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

Preparation and Characterization of (Tio_2-Sno_2) Thin Films by Pulsed Laser Deposition

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ABSTRACT

In this work, mixed oxide (TiO_2-SnO_2) thin films were grown on Si (111) and glass substrates by pulsed laser deposition (PLD) method. The influences of increasing amounts of SnO_2 were investigated. The X-ray diffraction results show the peaks position of the plane was shifted towards higher angle values with increasing amounts of SnO_2. The surface morphology of the deposits materials was also studied by using a scanning electron microscope(SEM) The results show that, the grain sizes decreases with increasing SnO_2 content from the largest value (53.6)nm to smallest value (25.5) nm. From UV-visible spectroscopy, the distinct variations in the transmission spectra, and optical energy gap, of the thin films were also observed.

Keywords: Pulsed Laser Deposition (PLD), (Tio_2-Sno_2) Thin Films, Structural Properties, Surface Morphology, Optical Properties

تحضيرودراسة اغشية رقيقة مكونة من خليط اوكسيد التيتانيوم واوكسيد القصديربطريقة الترسيب بالليزر النبضي

الخلاصة

يتضمن هذا العمل ترسيب اغشية رقيقة من خليط اوكسيد التيتانيوم واوكسيد القصديرعلى السيلكون والزجاج باستخدام طريقة الترسيب بالليزر النبضي وقد تم مناقشة تاثير زيادة نسبة اوكسيد القصديرعلى خصائص خليط اوكسيد التيتانيوم والقصدير.وقد بينت نتائج حيود الاشعة السينية ان موقع القمم انحرفت باتجاه قيم الزوايا الاعلى بزيادة نسبة اوكسيد القصدير.اما مورفولوجية السطح للمادة المترسبة فقد تم دراستها بواسطة المجهر الماسح الالكتروني .وقد بينت النتائج ان الحجم الحبيبي للجسيمات النانوية قل بزيادة نسبة اوكسيد القصديرمن الحجم الحبيبي (53.6 نانومتر) الى الحجم الحبيبي (25.5 نانومتر). وكذلك قد تم ملاحظة التغيرات الحاصلة لطيف النفاذية وكذللك فجوة الطاقةالبصرية بواسطة قياسات مطياف النفاذية للأشعة المرئية وفوق البنفسجية.

INTRODUCTION

Mixed oxide systems have attracted considerable attention The good stability of sensing properties of SnO_2 for reducing gases, combined with the good chemical stability of TiO_2 at high temperatures, stimulate the study on the applications of TiO_2–SnO_2 In particular, TiO_2–SnO_2 system combines the positive features of both materials being used in gas detection [1] and suggested to be applied as high-temperature resistors.[2].

It was concluded by K. Zakrzewska and co-workers that high operating temperatures of TiO_2 sensors could be reduced to about 770 K as a result of Sn incorporation. [3].

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 oxide films deposition[4],[5]., 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 films [6].

This technique is also suitable for depositing oxide films at a relative high deposition rate and low cost [7, 8]. In this work, we report on the growth of (TiO_2-SnO_2) deposits by PLD using10 ns pulses at 532 nm on Si (111) and glass substrates .The deposits were characterized by X-ray diffraction (XRD) to examine their crystallinity , scanning electron microscope (SEM) to observe the surface structure and UV-visible spectroscopy to investigate the optical properties of the films.

EXPERIMENTAL PROCEDURE

Film preparation

The deposition was carried out using a Q- switched Nd:YAG laser with a second harmonic generation (SHG) at wavelength is 532nm with pulse width 7ns and repetition rate 10Hz .The studied films were prepared by mixed oxides (TiO_2-SnO_2) films with different SnO_2 contents(25%,50%and75%) targets films were grown by pulsed laser deposition on Si(111) and glass substrates kept an on-axis distance of 4cm from the target. The chamber was kept at vacuum pressure of 10^{-5} mbar as shown in Figure (1). The (TiO_2-SnO_2) disc was ablated from 10-100 pulses (10-20 min) to get single layered thin films. Consequently, the films were deposited by PLD at 400 $^{\circ}$C substrate temperature in an O_2 pressure 5×10^{-1} mbar and laser fluance (1.4)J/cm^2.

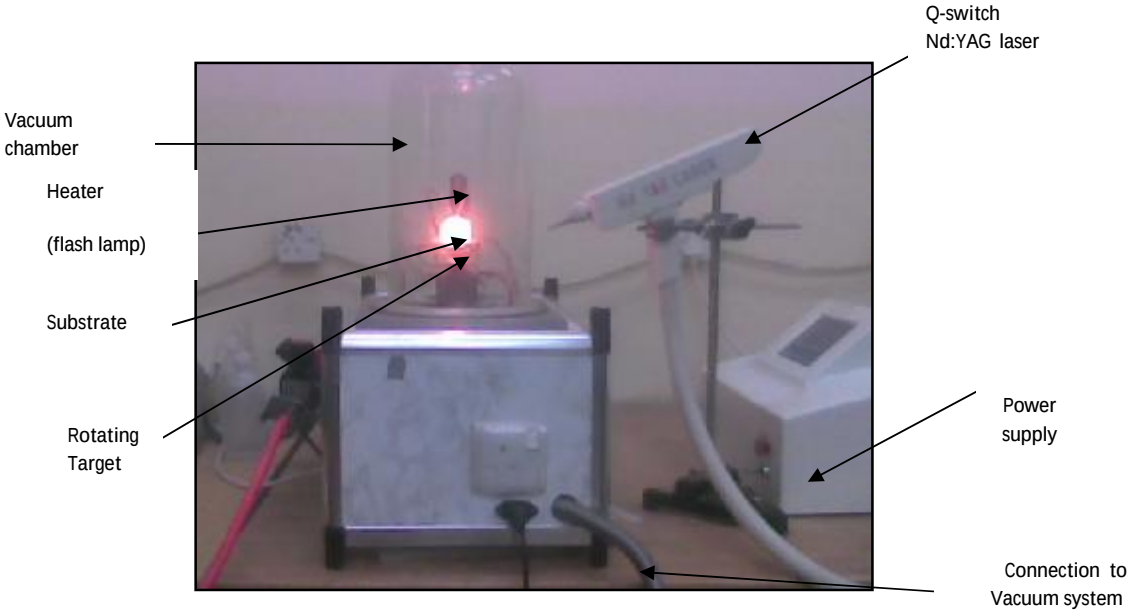


Figure (l) Experimental setup

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 ka . Transmission measurements were performed for a range 300-800 nm using UV-VIS-PV-8800 (Perkin Elemer Company) spectrophotometer. The characterizations included determination of the absorption as a function of incident photon energy, determination of the transmission as a function of incident photon energy and determination the value energy gap. The surface morphology was examined by Scanning Electron Microscopy (SEM–JEOL 7000).

RESULT AND DISCUSSION

Figure (2) shows the XRD patterns of the (TiO_2-SnO_2) films grown on Si (111) at T_s =400 $^{\circ}$C $^{\circ}$ at laser flounce 1.4 J/cm^2 ·diffraction peaks located at 2θ=28° corresponding to Silicon substrates are shown in the Figure below. At SnO_2 25% concentration, showed diffraction peaks located at 2θ=26.9 $^{\circ}$, 2θ=34°and 2θ=52.1°corresponding to the (110), (101) and (211), peaks respectively. At SnO_2 content to 50%, diffraction peaks were located at 2θ=27.0°, 2θ=34. 3°and 2θ=52.6°, corresponding to the (110),(101) and (211) peaks respectively .At 75% concentration , showed diffraction peaks located at 2θ=27.25°, 2θ=34.5° and 2θ=53° corresponding to the (110),(101) and (211) where the peaks position of the plane was shifted towards higher angle (2 θ) values with increasing amounts of SnO_2 content . It has been reported that TiO_2 crystallizes as anatase but even a small addition of Sn changes the crystallographic structure to that of tetragonal rutile. X-ray diffraction peaks are shifted from the positions characteristic to TiO_2-rutile due to the change in the lattice parameters upon the substitution of Sn for Ti. With the increasing tin content, X-ray diffraction lines shift systematically towards positions

typical for tetragonal, cassiterite form of SnO_2. All XRD patterns of films reflect that the crystal lattice of mixed oxide (SnO_2-TiO_2) did not undergo significant changes. XRD analysis also did not detect the TiO_2 phase, these due to the small molecular weight of TiO_2 as compared with that of SnO_2 and dispersion of this small-grain phase.

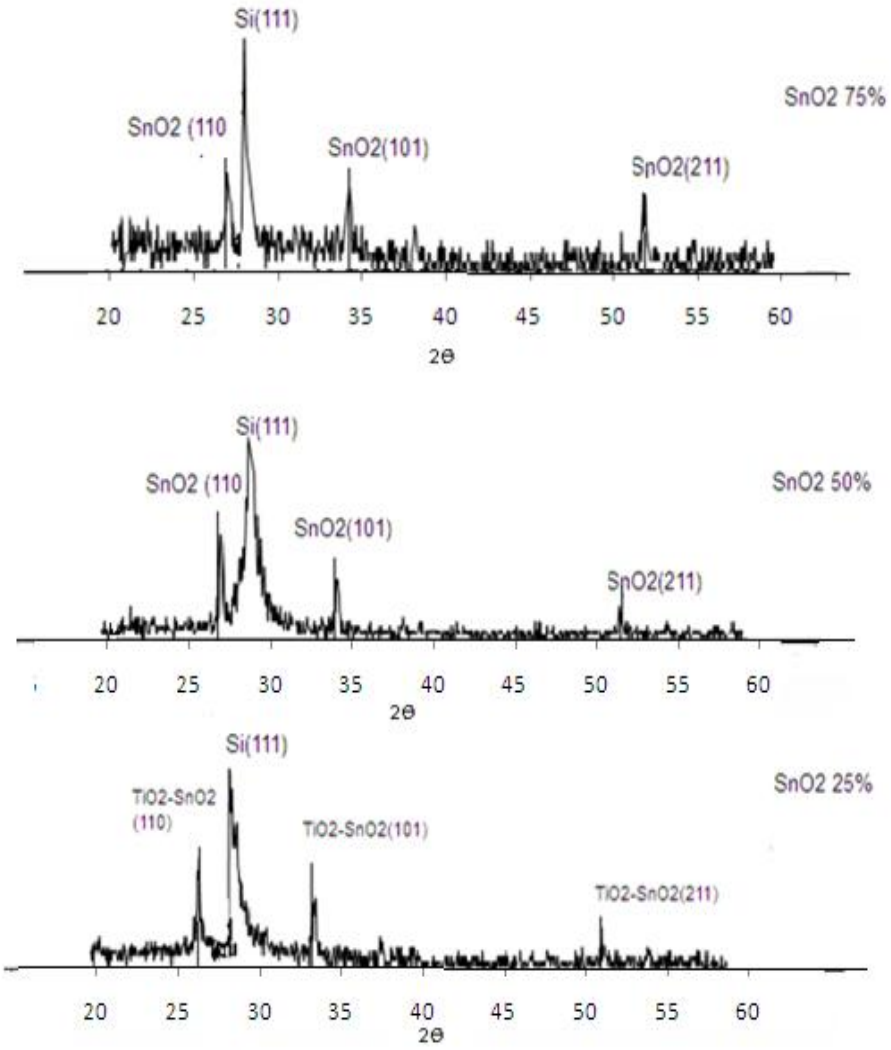


Figure (2) XRD patterns of (TiO_2 -SnO_2) films grown on Si at various SnO_2 content.

Table (1) the obtained result of the XRD for (TiO_2-SnO_2)/Si at T=400 °C.

sample	2θ(degree)	(hkl)	FWHM^0
(75%TiO2-25%SnO2)	26.9	R(110)	0.163
	34	R(101)	0.164
	52.1	R(211)	0.143
	28	Si(111)	0.305
(50%TiO2-50%SnO2)	27	R(110)	0.245
	34.3	R(101)	0.275
	52.6	R(211)	0.191
	28	Si(111)	0.305
(25%TiO2-75%SnO2)	27.25	R(110)	0.1
	34.5	R(101)	0.144
	53	R(211)	0.157
	28	Si(111)	0.305

SEM images of the TiO_2 mixed with different content of SnO_2 (25%, 50%, 75%) are presented in Figure (3) for film deposited at fixed substrate temperature of 400 ºC at Oxygen pressure of (5×10^{-1} mbar) and 1.4 J/cm^2 laser fluence. The grain size decreases with increasing SnO_2 content. SEM images show clearly that size and shape of grains are strongly affected by the chemical composition of SnO_2-TiO_2. Grain growth has been observed for TiO_2. Were Addition of SnO_2 reduces the grain size.

Table (2) The obtained result of the SEM for (TiO_2-SnO_2)/Si at T=400 °C.

sample	SEM of plane grain size (nm)
(75%TiO2-25%SnO2)	53.6
(50%TiO2-50%SnO2)	46.2
(25%TiO2-75%SnO2)	25.5

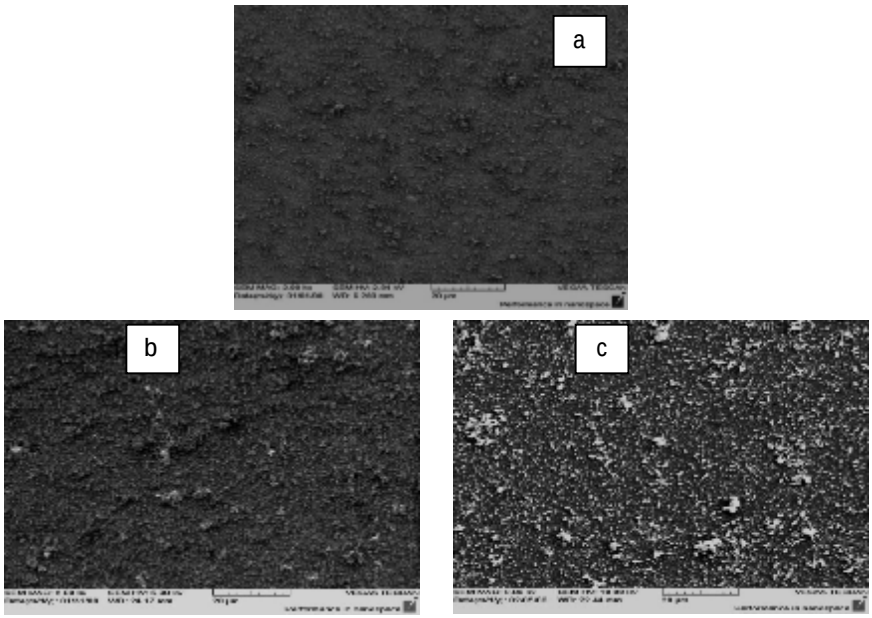


Figure (3) SEM images of (TiO_2 -SnO_2) films grown on Si at different SnO_2 content% a) 25% b) 50% c) 75.

Figure (4) shows the optical transmittance of the (TiO_2-SnO_2) films deposited on glass substrate at oxygen pressures (5×10^{-1}) mbar and at fixed substrate temperature of 400°C with 1.4 J/cm^2 laser fluence energy density. With average thickness (200) nm. It is found that the optical transmission of the (TiO_2-SnO_2) films increases as SnO_2 content is increased. This may be attributed to the fact that new defects are introduced after Sn atoms substitute Ti atoms and enter into TiO_2 lattice due to the electronegativity and ionic radius difference between Ti and Sn

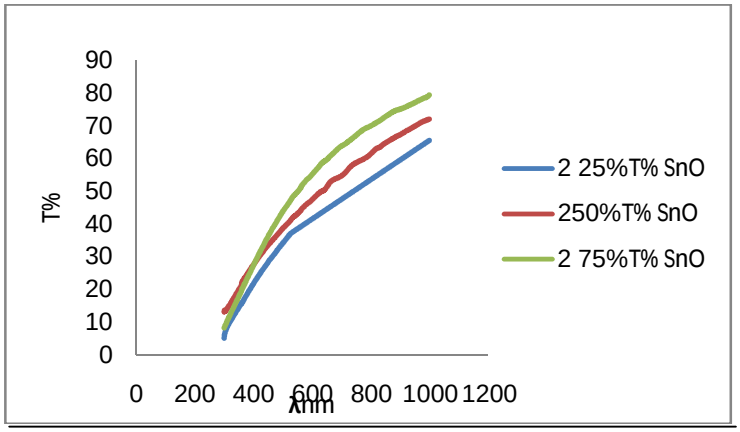
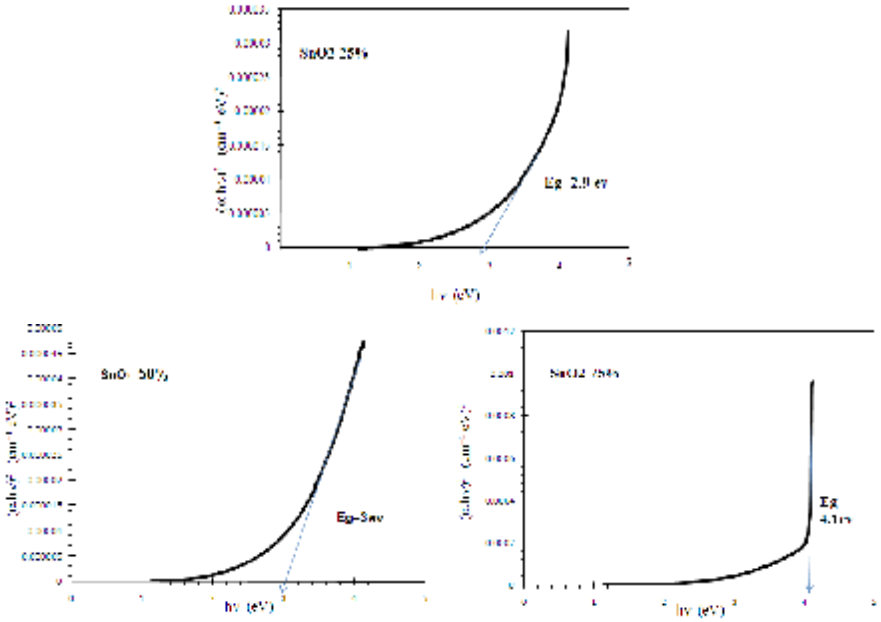


Figure (4) UV-VIS transmittance spectra of the (TiO_2-SnO_2) films at different SnO_2 content at 400 ° C substrate temperature with laser fluence 1.4J/cm^2.

The optical energy gap (Eg) values of the (TiO_2-SnO_2) films deposited on glass substrate at constant substrate temperature 400 ^oC,1.4J/cm^2 laser fluence, and oxygen pressure 5×10^{-1} mbar are determined and found to be increase from 2.9 to 4.1eV with SnO_2-content increased as shown in Figure (5). In other words, the optical energy band gap (TiO_2-SnO_2) thin films become wider as SnO_2 content increases and The reason for observed blue shift in the band gap could be attributed to the higher band gap energy of SnO_2 (≈ 4.3eV).



Figures (5) A plots of (αhν)^2 ^{2}verses photon enrgy (hν) of (TiO_2-SnO_2) thin films at different SnO_2 content at 400 $^\circ$ C substrate temperature with laser fluence 1.4 J/cm^2.

CONCLUSIONS

The (TiO_2–SnO_2) mixed oxide thin films have been prepared by PLD with different ratio with the ultimate aim to gain a deeper understanding of the properties of the system.

When the SnO_2 concentration further increased, the XRD analysis did not detect the TiO_2 phase, these due to the small molecular weight of TiO_2. SEM images show clearly that size and shape of grains are strongly affected by the chemical composition of (TiO_2-SnO_2). Were Addition of SnO_2 reduces the grain size to 25.5nm. The band gap energy of (TiO_2-SnO_2) films increases as SnO_2 concentration is increased because the higher band gap energy of SnO_2 (≈ 4.3eV).

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