

Effect of Substrate Temperature on Nanostructure Titanium Dioxide Thin Films Prepared by PLD

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ABSTRACT

In this work, a double frequency Q-switching Nd:YAG laser beam ($\lambda=532\text{nm}$, laser fluence 1.2 J/cm^2 , repetition rate 10 Hz and the pulse duration 7ns) has been used, to deposit TiO_2 thin films pure on glass and Si (111) substrates. The structure properties of pure TiO_2 were investigated by means of x-ray diffraction. As a result, it has been found that film structure and properties strongly depended on substrate temperature. X-ray diffraction (XRD) showed that at substrate temperatures higher than $300\text{ }^\circ\text{C}$ the structure of the deposited thin films changed from amorphous to crystalline corresponding to the tetragonal TiO_2 anatase phase. The surface morphology of the deposits materials have been studied using scanning electron (SEM) and atomic force microscopes (AFM). The grain size of the nanoparticles observed at the surface depended on the substrate temperature, where $500\text{ }^\circ\text{C}$ was the best temperature and partial pressure of oxygen $5\times 10^{-1}\text{ mbar}$ was the best pressure during the growth process. RMS roughness increased with increasing substrate temperature (T_s) which are (11.2nm) for thin films deposited at (500)C. UV-VIS transmittance measurements have shown that our films are highly transparent in the visible wavelength region, with an average transmittance of $\sim 90\%$ which makes them suitable for sensor applications. The optical band gap of the films has been found to be 3.2 eV for indirect transition and 3.6 eV for direct transition at $400\text{ }^\circ\text{C}$. The sensitivity toward CO gas has been measured under 50 ppm.

Keywords: Pulsed Laser Deposition (PLD), TiO_2 Thin Films, Nonstructural. Gas Sensor.

دراسة تأثير درجة حرارة القاعدة على اغشية اوكسيد التيتانيوم ذات التركيب النانوي المحضرة بطريقة الترسيب بالليزر النبضي

الخلاصة

في بحثنا هذا تم استعمال ليزر نيدميوم ياك النبضي ذو الطول الموجي (532 nm) ويعمل بتقنية عامل النوعية ذو معدل تكرارية (10 هرتز) و امد نبضة 7 نانو ثانية لترسيب اغشية اوكسيد التيتانيوم النقية على قواعد من الزجاج والسليكون (111). وتم دراسة الخصائص التركيبية لاغشية اوكسيد التيتانيوم باستخدام حيود الاشعة السينية. وأثبتت نتائج الاشعة السينية الخصائص التركيبية لاوكسيد التيتانيوم النقي حيث اظهرت النتائج ان تراكيب الاغشية وخصائصها تعتمد بشدة على درجة حرارة القاعدة حيث اظهرت نتائج حيود الاشعة السينية انه عند درجة حرارة قاعدة أكثر من 300 °C يتحول تركيب الاغشية من عشوائي إلى بلوري مساوي إلى طور الأناثاس الرباعي لاوكسيد التيتانيوم. تم دراسة طوبوغرافية السطح باستخدام المجهر الالكتروني الماسح (SEM) ومجهر القوى الذرية (AFM). والحجم الحبيبي للجسيمات النانوية التي ظهرت عند السطح اعتمد على درجة حرارة القاعدة، وكانت افضل درجة حرارة قاعدة هي 500 °C وافضل ضغط اوكسجين عند انماء الغشاء كان (10⁻¹ ملي بار). كما ادت زيادة درجة حرارة القاعدة الى زيادة خشونة السطح فبلغت قيمتها (11.2 نانومتر) عند درجة حرارة قاعدة 500 °C. كذلك تم دراسة الخصائص البصرية بواسطة قياسات مطياف النفاذية للأشعة المرئية وفوق البنفسجية. كانت نتائج النفاذية البصرية أعلى من 90% مما يجعلها ملائمة لتطبيقات التحسية. وعند اشابة اوكسيد التيتانيوم بمعدي الفضة والبلاتين نلاحظ حدوث ازاحة بحافة الامتصاص نحو المنطقة المرئية. بلغت قيمة فجوة الطاقة البصرية الغير مباشرة (3.2 eV) و فجوة الطاقة البصرية المباشرة (3.6 eV) عند درجة حرارة قاعدة 400 °C. تم حساب التحسية لغاز CO تحت تركيز 50 جزء لكل مليون.

INTRODUCTION

Titanium dioxide TiO₂ (titania) is a cheap, non-toxic and one of the most efficient semiconductor photocatalysts for extensive environmental applications because of its strong oxidizing power, high photochemical corrosive resistance and cost effectiveness^[1]. Due to these inherent properties, TiO₂ is the most suitable candidate for degradation and complete mineralization of toxic organic pollutants in water^[1,2]. It is well known that TiO₂ exists in three crystalline structures: rutile, anatase and brookite^[3,4]. The anatase phase is especially adequate for those applications due to its crystal structure and a higher band gap of 3.2 eV compared to the 3 eV in rutile. Anatase and rutile have properties of interest for sensing applications^[5]. Gas sensors based on semiconductor metal oxide thin films focused numerous research efforts during the last few years. Among them, titanium dioxide (TiO₂) has been investigated due to its sensing properties in front of hydrogen [1], carbon monoxide and oxygen [2], hydrocarbons [3,4], or humidity detectors [5].

Unwanted crystallites growth or phase transformation [6,7]. Many deposition techniques for TiO₂ films have been explored such as chemical vapor deposition (CVD) [8], atomic layer deposition (ALD) [9], and pulsed laser deposition (PLD) [19,20]. Recently, sputtering [10-13] has become the most commonly used technique for the deposition of titania due to its controllability and simplicity. Different processes may lead to different microstructure in the films prepared [12, 13].

In this paper, we report the successful growth of pure TiO₂ thin films on (0 0 1) SiO₂ and Si (111) substrates by PLD. Besides the structure and Morphology as a

function of substrate temperature, we investigated the gas sensor properties of the deposited thin films.

EXPERIMENTAL PROCEDURE

film preparation

The deposition was carried out using a Q switched Nd: YAG laser with a frequency second harmonic generation radiation at 532nm (pulse width 7nsec repetition rate 10HZ) and fluence energy 1.2 J/cm^2 . The studied films were prepared from pure TiO_2 targets. Films were grown by pulsed laser deposition on optically flat glass substrates kept on-axis distance of 4cm from the TiO_2 target. The chamber was kept at vacuum pressure of 10^{-3} mbar as shown in Figure (1). The TiO_2 disc was ablated by 10-100 pulses (10-20 min) to get single layered thin films. Consequently, the films were deposited by PLD at 500°C substrate temperature in an O_2 pressure at 10^{-1} Torr. The deposited film had a thickness of approximately 200 nm.

Film characterization

The crystalline structure of the films was determined by X-Ray Diffraction (XRD) measurements (Philips PW 1050, $\lambda=1.54 \text{ \AA}$) using $\text{Cu K}\alpha$. Transmission measurements were performed for a range 400-900nm using UV-VIS-PV-8800 (Perkin Elemer Company) spectrophotometer. The characterizations included determination of the absorption coefficient as a function of incident photon energy, determination the value energy gap. The surface morphology was examined by scanning electron microscopy (SEM-JEOL 7000) and by atomic force microscopy (AFM-Digital Instruments NanoScope) working in tapping mode. The gas sensor measurement by A Hewlett-Packard Systems 5890 Series II GS system. The produced thin films in this study have been exposed to 50 ppm CO gas concentration. The setting in laboratory at University of Technology in Malaysia.

RESULT AND DISCUSSION

Figure (2) shows the XRD measurements results of different TiO_2 films formed at substrate temperatures of 200°C , 300°C and 400°C on glass substrate. It can be seen that the film is amorphous at $T_s = 200^\circ\text{C}$. When the temperature (T_s) increased to 300°C , as shown in curve (b), two diffraction peaks located at $2\theta=25.28^\circ$ and $2\theta=37.8^\circ$ are found, which belong to anatase: (A)(101) and (A) (004) peaks, respectively. When the temperature is 400°C as shown in curve (c), the anatase (101) peak and (004) peak is becoming sharper, suggesting that pure c-oriented TiO_2 films are obtained. The above XRD results indicate that the structure of the films changed from amorphous to anatase phase with the increasing of the temperature (T_s) at 300°C .

Figure (3) shows the SEM images of the TiO_2 thin films deposited at substrate temperatures of (300, 400 and 500°C), respectively. TiO_2 thin films have a quite uniform and hole-free surface. At (300- 500) $^\circ\text{C}$ the film has homogeneous surface morphology, with a wide size distribution of the particles from about (29-40 nm). With increasing substrate temperature, the average size of aggregated particles increases. When the substrate temperature reaches 500°C , the particle size increases obviously.

Figure (4) shows the AFM images of the TiO_2 thin films deposited at substrate temperatures of (300, 400 and 500°C). From the topographic images it can be seen that the films deposited at 300°C appears to be more uniform than the topography of

the sample deposited at 400 and 500°C. The RMS (root mean square) roughness also increased with increasing substrate temperatures (T_s), the section analysis shows that RMS roughness values are (2.1, 4 and 11.2nm) for thin films deposited at (300, 400 and 500)°C respectively.

The UV-Vis optical properties in the range from 300nm to 900nm at various temperatures from (200- 400) °C, reveal that the transmittance depends strongly on the temperature as shown in Figure (5). It is also found that the average transmittance of the TiO₂ film exceeded 90% in the near-infrared region. This indicates that TiO₂ film can be used as a window material in solar cells. For all the films analyzed it is observed that the optical transmittance decreases slightly with increasing the substrate temperature. This is consistent with the increase of the surface roughness promoting the increase of the surface scattering of the light.

The energy gap values depend in general on the films crystal structure, the arrangement and distribution of atoms in the crystal lattice; also affected by crystal regularity. It was found in literature that TiO₂ has a direct and indirect band gap and the band gap values change according to the preparation parameters and conditions. The graphs of $(\alpha h\nu)^2$ vs E (eV) and $(\alpha h\nu)^{1/2}$ vs E(eV) for direct and indirect band gap for TiO₂ thin film are shown in Figure (6 a,b). Graphs obtained for all the other thin films have a similar type of curve. The respective values of E_g were obtained by extrapolation to $(\alpha h\nu)^n = 0$. The E_g values for direct and indirect band gap for all the thin films are summarized in Table (1). Substrate temperature having different effect leads to increase in the optical energy gap values, because the increasing substrate temperature process decreases from the secondary levels and the structure defects which lead to the contract tails region. This leads to expand in the optical energy gap as shown in the Figure (6).

Figure (7) shows the sensitivity of the films that the sensitivity increases with the increasing in the operating temperature, reaching a maximum value corresponding to an optimum operating temperature which is 250°C for all the samples. Above this temperature, the sensitivity to CO gas for all samples decreases at about 400°C. The high temperature operation of the sensor makes the life time of the sensor become shorter and increasing resistance thus required more electricity for operation. It is believed that the oxygen could be removed or lost from the bulk of the metal oxide materials at high temperatures. This suggests that the response of the sensor may decrease at higher temperatures since there will be more oxygen vacancies which led to less occurrence of CO oxygen reaction.

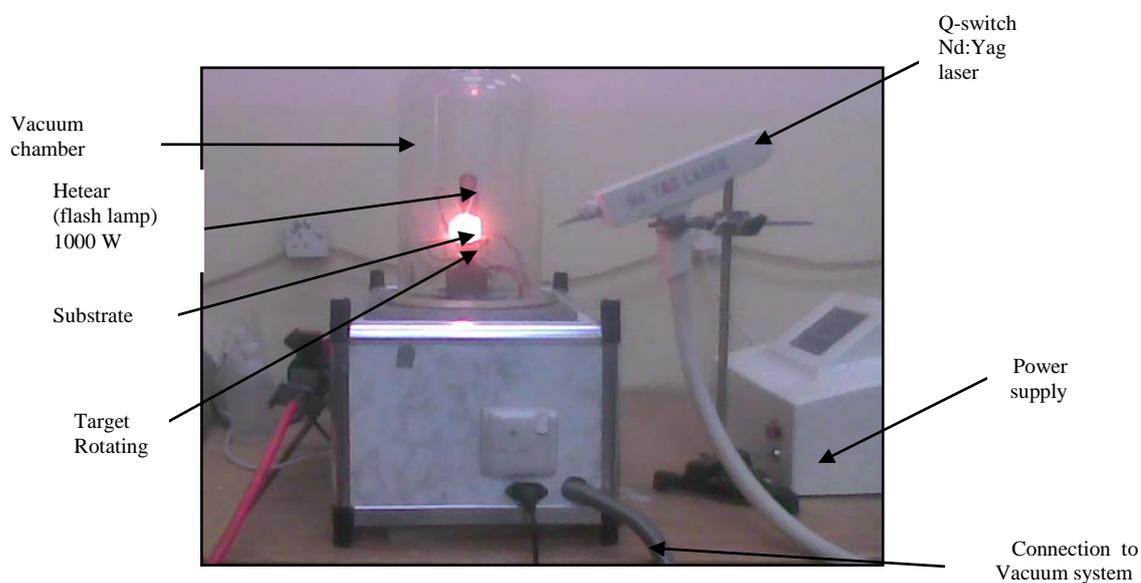


Figure (1) Experimental setup.

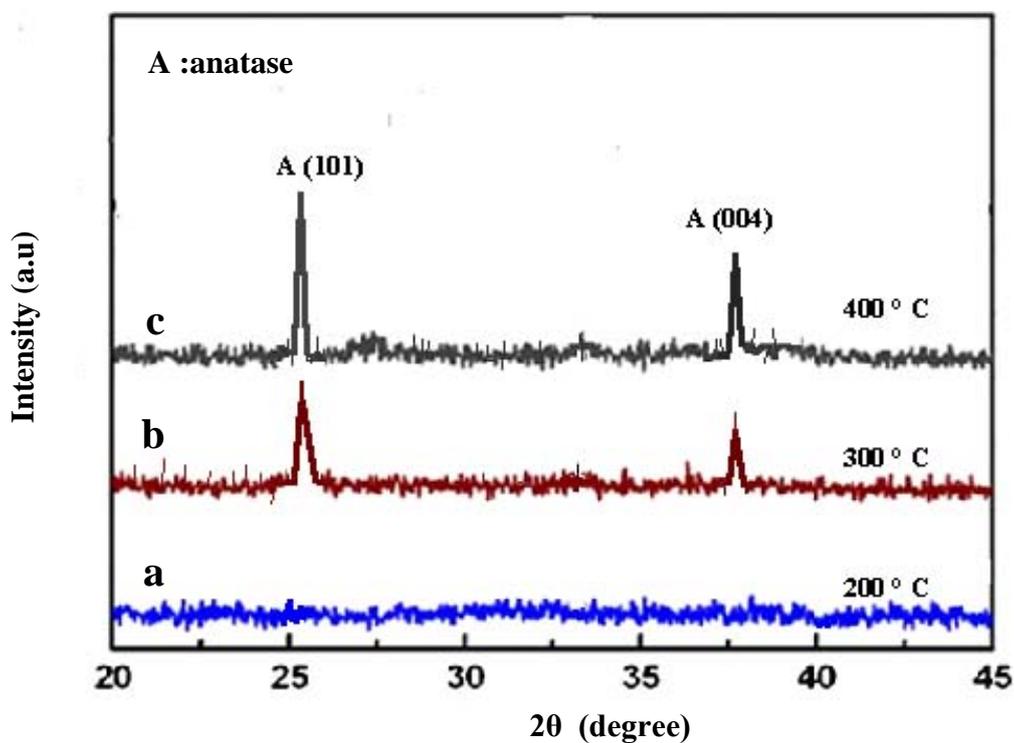


Figure (2) XRD spectra of $\text{TiO}_2/\text{glass}$ at different temperature a) 200°C b) 300°C, c)400°C.

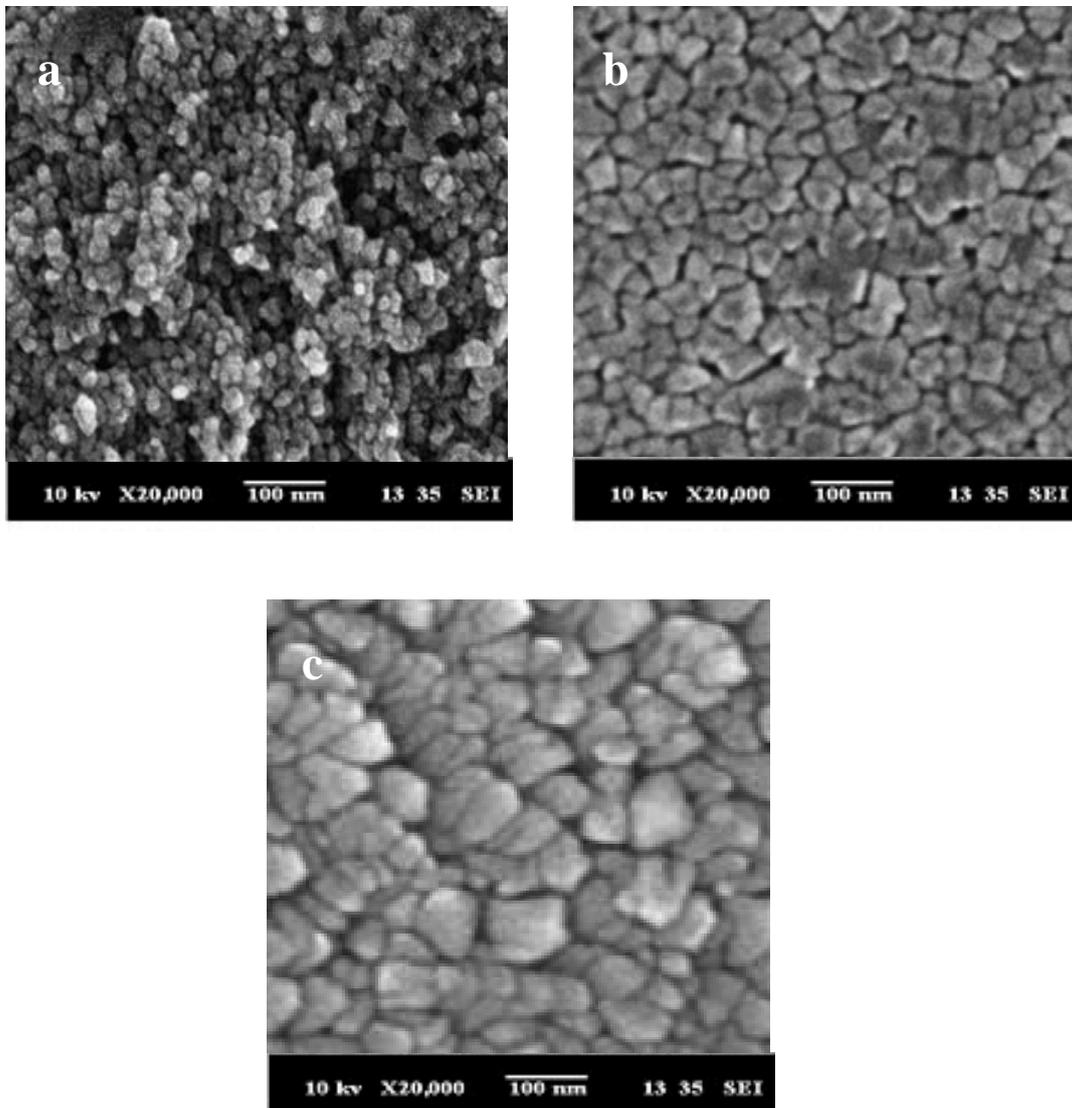


Figure (3) SEM image of the TiO_2/Si thin films deposited at various temperature of a) 300°C , b) 400°C , c) 500°C , and laser fluence 1.2 J/cm^2 , O_2 pressure= $5*10^{-1}$ mbar.

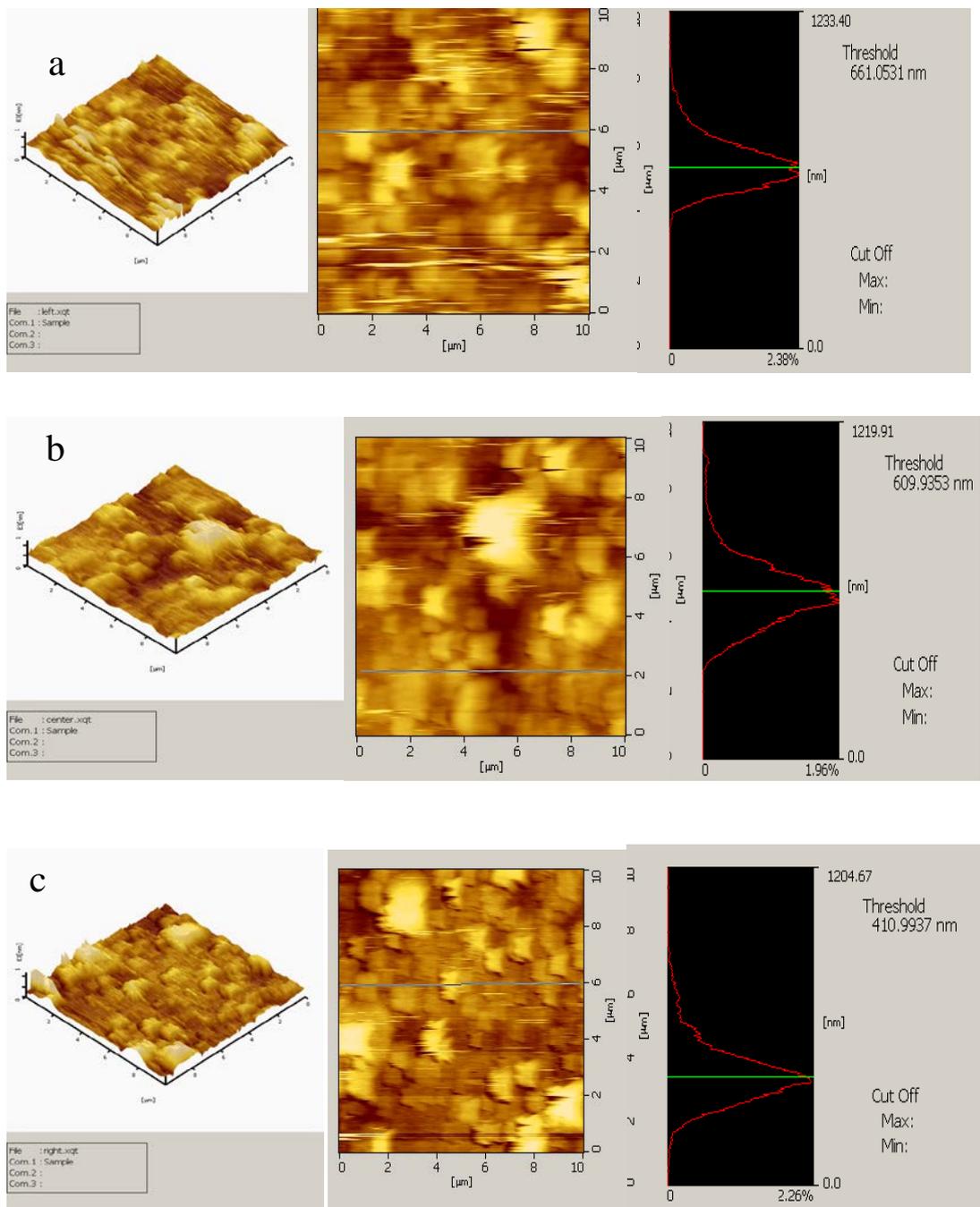


Figure (4) AFM image of the TiO_2/Si thin films deposited at various substrate temperature of a) 300°C, b) 400°C, c) 500°C, and laser fluence 1.2 J/cm^2 , O_2 pressure $5 \cdot 10^{-1}$ mbar.

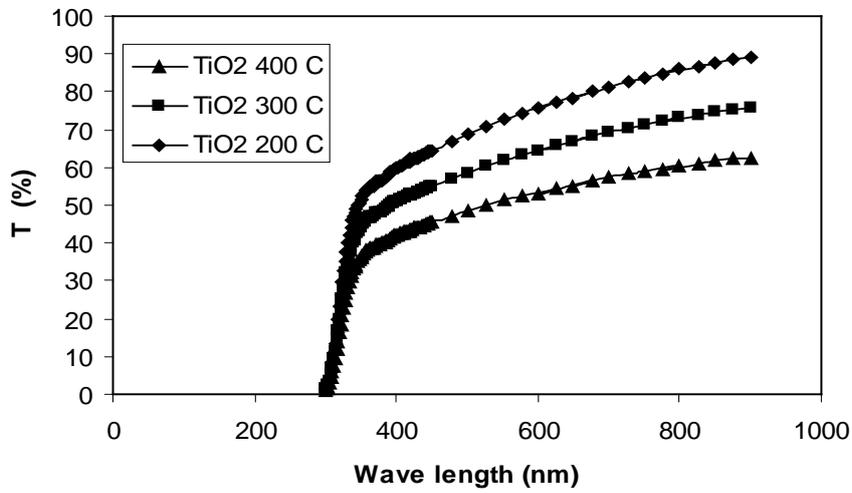
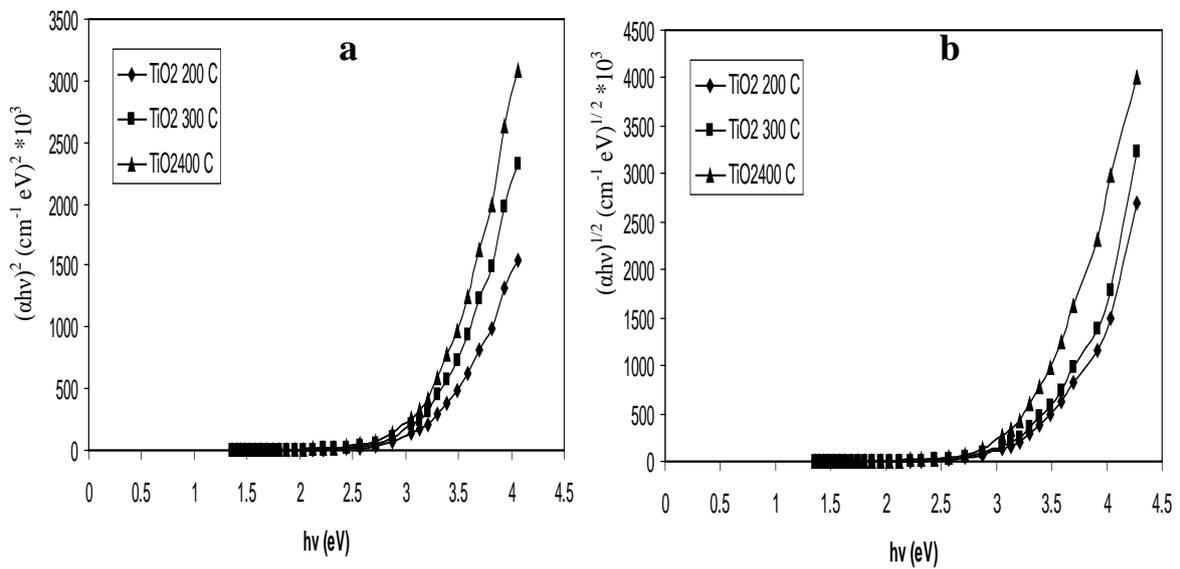


Figure (5) UV-VIS transmittance spectra of the TiO₂/glass films at different substrate temperature with laser fluence 1.2 J/cm², O₂ pressure 5*10⁻¹ mbar.



Figures (6). A plots of a) $(\alpha hv)^2$ and b) $(\alpha hv)^{1/2}$ verses photon energy (hv) of TiO₂ thin films with various Substrate Temperature and laser fluence 1.2 J/cm², O₂ pressure=5*10⁻¹ mbar.

Table (1) Physical and optical measurements for pure and doped TiO₂ films.

Samples	Optical energy gap E _g (eV) (direct)	Optical energy gap E _g (eV) (indirect)
TiO ₂ Pure at 200 °C	3.4	3.03
TiO ₂ Pure at 300 °C	3.5	3.1
TiO ₂ Pure at 400 °C	3.6	3.2

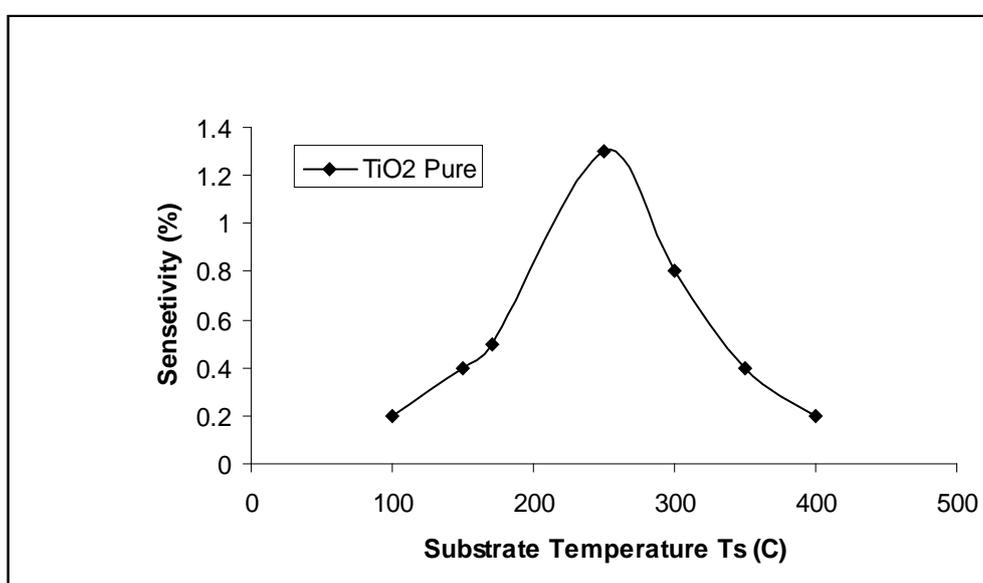


Figure (7) Sensitivity for TiO₂/glass pure films for CO gas at different operation temperature and laser fluence 1.2 J/cm² with O₂ pressure 5*10⁻¹ mbar.

CONCLUSIONS

In this study the film structure and the surface morphology of the deposits materials have been studied using scanning electron (SEM) and atomic force microscopes (AFM) strongly depended on substrate temperature. X-ray diffraction (XRD) showed that at substrate temperatures higher than 300 °C the structure of the deposited thin films changed from amorphous to crystalline corresponding to the tetragonal TiO₂ anatase phase. UV-VIS transmittance measurements have shown that our films are highly transparent in the visible wavelength region, with an average transmittance of ~90% which makes them suitable for sensor applications. The optical band gap of the films has been found to be 3.2 eV for indirect transition and 3.6 eV for direct transition at 400°C. The sensitivity toward CO gas has been measured under 50 ppm concentration.

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