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Preparation and Characterization of High Quality SnO_2 Films Grown by (HPCVD)

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ABSTRACT

In this research SnO_2 thin films have been prepared by using hot plate atmospheric pressure chemical vapor deposition (HPCVD) on glass and Si (n-type) substrates at various temperatures. Optical properties have been measured by UV-VIS spectrophotometer, maximum transmittance about (94%) at 400 ^{0}C. Structure properties have been studied by using X-ray diffraction (XRD) , its shows that all films have a crystalline structure in nature and by increasing growth temperature from(350-500) ^{0}C diffraction peaks becomes sharper and grain size has been change. Atomic force microscopy (AFM) uses to analyze the morphology of the Tine Oxides surface structure. Roughness & Root mean square for different temperature have been investigated. The results show that both increase with substrate temperature increase this measurements deal with X-Ray diffraction results, that there is large change in the structure state of SnO2 thin f film by changing temperature parameter.

Keywords: Sno_2, Thin Films, Hpcvd

تحضيراغشية اوكسيد القصدير عالية النوعية باستخدام الترسيب الكيمياوي ذو الاساس الحار

الخلاصة

في هذا البحث تم تحضير أغشية اوكسيد القصدير بطريقة الترسيب الكيماوي بالبخار بالضغط الجوي على قاعدة ساخنة من الزجاج وسيلكون لدرجات حرارة مختلفة. الخصائص البصرية للغشاء تم قياسها باستخدام جهاز مطياف (UV-Vis.) اقصى نفاذية كانت بحدود (94%) عند 400 ^{0}C . أما الخصائص التركيبية تم دراستها باستخدام حيود الأشعة السينية التي أوضحت انه جميع الاغشية هي ذات تركيب بلوري بطبيعتها وبتغيير حرارة نمو الغشاء لمدى ^{0}C (300-500) فان قمم الحيود أصبحت اكثر حدة والحجم الحبيبي يتغير. استخدم مجهر القوى الذرية لتحليل طوبوغرافية وتركيب سطح أغشية اوكسيد القصدير حيث تم حساب الخشونة ومعدل الجذر التربيعي للعينات المحضرة ولدرجات حرارة مختلفة واظهرت النتائج بأن كلاهما يزداد مع ازدياد درجة حرارة الاساس وهذا يتفق مع نتائج حيود الاشعة السينية كما ان هنالك تغيير كبير بالحالة التركيبية لغشاء SnO_2 مع تغيير مؤثر الحرارة.

INTRODUCTION

Tin oxide (SnO2) is one of the transparent conductive oxides (TCOs) where they are stable with good adherent to the substrate, hard mechanically and have large transmittance in visible region [1]. It is a very important wide-band-gap semiconductor (e.g., 3.6 eV at 300 K). Owing to its excellent optical and electrical properties, it has a broad range of high technology applications, such as optoelectronic devices, chemical sensors, solar cells, lithium batteries [2]. It is well known that the particle size and morphology of materials have a great influence on their properties. The most common form of SnO_2 in these films is the tetragonal rutile form consisting of a unit cell with a tin atom surrounded by six oxygen atoms in a octahedral coordination and oxygen atoms surrounded by three tin atoms in a triangular fashion as shown in Figure(1). Pure SnO2 is generally regarded as an oxygen-deficient n-type wide-band semiconductor but this effect can be enhanced by doping where atomic impurities of i. e. Sb, F or Cl are incorporated in tin oxide lattice [3, 4, 5].

Physical properties of SnO2 are summarized in Table (1) which gives tin oxide the following daily-life properties:

• low electrical resistance
• transparent for visible light but reflective for infrared light
• environmental stable
• high hardness

These properties make thin films of SnO2 good candidates for applications where transparency and conductivity of electricity are required. Currently, tin oxide films are used as heterogeneous catalyst in oxidation reactions [5, 6], as infrared reflector in low-energy glass and anti-static layer [7], as transparent electrode in displays or solar cells [8], as protective layer on glass containers [4, 9] or as solid-state gas sensor for the detection of a wide range of gasses [10, 11]. SnO2 has been synthesized by different methods such as the sol–gel method, chemical vapor deposition (CVD), magnetron sputtering and hydrothermal treatment [12-13].

The aims of the present work are to prepare SnO_2 thin films by using a hot plate atmospheric pressure chemical vapor deposition (HPCVD) on glass and Si(n-type) substrates at various temperatures.

Table (1) Physical properties of tin dioxide [4, 5].

Property	SnO_2
Mineral name	Cassiterite
Crystal structure	Tetragonal, rutile
Space group	D^{14}_{4h} or P_{42}/mnm
Lattice constants [nm]	a=0.474 b= 0.319
Oxidation states	Sn^{4+}, O^{2-}
Molar mass [g mol-1]	150.71
Density p [g cm-3]	6.85
Mohs hardness [-]	6.5
Melting point	1630
Band gap [eV]	3.6
Common extrinsic n-type dopants	Sb,F,Cl

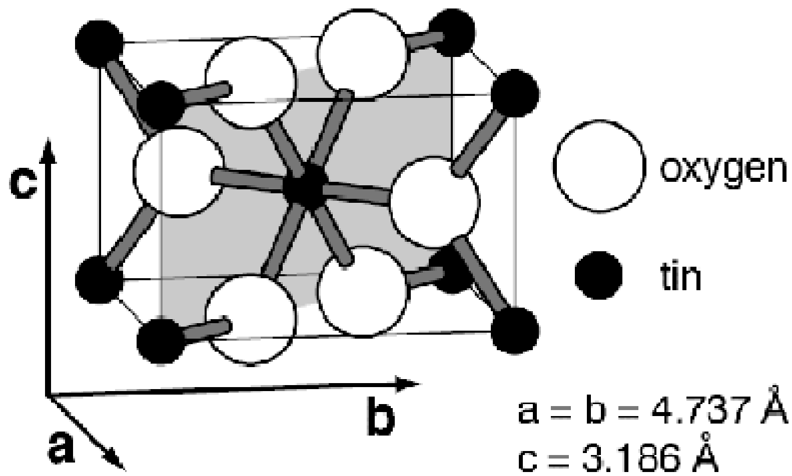


Figure (1) The rutile structure of SnO_2 unit cell.

EXPERIMENTAL WORK

The salt hydrated tin dichloride ($SnCl2H_2O$) was used as start material mixing with methanol (CH3OH) and use N_2 gas as carrier gas, tin oxide thin films were prepared by homemade HPCVD, the schematic diagram of the Hot Plate Atmospheric Pressure Chemical Vapor Deposition system is given in Figure (2).The reaction chamber composes of Pyrex funnel put upside down on hot stainless steel plate. The glass slides and silicone substrate were cleaned ultrasonically by Trichloroethylene (TCE), acetone, ethanol followed by de-ionized water and dry with N_2.

Before using Si wafer it etches with HF (10%). The vapor of the precursor reactance carried on the glass substrate by the N_2 gas. The operating parameters are shown in Table (2). X-Ray diffraction (CuKα) radiation with a wavelength λ =0.154060 nm at 2θ (20-60) was use to study crystal structure. Atomic force microscopy (AFM) was used for investigate the morphology and roughness of surface, optical properties was studied by UV-Visible spectrophotometer (Shimadzu).

Table (2) Deposition parameters of tin oxide film

Thin film	SnO2
Substrate	Glass , Si
Temperature (^{0}C)	350-500
N2 gas flow rate	2L/min
$SnCl_2$2H2O	2g
CH_3OH	20 ml
HF	10%

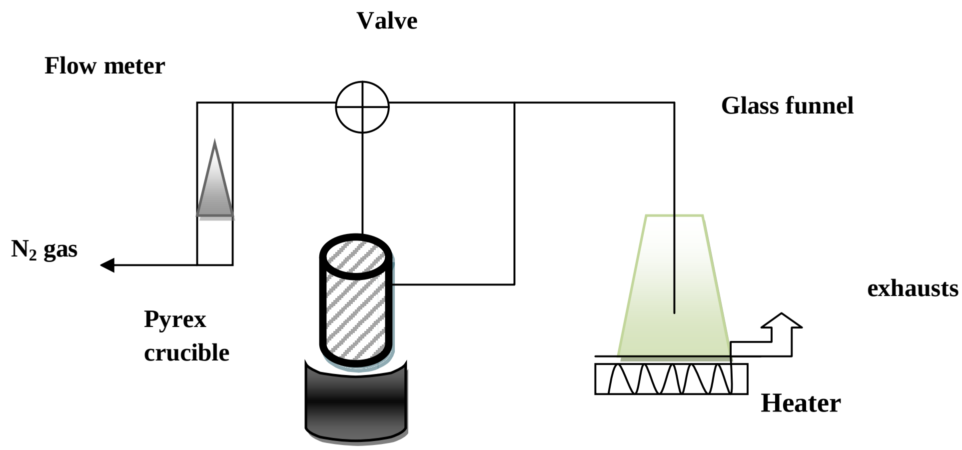
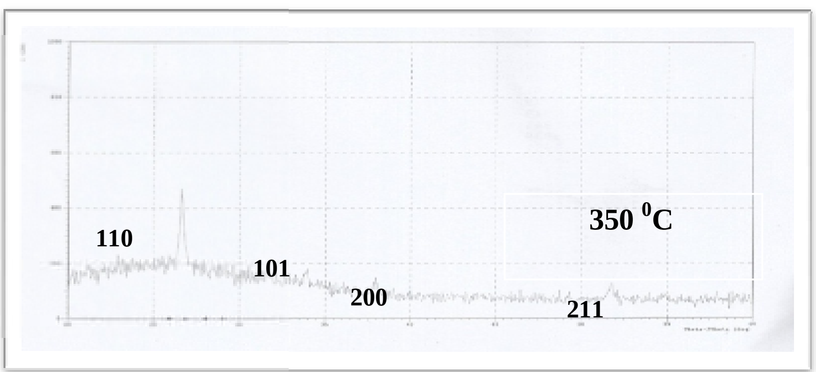


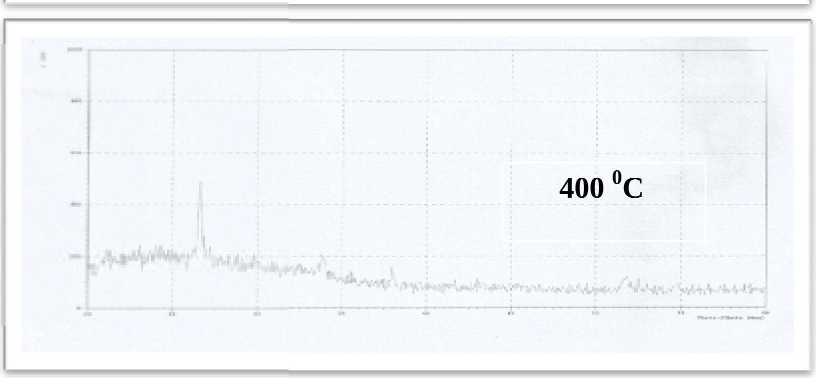
Figure (2) Schematic diagram of HPCVD system.

RESULTS AND DISCUSSION

Structural properties

XRD measurement were made to SnO2 films deposited on glass substrate are shown in Figure (3). It's clear that there are four X-ray diffraction patterns (110),(101),(200),(211) at various temperature $(350\text{-}450)^0$C ,the max. Peak at 2θ values of 26.6° is (110).The results show that at a temp of $(500)^0$C there are more than five peaks this improvement for crystalline structure . A matching of the observed and standard (hkl) planes confirmed that the product is of SnO2 having a tetragonal structure.





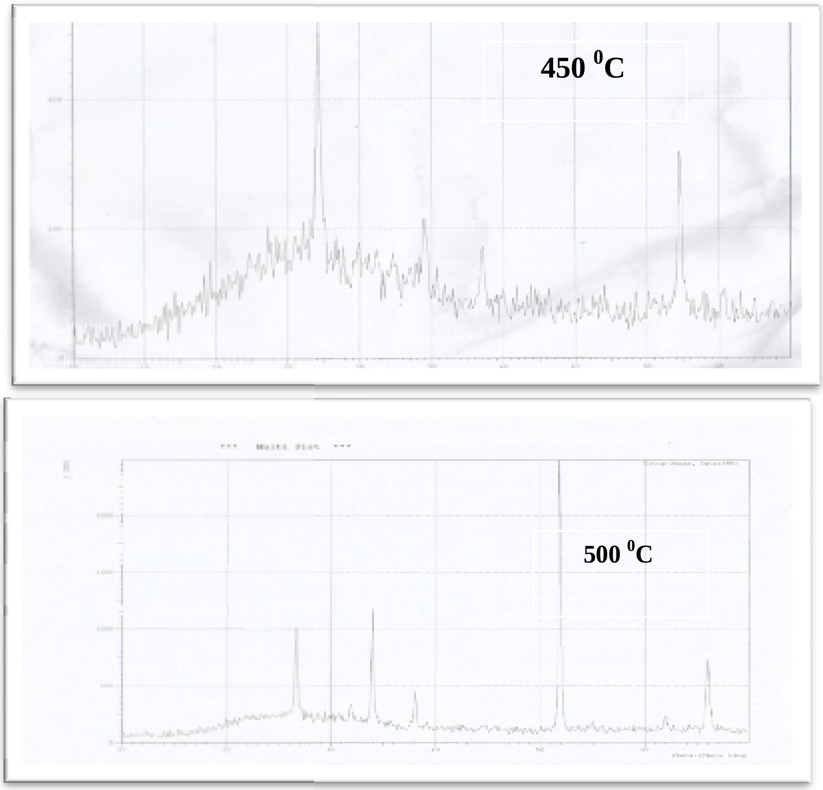
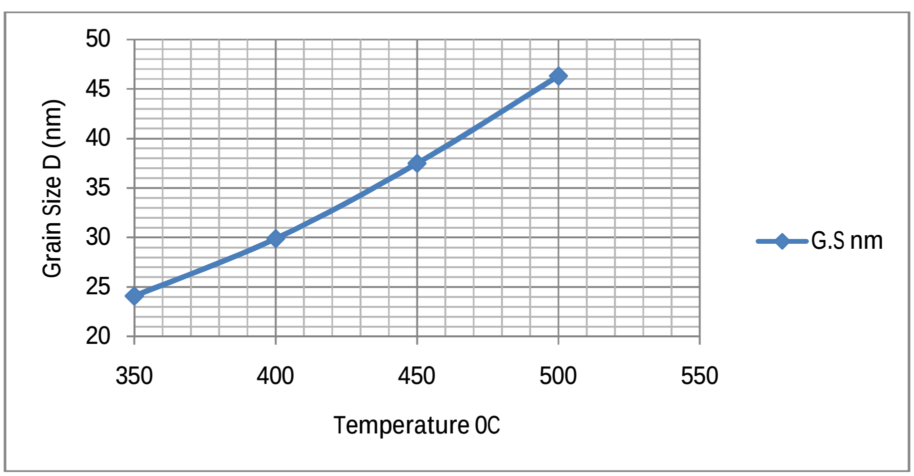


Figure (3) The XRD pattern of the SnO_2 film prepared at various substrate temperature (350-500 ^{0}C).

It was noted that the grain particle size became larger with temperature increase for SnO_2 film as shown in Figure (4).



Figure(4) SnO2 thin film grain size deposit on glass substrate variation with temperature.

Figure(5) shows XRD pattern for SnO2 film on Si (n-type) in deposition temperature (490 0C),the measurement show that there is only two peaks observed.

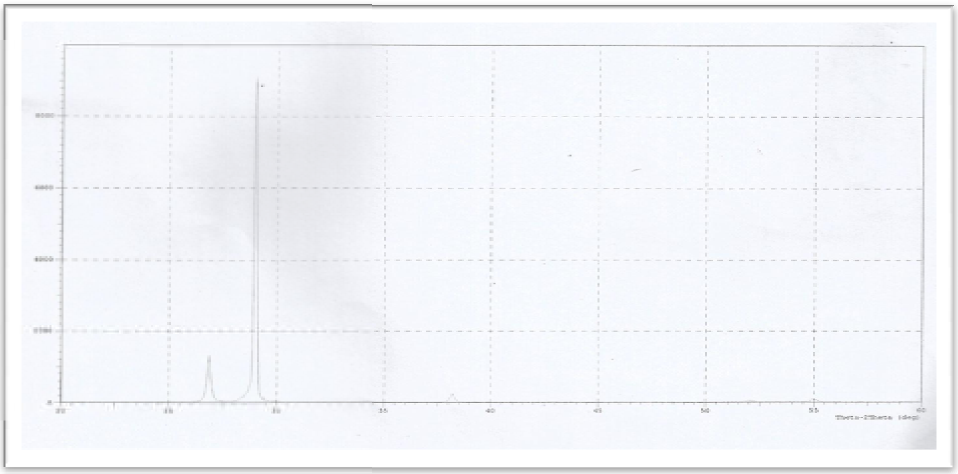


Figure (5) Shows XRD pattern for SnO2 film on Si (n-type) substrate.

OPTICAL PROPERTIES

SnO_2 thin film deposited on to glass substrate by using wet chemistry results refer to have a bright yellow thin film with high quality and were very transparent. The optical transmission of the samples is investigated in the range of 280 to 1100nm using UV-VIS spectrophotometer as shown in Figure (6).The measurements are taken in the wavelength scanning mode for normal incidence with max. transmittance about (94%) at 400 ^{0}C. It is noted that the average permeability of Tin Oxide films be high for each temperature at a higher rate (80%), and this is proof that we get visually permeable membranes with excellent quality possible to use different applications such as poles transparent or other.

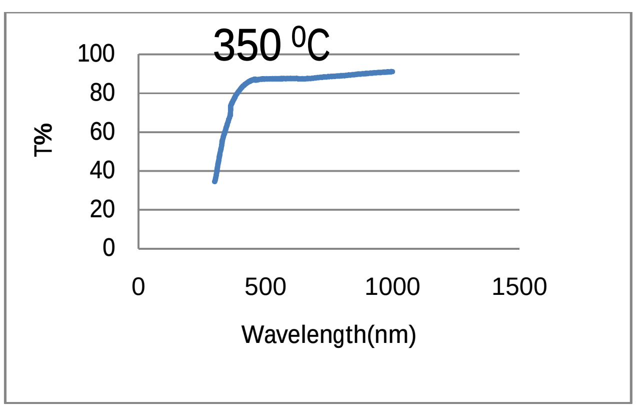
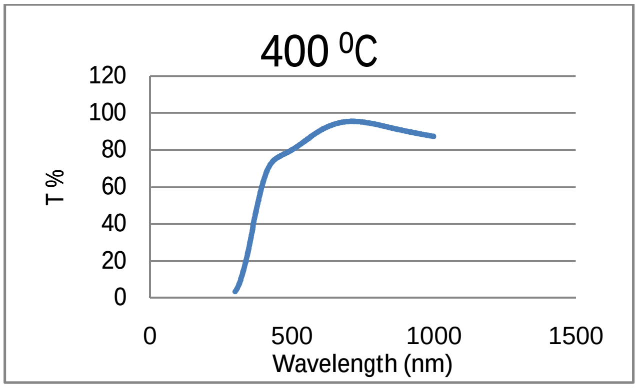
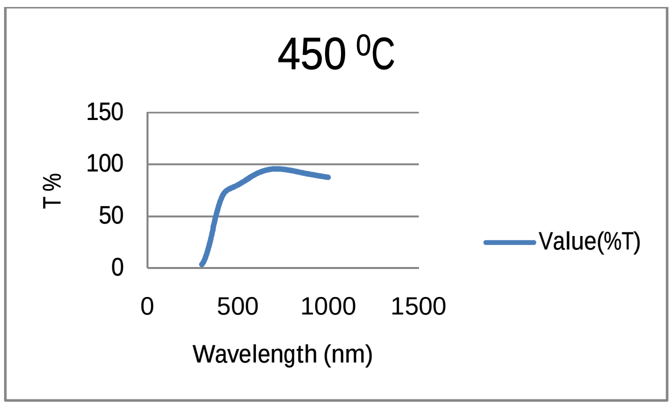


Figure (6) To be Continued





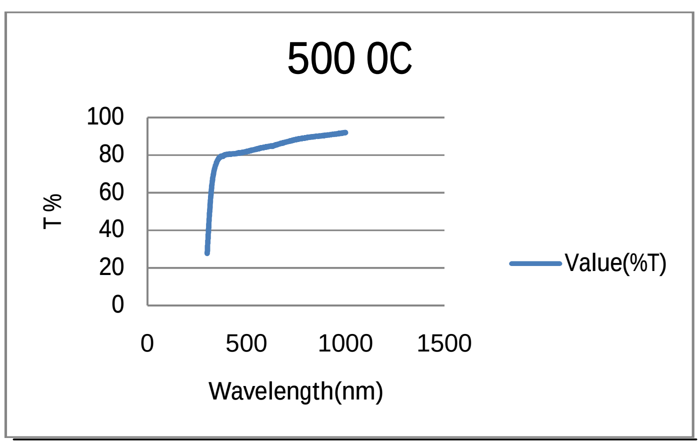
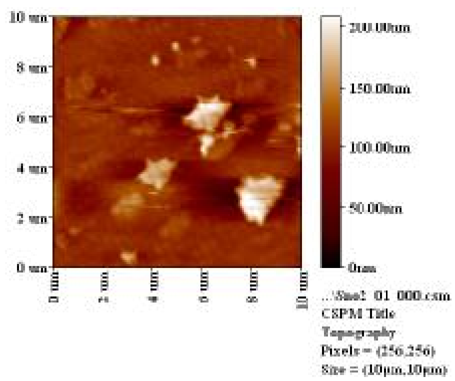


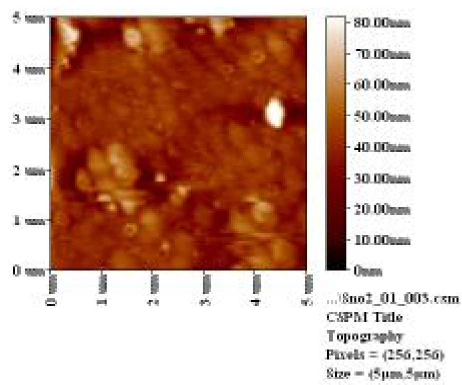
Figure (6) Transmittance and absorbance spectrum for SnO_2 films for various substrate temperatures.

MORPHOLOGY OF THE TINE OXIDES SURFACE STRUCTURE

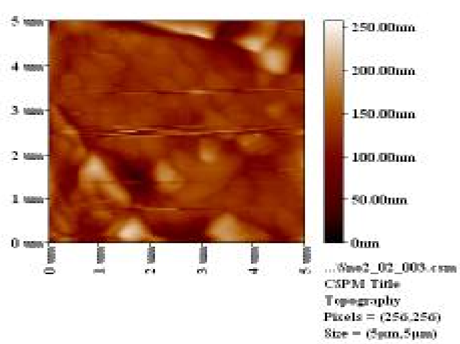
Atomic force microscopy (AFM) was used to study the morphology of SnO_2 thin films deposit by (HPCVD) as shown in Figure(7) in (2D) and (3D). The results show that the roughness and rout mean square of tine oxides surface increase with substrate temperature increase this measurements agree with X-Ray diffraction results, that there is large change in the structure state of SnO2 thin film by changing temperature parameter . The surface topography and surface roughness will change with all temperature AFM images show, thin layers consist of isolated islands, it grow with temperature this is obvious in (2D) and (3D) images.



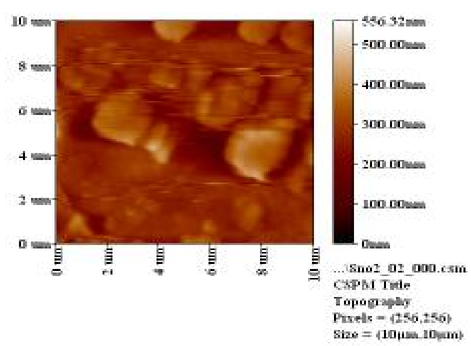
(350 ^{0}C)



(400 ^{0}C)

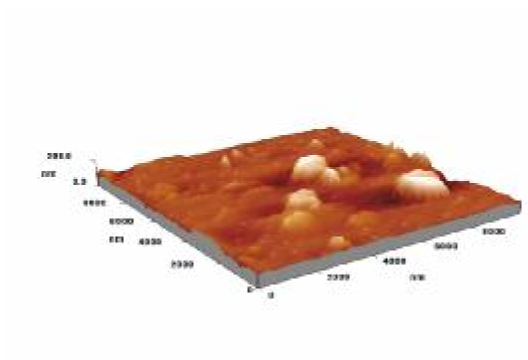


(450 ^{0}C)

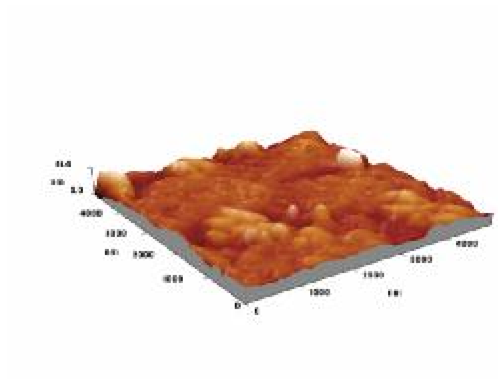


(500 ^{0}C)

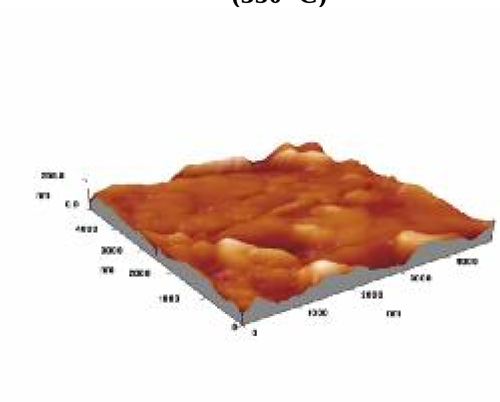
Figure (7)Atomic force microscopy(AFM) of Sno2 thin films deposit by (HPCVD in (2D).



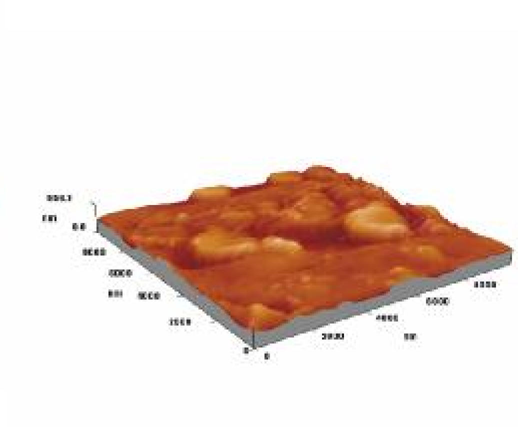
(350 ^{0}C)



(400 ^{0}C)



(450 ^{0}C)



(500 ^{0}C)

Figure (8) Atomic force microscopy (AFM) of Sno2 thin films deposit by (HPCVD in (3D).

Table (3) show AFM data that we gate each measurement form surface morphology of SnO_2 thin films images.

Table (3) AFM measurement for different temperature.

Temperature (T ^{0}C)	Roughness average (sa)nm	Rout mean square(sq) nm	Surface Skewness (Ssk)	Surface Kurtosis (Sku)	Peak-Peak (sy)nm	Grain Size (g.s)nm
350	5.87	8.37	0.477	6.2	81.4	24.1
400	13.9	23.4	0.945	7.89	197	29.95
450	18.9	26.9	0.0146	4.71	223	37.5
500	34.5	48.4	-0.121	4.3	358	46.3

CONCLUSIONS

Tin oxide thin film have been successfully deposited at glass substrate by using HPCVD method. Structural investigations using .XRD reveal that the layers are composed of SnO2, grain size was (24-46.6) nm measured by Scherrer equation. The results show that at a different temp. There are more than five peaks this improvement for crystalline structure Max. Transmittance was 94% in a visible light spectrum, the average roughness of thin film surface is about(5.3 nm). The results show that the roughness and rout mean square of tine oxides surface increase with substrate temperature increase.

REFERENCES

[1]. Vasiliev, R. B. M. N. Rumyantseva, S. E. Podguzova, A.S. Ryzhikov, L. I. Ryabova, and A. M. Gaskov, "Effect ofinterdiffusion on electrical and gas sensor Properties ofCuO/SnO2 heterostructure,"Materials Science and Engineering B, vol. 57, no. 3, pp. 241–246, 1999.

[2]. Wager, J. F. "Transparent electronics," *Science*, vol. 300, no. 5623, pp. 1245–1246, 2013.

[3]. Jarzebski and J. P. Marton. Z. M. Physical properties of SnO2 materials. *1*.– Preparation and defect structure. Journal of the Electrochemical Society, 123 (7), C199–C205 (1976).

[4]. Greenwood and A. Earnshaw. N. N. Chemistry of the elements. Butterworth-Heinemann,2nd edition (1997).

[5]. Batzill and U. Diebold. M. The surface and materials science of tin oxide. Progress in Surface Science, **79** (2–4), 47–154 (November 2005).

[6]. Harrison, P. G. C. Bailey, and W. Azelee. Modified tin (IV) oxide (M/SnO2, M = Cr, La, Pr, Nd, Sm, Gd) catalysts for the oxidation of carbon monoxide and Propane. Journal of Catalysis,**186** (1), 147–159 (August 1999).

[7]. van Mol, A. M. B. Y. Chae, A. H. McDaniel, and M. D. Allendorf. Chemical vapor deposition of tin oxide: fundamentals and applications. Thin Solid Films, **502** (1-2), 72–78 (April 2006).

[8]. Granqvist. C. G. Transparent conductors as solar energy materials: A panoramic review.Solar Energy Materials and Solar Cells, **91** (17), 1529–1598 (October 2007).

[9]. Gordon.R. Chemical vapor deposition of coatings on glass. Journal of Non-Crystalline Solids, **218**, 81–91 (September 2007).

[10]. Göpel and K. D. Schierbaum. W. SnO2 sensors: Current status and future prospects. Sensors and Actuators B: Chemical, **26** (1–3), 1–12 (May 1995).

[11]. Barsan, N. M. Schweizer-Berberich, and W. Göpel. Fundamental and practical aspects in the design of nanoscaled SnO2 gas sensors: a status report. Fresenius' Journal of Analytical Chemistry, **365** (4), 287–304 (October 1999).

[12]. Haynes,W. M. editor. CRC handbook of chemistry and physics. CRC, 93rd edition (2012).

[13]. J. Mater Synthesis and characterization of nanostructure SnO2 film Sci: Material in Electronics, 22:pp.1681-1684 (2011)(nano technology center) .