

Study the Effect of Ambient Oxygen Pressure on Structural and Optical Properties of Pure SnO₂ Thin films Prepared by Pulsed Laser Deposition

دراسة تأثير ضغط الاوكسجين على الخواص التركيبية والبصرية لآغشية الرقيقة لثاني اوكسيد

القصدير النقي المحضر بواسطة الترسيب بالليزر النبضي

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Abstract

Polycrystalline pure SnO₂ thin films were deposited on glass substrates at fixed substrate temperature (400C°) by (Nd-YAG)pulsed laser deposition (PLD) with pulse energy(5000 mJ), pulse width(10ns) at a different ambient oxygen pressure ($10^{-1}, 10^{-2}, 10^{-3}$) torr. The effect of ambient oxygen pressure on the structural and optical properties of SnO₂ thin films was studied. (XRD) X-ray diffraction and AFM (atomic force microscopy) methods were used to examine the structure and morphology of the films in this work. From (XRD) X-ray diffraction of the SnO₂ films, it was found that the deposited films showed some differences compared with the oxygen pressure and the intensities of the peaks of the crystalline phases decreased with the increase of oxygen. From AFM images, the distinct variations in the morphology of the thin films were also observed, from the transmittance of SnO₂ it was found that the optical transmission of SnO₂ films at high oxygen pressure is low than for low ambient oxygen pressure.

الخلاصة:

الغشاء الرقيق متعدد البلورات ثاني اوكسيد القصدير النقي تم ترسيبه على ارضيات زجاجية عند درجة حرارة اساس 400 سيلزية بواسطة الترسيب بليزر النديميوم ياك النبضي بطاقة 5000 ملي جول ,وعرض نبضة الليزر 10 نانو ثانية عند ضغوط مختلفة للاوكسجين ($10^{-1}, 10^{-2}, 10^{-3}$) ملم.زئبق. تمت دراسة تأثير ضغط الاوكسجين على الخواص التركيبية والبصرية لآغشية ثاني اوكسيد القصدير في هذا العمل تم فحص تركيب وطوبوغرافية الأغشية بأستعمال حيود الأشعة السينية (XRD) ومجهر القوى الذرية (AFM). من انماط حيود الأشعة السينية لآغشية ثاني اوكسيد القصدير وجد أن الأغشية المرسبة أظهرت بعض الاختلافات بتغير ضغط الاوكسجين وشداث القمم للأطوار البلورية تقل بزيادة الاوكسجين . من صور مجهر القوى الذرية لاحظنا أختلافات متميزة في طوبوغرافية الأغشية الرقيقة . من نفاذية ثاني اوكسيد القصدير وجدنا انه النفاذية البصرية لغشاء ثاني اوكسيد القصدير عند ضغط الاوكسجين العالي اقل مما في حالة ضغط الاوكسجين القليلة.

1-Introduction:

Pulsed laser deposition (PLD) is a thin film deposition method which uses short and intensive laser pulses to evaporate target material. The ablated particles escape from the target and condense on the substrate. The deposition process occurs in a vacuum chamber to minimize the scattering of the particles[1,4].

Earlier a seemingly esoteric technique of Pulsed Laser Deposition (PLD) has emerged as a potential methodology for growing nanostructures of various materials including semiconductors[1]. Since it is a cold-wall processing, which excites only the beam focused areas on the target enabling a clean ambient, it is highly suited for the growth of nanostructures with high chemical purity and controlled Stoichiometry.

The other characteristics of PLD such as its ability to create high-energy source particles, permitting high quality film growth at low substrate temperatures [2], simple and inexpensive experimental setup, possible operation in high ambient gas pressure, and sequential multi-target and multi-

component materials' congruent evaporation make it particularly suited for the growth of oxide thin films and nanostructures.

Tin oxide (SnO_2) is an n-type semiconductor with band gap of $E_g = 3.62\text{--}4.00\text{eV}$ at room temperature [3]. The (SnO_2) research for its applications has been mainly focused on this films. Up to date, (SnO_2) thin films have been achieved by a variety of deposition techniques such as chemical vapor deposition (CVD) [5,6], sol-gel processing [7,8], reactive sputtering [9] and pulsed laser deposition (PLD) [10,11]. Among these fabrication techniques, PLD has attached much attention. It is well known that ambient oxygen pressure is one of the key experimental parameters in the process of PLD. In this paper, (SnO_2) thin films were prepared by PLD and the influence of ambient oxygen pressure ($10^{-1}, 10^{-2}, 10^{-3}$) torr on structural and optical properties of SnO_2 thin films were reported.

2-Experimental procedures:

SnO_2 thin films were prepared by pulsed laser deposition system with a titanium target of 99.99% purity on microscope glass slides as substrates. The target was pressed less than 5 ton to form a target with 2.5 cm diameter and 0.4 cm thickness. Microscope glass slides were used as the substrates for thin films. Prior to deposition, the glass slides were sequentially cleaned in an ultrasonic bath with ethanol. Finally they were rinsed with distilled water and dried. The substrate is placed in front of the target with its surface parallel to that of the target the substrate deposited at temperature 400°C with Oxygen pressure ($10^{-1}, 10^{-2}, 10^{-3}$) torr. The pulsed laser deposition is carried out inside a vacuum chamber generally at three different oxygen pressures. Nd-YAG laser (Huafei Tangda Technology-Diamond-288 pattern EPLS) second harmonic generation with laser wavelength (1064/532)nm, pulse energy (100-1000)mJ, pulse width (10ns). The focused Nd-YAG SHG Q-switching laser beam coming through a window is incident on the target surface making an angle of 45° with it, given in Fig (1) below.



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

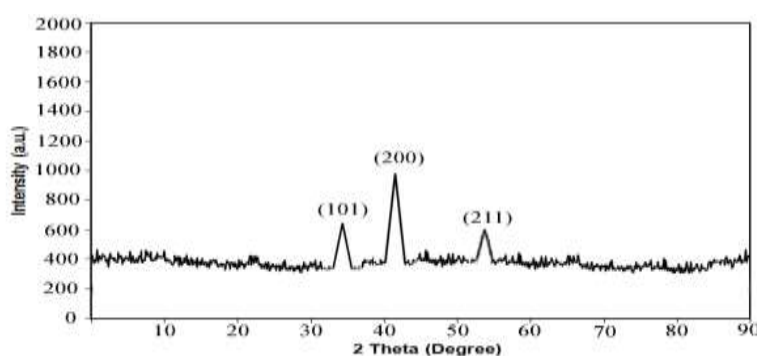
Figure (1): Pulsed laser deposition (PLD) system

3-Results and Discussion:

3-1 Effect of the Ambient Oxygen Pressure on Structural Properties of Pure SnO₂ Thin Films:

Structure and Morphology:

The oxygen pressure also plays an important role in the film crystallinity, in this work the crystalline properties of the SnO₂ films were analyzed by an X-ray diffractometer (Model-PW1050, Philips) using Cu-K α radiations ($\lambda=1.54$ Å). Data were acquired over the range of 2θ from 10° to 90° . The XRD method was used to study the change of crystalline structure, at fixed substrate temperature under three different ambient oxygen pressure (10^{-1} , 10^{-2} , 10^{-3}) torr as shown in Fig (2), (3) and (4). Fig. (2) shows the XRD measurements results of the different SnO₂ films deposition at 400°C on glass substrate at laser fluence 0.8 J/cm^2 . While the oxygen pressure was 10^{-3} torr. It can be seen that the film is crystalline. three diffraction peaks located at $2\theta=33.28^\circ$, $2\theta=41.5^\circ$ and $2\theta=53.5^\circ$ are found, which belong to (R) rutile (101), (200) and (211) peaks, respectively. When the Oxygen reached to 10^{-2} torr, as shown in curve fig.(3) the peak becomes small stronger and sharper, Like this as shown in curve fig.(4).



Fig(2)the XRD measurements results of the different SnO₂ films deposition at 10^{-3} torr deposited on glass substrate at 400°C .

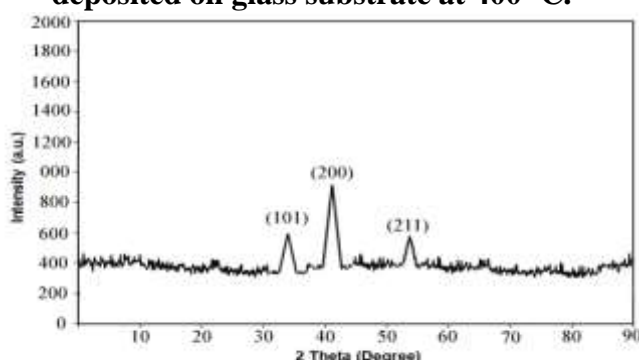


Fig (3) The XRD measurements results of the different SnO₂ films deposition at 10^{-2} torr deposited on glass substrate at 400°C .

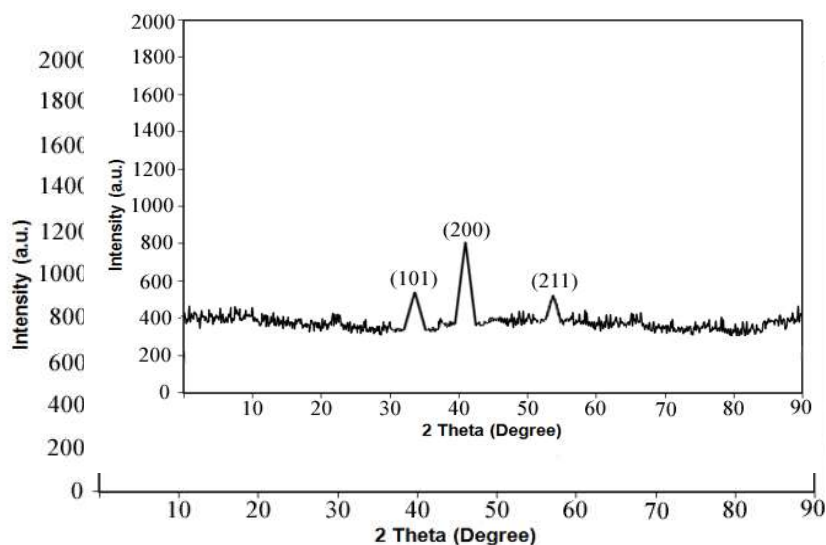


Fig (4) The (X-ray diffraction) XRD measurements results of the different SnO₂ films deposition at 10⁻¹ torr deposited on glass substrate at 400 °C.

In order to reveal a possible reason for the deterioration in crystalline quality for the SnO₂ film grown at high oxygen pressure 10⁻¹, 10⁻² torr, we first considered the strain that may be accumulated in the film. The (200) lattice spacing of the SnO₂ films was estimated from the XRD (X-ray Diffraction) (200) peak position in order to calculate how much strain was present in the films, the lattice spacing for the films deposited at 10⁻¹, 10⁻² is large. In general, SnO₂ films are deficient in oxygen. This deficient may be alleviated by high ambient oxygen in the growth chamber during deposition. The higher the O₂ pressure in the growth chamber, the more oxygen is incorporated into the SnO₂ film lattice. When oxygen is excessively incorporated due to a high O₂ pressure, lattice expansion is likely to happen.

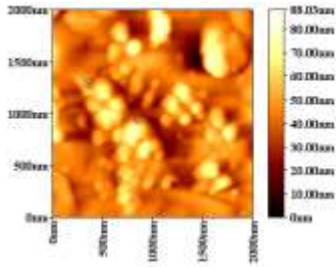
The crystalline quality can be also affected by the kinetic energy, as the oxygen pressure increases; the crystalline quality of the films becomes worse. The ablated species suffer more collision in the gas phase and thereby their velocity of the ablated species is decreased. At lower oxygen pressure, the ablated species have sufficient kinetic energy for diffusion and can thus diffuse to the right crystallographic sites. However at higher oxygen pressure, the ablated species have lesser kinetic energy which results in lesser diffusion resulting in poor crystalline quality of the films.

For morphological investigations, AFM (atomic force microscopy) images were recorded using Nanoscope IIIa and Dimension 3100 scanning probe microscope controller in a tapping mode. The surface morphology of all the SnO₂ films is presented by AFM images in tapping mode shown in Fig. (5) shows AFM images of the SnO₂ pure thin films deposition at pressure (10⁻¹, 10⁻², 10⁻³) torr. From the topographic images it can be seen that the films deposition at 10⁻¹ torr appears to be more uniform than the topography of the sample deposition at 10⁻² torr and 10⁻³ torr. The RMS roughness also increased with increasing Oxygen, the section analysis shows that RMS (root mean square) values are (8.3, 20.4, 55.4) for thin films deposition at pressure (10⁻¹, 10⁻², 10⁻³) torr.

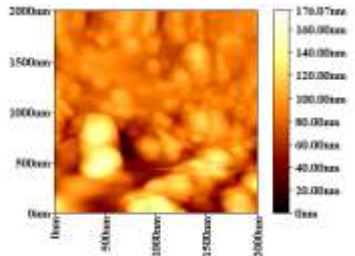
The growth at high O₂ pressure of 10⁻¹ mbar consists of much larger grains and exhibits a rougher surface than the film grown at the low O₂ pressure of 10⁻², 10⁻³ torr [11].

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

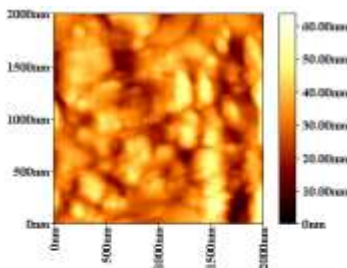
particles lose energy to the level adequate for forming ionic complexes or molecules. If these clusters reach the substrate surface, small grains, start to grow as they become the nucleus. On the other hand, most of the ablated particles can reach the substrate in the state near the single atoms if the ambient pressure is extremely low [12].



a



b



c

Fig (5) AFM images of SnO₂ thin films deposition at a) 10⁻³ torr, b) 10⁻² torr and , c)10⁻¹ torr respectively deposited on glass substrate at 400 °C.

3-2 Effect of the Ambient Oxygen Pressure on optical Properties of Pure SnO₂Thin Films:

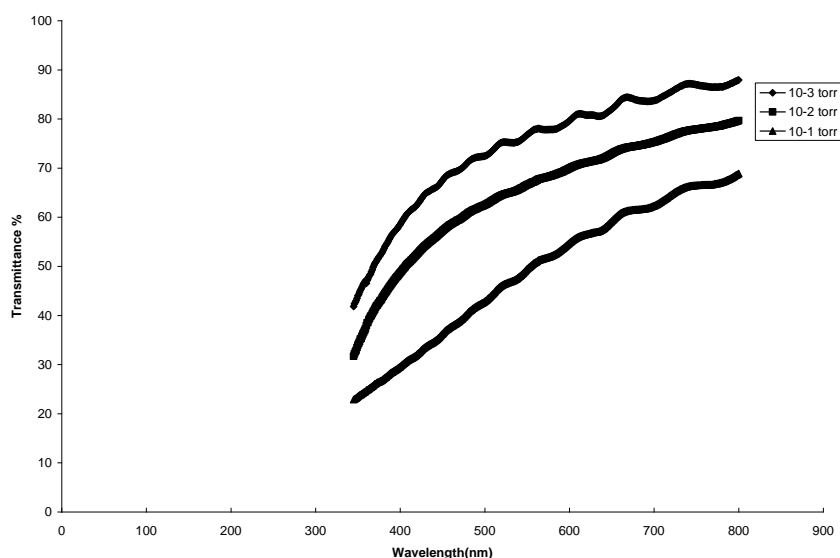


Fig.(6) Transmittance of SnO₂thin films as a function of oxygen pressure

The optical properties of the films deposited by ns-PLD were measured by UV-VIS spectrophotometer. In order to measure the optical transmittance, the laser fluence energy density was set to be 0.8 J/cm² and the oxygen pressure varies from ($10^{-3}, 10^{-2}, 10^{-1}$) torr the UV- VIS optical properties in the range from 190 nm to 800nm at fixed substrate temperature 400C° the mean transmittance (%) is large than 87% in the visible range. It is found that the optical transmission of the SnO₂ films at high oxygen pressure is low than for low oxygen pressure, this is indicate that the decreases in optical transmission with increases oxygen pressure is due to the grain size cause, the lower oxygen pressures inducing smaller grain size[11,13].

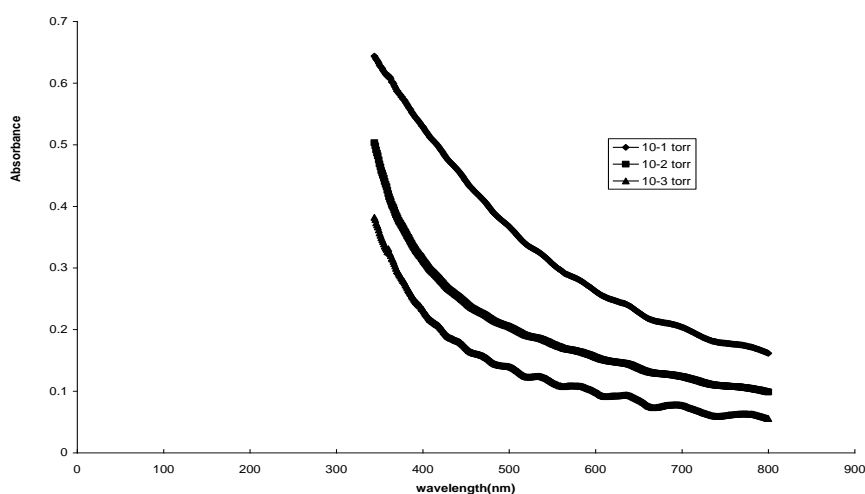


Fig.(7) Absorbance of SnO₂thin films as a function of oxygen pressures.

In fig (7) represents the absorbance spectrum of SnO_2 thin films as a function of wavelength under different oxygen pressure, it found that the value of absorbance decreased with increasing wavelength and the absorbance decreased slightly at the low energies region (long wavelengths) while it decreased clearly at high energies region (short wavelengths).

4- Conclusions:

The structural and optical properties of polycrystalline tin oxide SnO_2 thin films by PLD have been investigated as a function of oxygen pressure. The surface roughness increased as the oxygen pressure increased. The transmittance of the thin films is larger than 80% at VIS and NIR so it used as a window layer and heat reflectors in solar cells.

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