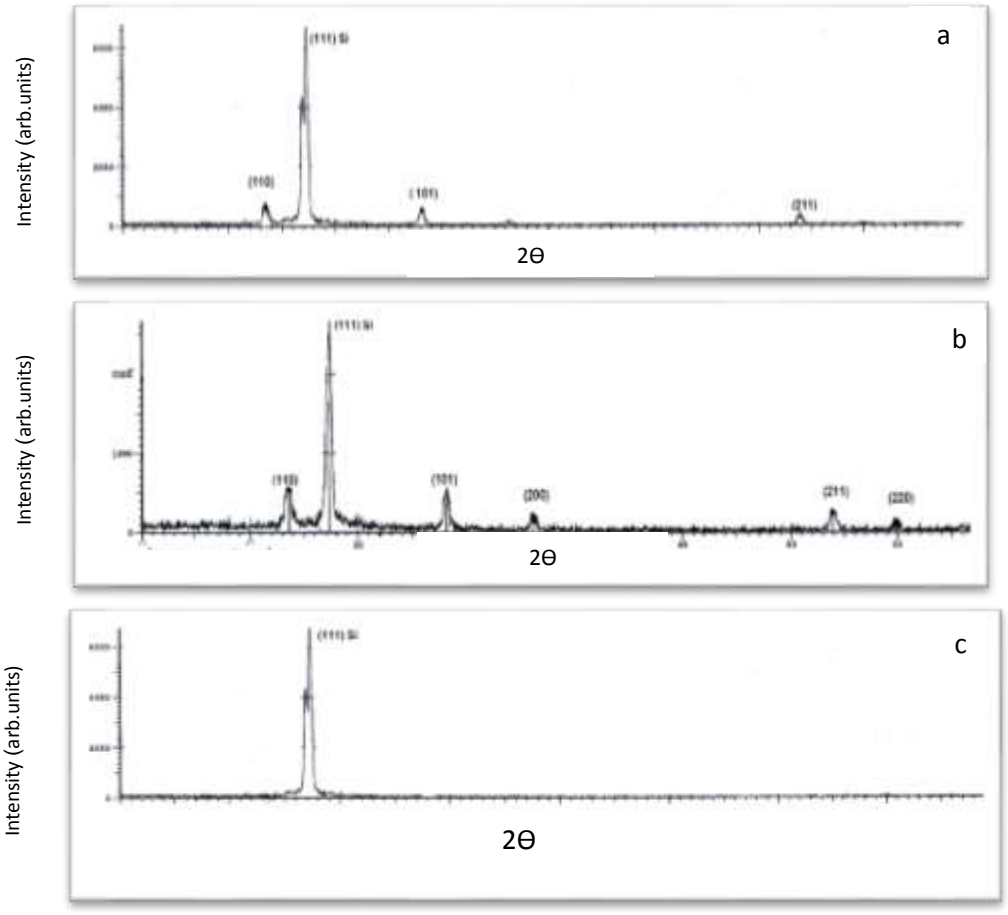
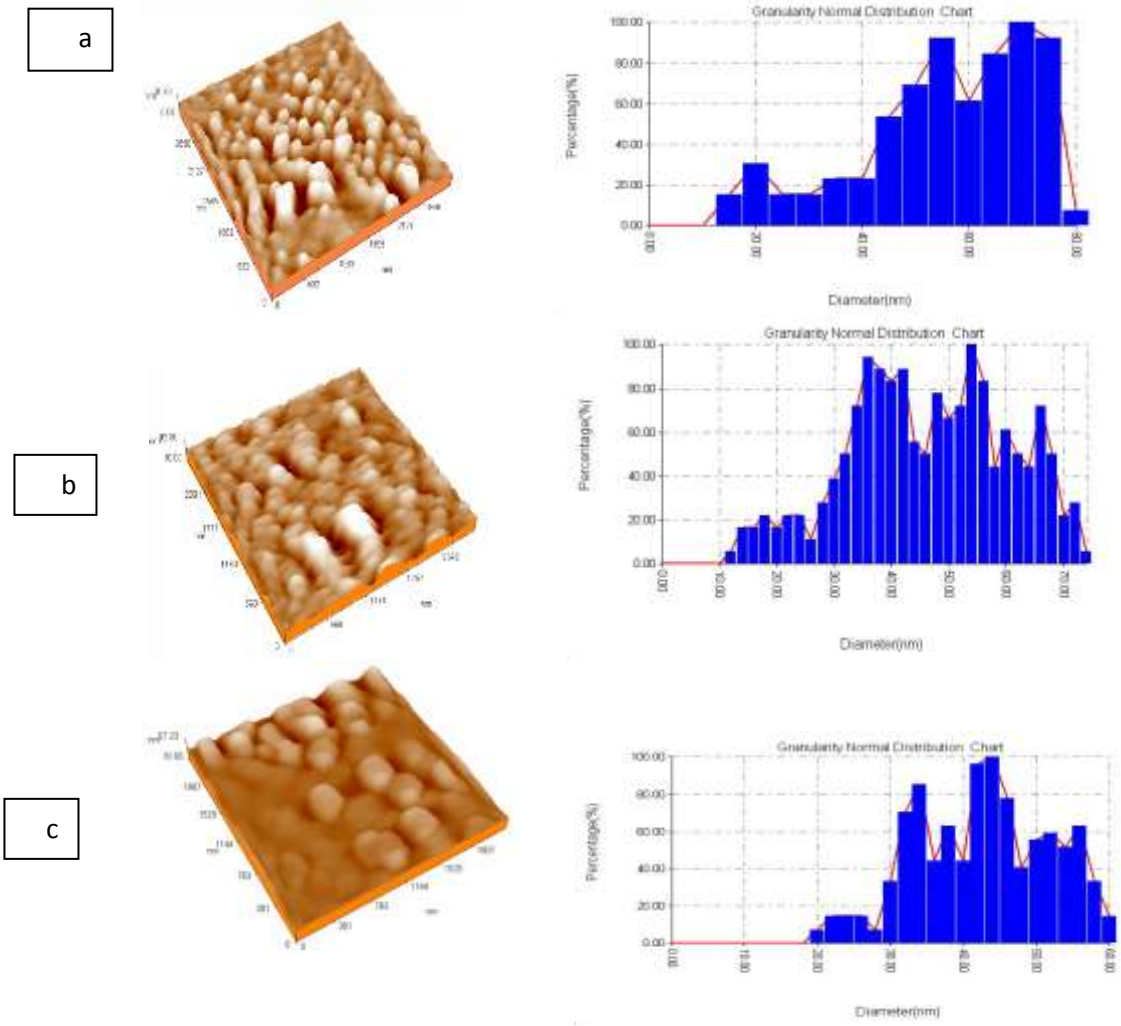


Figure (2) XRD patterns of SnO_2 films grown on Si at various oxygen pressures a) 5×10^{-2}mbar b) 5×10^{-1} mbar c).

The AFM images of the pure SnO_2 /Si films deposited at substrate temperature 300°C and at oxygen pressures of (5×10^{-2} , 5×10^{-1} and 10 mbar) and 1.2 J/cm^2

laser fluence energy are shown in figure (3). The AFM images of the pure SnO_2 thin films observed increasing O_2 pressure which probably leads to the sharp increase of the surface roughness. The RMS roughness values are

(7.5, 11.3 and ..4.3 nm) for thin films deposited at (a=5 $\times 10^{-2}$,b= 5 $\times 10^{-1}$ and c=10 mbar) respectively .The increasing of oxygen pressure presents a very homogeneous distribution of the nanoparticles. For that morphology, the buffer O_2 gas pressure has influence on the nanostructure of the film surface at the range of several nm. It means that the interaction of the evaporated particles Sn with buffer O_2 gas produced nanoparticles consisting of Sn and O_2 low [8]as shown in Table (1).



Figure(3)AFM image of theSnO_2/Si thin films deposited at various oxygen pressure a) 5*10^{-2} mbar, b) 5*10^{-1} mbar and c) 10 mbar at substrate temperature 300 ˚C and 1.2 J/cm^2 laser fluence energy

The SEM images of the films deposited at fixed substrate temperature of 300 °C and at oxygen pressures of (5×10^{-2} , 5×10^{-1} and 10 mbar) and 1.2 J/cm^2 laser fluence energy are shown in figure (4). It is evident that quite different surface morphologies are evolved depending on O_2 pressure during film growth.

As shown in Fig(4) the growth at O_2 pressure of 5×10^{-1} mbar consists of much larger grains and exhibits a rougher surface than the film grown at the low O_2 pressure of 5×10^{-2} mbar.

The mechanism for the grain formation is described as follow. After initial free expansion from the target surface, the mean free path of the ablated particles is reduced in the presence of gas. More specifically, at higher ambient pressure, the more collisions and scatterings occur. Then the particles lose energy to the level adequate for forming ionic complexes or molecules. If these clusters reach the substrate surface, small grains, start to grow as they become the nucleus. On the other hand, most of the ablated particles can reach the substrate in the state near the single atoms if the ambient pressure is extremely low [9]

The SEM image shows a smooth, featureless surface in agreement with the amorphous structure observed by XRD [10] in Table (1).

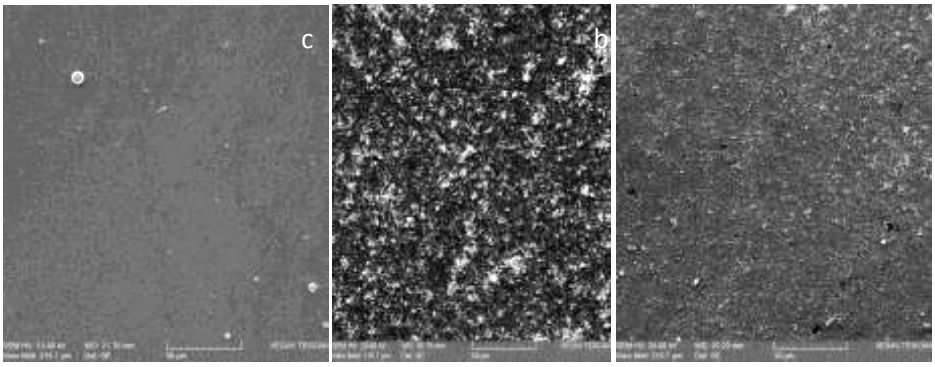


Figure (4) SEM image of theSnO_2/Si thin films deposited at various oxygen pressure a) 5*10^{-2} mbar, b) 5*10^{-1} mbar and c) 10 mbar at substrate temperature 300 °C and 1.2 J/cm^2 laser fluence energy

Table (1). morphological characteristics of the SnO_2 Pure films deposited at different Oxygen pressure with 300 °C substrate temperature and 1.2 J/cm^2 laser fluence

sample	*(O_2) Pressure mbar*	*SEM of plane grain size (nm)*	*AFM of plane grain size (nm)*	*RMS roughness*
SnO_2/Si	**5×10^{-2}**	**35**	**41.6**	**4.5 nm**
SnO_2/Si	**5×10^{-1}**	**36**	**45.41**	**11.3nm**
SnO_2/Si	**10**	**50**	**53.27**	**7.3 nm**

CONCLUSIONS

at the pressure $5*10^{-1}$ mbar The films exhibit a dominant peak on $2\theta = 27^{\circ}$, $2\theta = 34^{\circ}$, $2\theta = 52^{\circ}$ corresponding to the (110) ,(101),(211) peaks respectively with high intensity and a appearances of peak on $2\theta = 38^{\circ}$, $2\theta = 54.3^{\circ}$ corresponding to the (200),(220) peaks respectively The increase in peak intensity indicates an improvement in the crystallinity of the films. This leads to decrease in Full Width at Half Maximums (FWHM) of peak and increase in grain size where as , at the pressure 10 mbar as the films became amorphous .The SEM image shows a smooth agreement with the amorphous structure observed by XRD.. The AFM image shows The growth at O_2 pressure of $5*10^{-1}$ mbar consists of much larger a rougher surface reach to 11.3nm than the film grown at O_2 pressure of 5×10^{-2} and 10 mbar As the pressure of the O_2 gas increases.

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