

Laser Energy Effects on Optical Properties of Titanium Di-Oxide Prepared by Reactive Pulsed Laser Deposition

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Received on: 4/3/2012 & Accepted on: 7/6/2012

ABSTRACT

In this Work, Laser energy effects on optical and morphological properties of TiO₂ thin film has been carried out using Reactive Pulsed Laser as a Deposition technique (RPLD). Q-switched Nd-YAG laser with ($\lambda=1.06\mu\text{m}$, $t =7\text{nsec}$) and different energies have been used to ablate pure Titanium target and deposited thin films on glass substrates with constant substrate temperature of (343K). The optical properties of the films prepared include Optical transmit ion and absorption measurement, surface uniformity measurement and FTIR structure of these films. The results films show that high transparency reached to about (85-98) % can be achieved with TiO₂ film which itself decreases sharply with the increasing of Laser energy while the optical band gap is (3.7-3.9) eV at optimum Laser energy in all results (800mJ), the FTIR structure result at 800 mJ is the optimum and peaks absorption of TiO₂ are (408.91, 439.77, 524.64) cm⁻¹.

Keywords: Titanium di-oxide, Thin films, Laser deposition.

تأثير طاقة الليزر على الخصائص البصرية لآغشية اوكسيد التيتانيوم المحضرة باستخدام تقنية الترسيب بالليزر النبضي

الخلاصة

في هذا العمل، تم دراسة تأثير طاقة الليزر على الخصائص البصرية والشكلية لآغشية ثاني أكسيد التيتانيوم TiO₂، الرقيقة المنمأة باستخدام تقنية الترسيب بالليزر النبضي (RPLD). حيث تم استخدام ليزر النديميوم-ياك النبضي Nd-YAG الذي يعمل بتقنية عامل النوعية ذو طول موجي ($\lambda=1.06\text{nm}$) و امد نبضة ($t=7\text{nsec}$) عند طاقات مختلفة لتشظية اهداف معدن التيتانيوم وترسيبه على قواعد زجاجية عند درجة حرارة (343K). ان الخصائص البصرية للآغشية المنمأة تشمل حساب الامتصاصية و النفاذية و معرفة مدى انتظامية السطح و كذلك الخصائص التركيبية للمادة حيث اظهرت نتائج الخصائص البصرية لآغشية اوكسيد التيتانيوم ان نسبة النفاذية عالية و

تتراوح ما بين (85-98) % وانها تقل بحدّة مع زيادة طاقة الليزر. كما و ان فجوة الطاقة البصرية تتراوح ما بين (3.7-3.9)eV و ان افضل النتائج كانت عندما طاقة الليزر تساوي (800 mJ). اما نتائج الخصائص التركيبية للاغشية (FTIR) تبين ايضا اعلى قمة امتصاص لأكسيد التيتانيوم عند طاقة ليزر تساوي 800 mJ.

INTRODUCTION

Pulsed laser deposition (PLD) is extensively used in the deposition of various materials including oxides, nitrides, superconductors, self organized complex oxide quantum dot etc. [1]. The quality of the film deposited depends on various parameters like laser wavelength, energy, fluency, ambient pressure of the gas, substrate, target-substrate distance, and thermo physical properties of the target material which include density, mass, absorption coefficient etc. the optimization of these parameters to obtain a high quality film for a desired application is therefore an integral part for PLD.

In recent years, TiO₂ thin film has attracted much attention because of its chemical, electrical and optical properties [2-3]. It is known that the TiO₂ crystal usually has three different crystallographic structures: rutile (tetragonal), anatase (tetragonal), and brookite (orthorhombic) [4]. Two of them, rutile and anatase, are commonly used in photocatalysis and the TiO₂ with anatase structure shows a higher photocatalytic activity [5-6]. This unique photocatalytic property makes it suitable for the oxidation of organic pollutants and other contaminants from wastewater or drinking water supplies [7-8].

EXPERIMENTAL WORK

Undoped TiO₂ thin films were deposited on cleaned glass substrates by using pulsed Nd: YAG laser by pulsed laser deposition technique, Fig. 1 shows the schematic diagram of PLD system used in this study [9, 10]. Pulses of Q-switched Nd:YAG laser with pulse duration 7 ns and $\lambda = 1064$ nm were focused through 12 cm focal length of converging lens onto a high purity titanium target (99.999% provided from Fluka com.) at 45° angle of incidence. The target rotated with frequency of 1 Hz. The pulse laser energy between (700 – 1000)mJ was used. All films were produced using 70 laser shots and deposited at substrate temperature of 70°C (this growth temperature was optimum) in background gas oxygen with a pressure 50 mbar, this background gas was let into the vacuum chamber through a needle valve. The film thickness was measured by a stylus profilometer. The transmittance of the films was investigated in spectral range (300-800) nm using UV-VIS (SP8001) Shimadzu double beam spectrophotometer. The crystal structure of the grown films was analyzed with FTIR system (Shimadzu 8400 S). The morphology of the films was studied using optical microscope. The Atomic Force Microscope of these films was studied using Shimadzu AA3000 Scanning Probe Microscope.

RESULTS AND DISCUSSION

The optical absorption of TiO₂ films on glass prepared by reactive PLD were measured by UV-Vis spectrophotometer. Figure (2) shows the optical Absorption peaks, these peaks have as lightly blue shift with the increase of laser power due to

increase in particle size. In fact, increasing the fluency means delivering more energy that implies ablating larger amount of material, because of the plasma plume becomes more intense and the TiO₂ particles cloud becomes bushy. Most likely, this means that big particles will be present due to longer growth time and to the high probability of deposited particles muster. In other words, atoms and nanoscale particles deposited under laser radiation tend to muster during and after the laser pulse. This reality leads to generate of larger particles that becomes more distinguished when the density of the TiO₂ particles increases further with increasing the fluency.

The band gap energy E_g is found by plot $(\alpha h\nu)^2$ vs. $h\nu$ as shown in figure (3). The calculated band gap energies are among (3.7- 3.9) corresponding to the (1000, 900, 800, and 700 mJ) are higher than the bulk TiO₂, because of increasing in particle sizes reason due to the quantum confinement effect and increase of surface/volume ratio.

The TiO₂ has been grown on a glass substrate at oxygen pressure 20mbar and substrate temperature 70 °C. Figure (4 (a & b)) shows the AFM images of the TiO₂ thin films deposited at different laser energies (800, and 1000) mJ. The surface morphology of the TiO₂ thin films as observed from the AFM micrographs proves that the grains are uniformly distributed with individual columnar grains extending upwards. This surface characteristic is important from the topographic images it can be seen that the films deposited at 800 mJ appears to be more uniform than the topography of the sample deposited at 1000 mJ. The Root Mean Square (RMS) roughness and Roughness average (R_a) increased with increasing laser energy, the section analysis shows that RMS roughness values are (18 & 26.3) nm, Roughness average (11.2 & 16.5) nm and the average diameter of particles size (229.95 & 243.20) nm for thin films deposited at (800, 1000) mJ respectively. The particle size shown in figure (5 (a & b)).

In figure (6(a)) gives the FTIR result for film prepared at laser energy 800 mJ, we can recognize the absorption peak at (408.91, 439.77, 524.64) cm⁻¹ which related to the Ti-O-Ti bonds, beside the absorption bonds between 563.21 cm⁻¹ & 740.6 cm⁻¹ are assigned for O-N=O deformation which are very intense in IR spectra and the absorption pick at 1080.14 cm⁻¹ is relate to C-O=Ti bands, also the O-H Figure (6(b)) gives the FTIR result for film prepared at laser energy 1000 mJ, we can recognize the absorption peak at (408.91) cm⁻¹ which related to the Ti-O-Ti bonds, beside the absorption bonds 594.08 cm⁻¹ & 686.66 cm⁻¹ are assigned for O-N=O deformation which are very intense in IR spectra and the O-H group and the band around 1589.34 cm⁻¹ for bending vibration of H-O-H group it indicates the existence of water on the surface of TiO₂ [11,12]. An increasing the formation ability of the TiO₂ molecule could be recognize obviously by using the optimum laser energy (800 mJ). We can recognize the other peaks in figure 6(a & b) is related to glass substrate.

CONCLUSIONS

Highly transparent of TiO₂ films have been prepared on glass substrates by reactive PLD. Structural, and optical, characteristics of the films as a function of laser energy had been investigated. The FTIR structure result at 800 mJ is the

optimum and peaks absorption of TiO₂ are (408.91, 439.77, 524.64) cm⁻¹. The films deposited at oxygen pressure of 50 mbar have increasing band gap energies with increasing laser energies but at 800 mJ show the best results in all measurements so this laser energy is the optimum under the conditions used in this work.

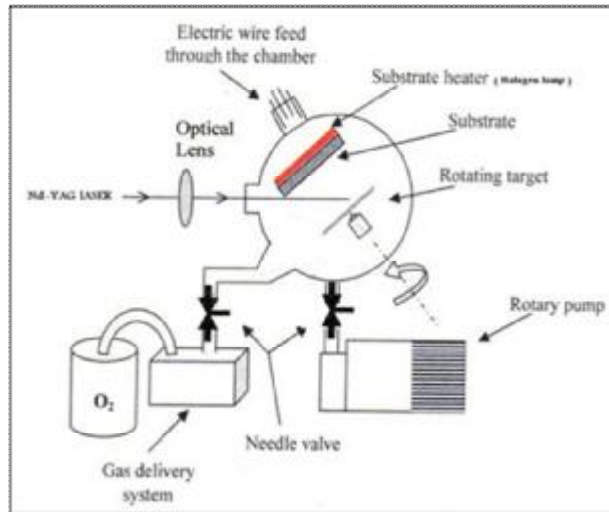


Figure (1). A-Schematic diagram of the PLD System used [9, 10].

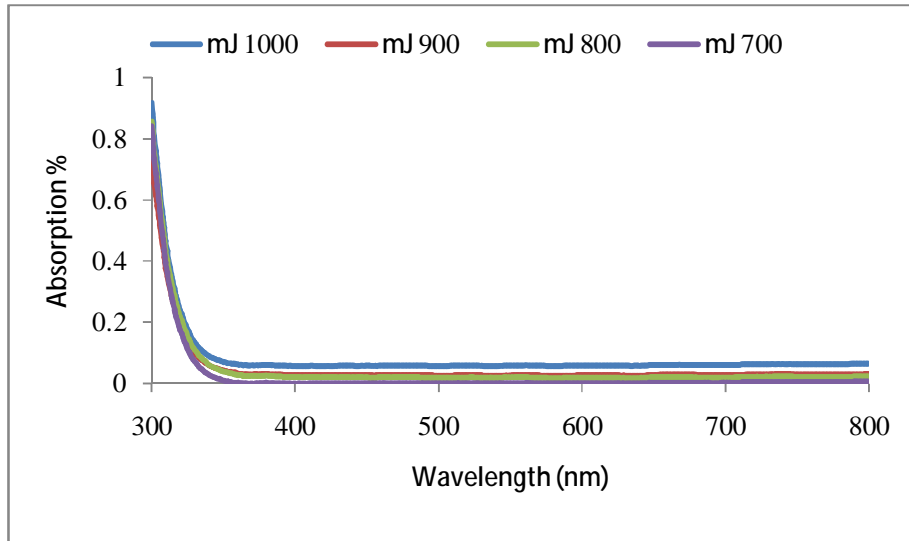


Figure (2): Optical Absorption as a function of wavelength for TiO₂/glass at different laser energy between (1000-700) mJ.

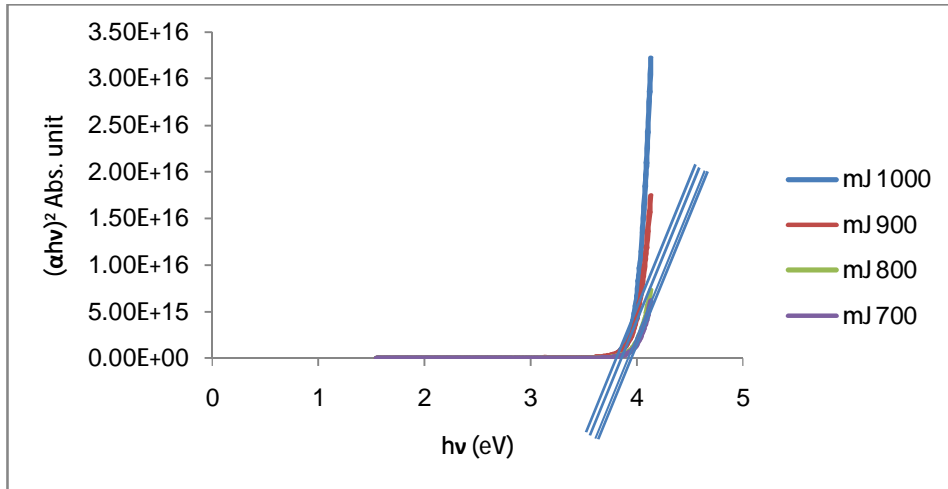


Figure (3): A plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of the $\text{TiO}_2/\text{glass}$ thin films at different laser energy between (1000-700) mJ.

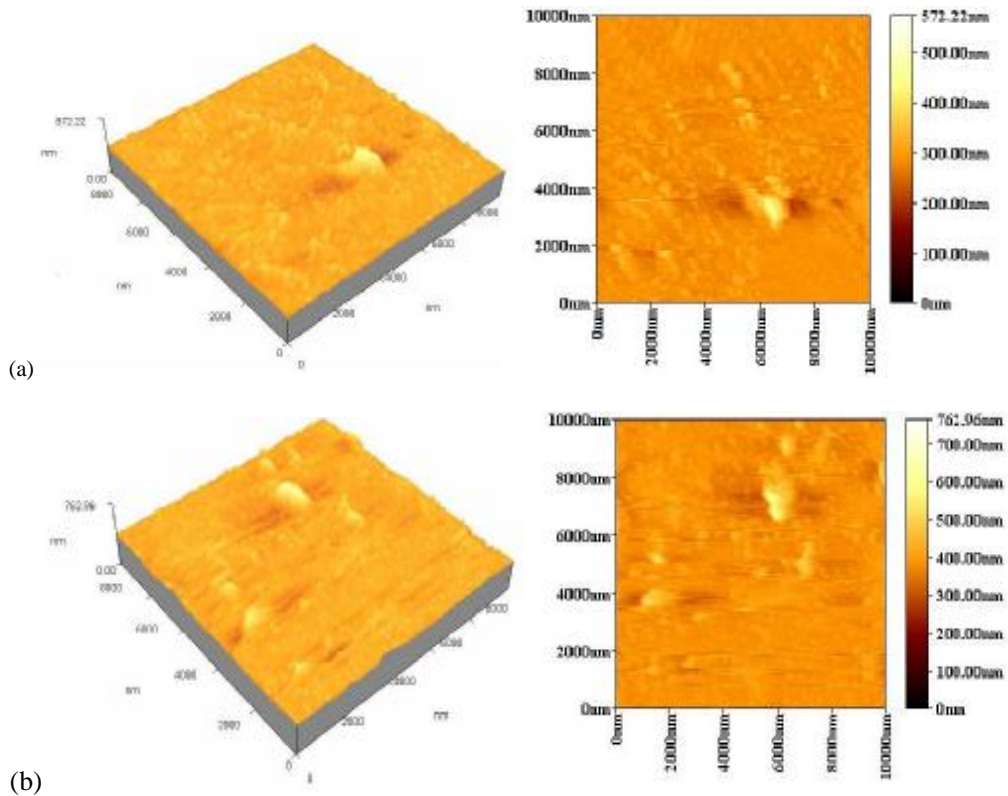


Figure (4): AFM micrographs of the $\text{TiO}_2/\text{glass}$ thin films at different laser energy a) 800mJ, b) 1000 mJ.

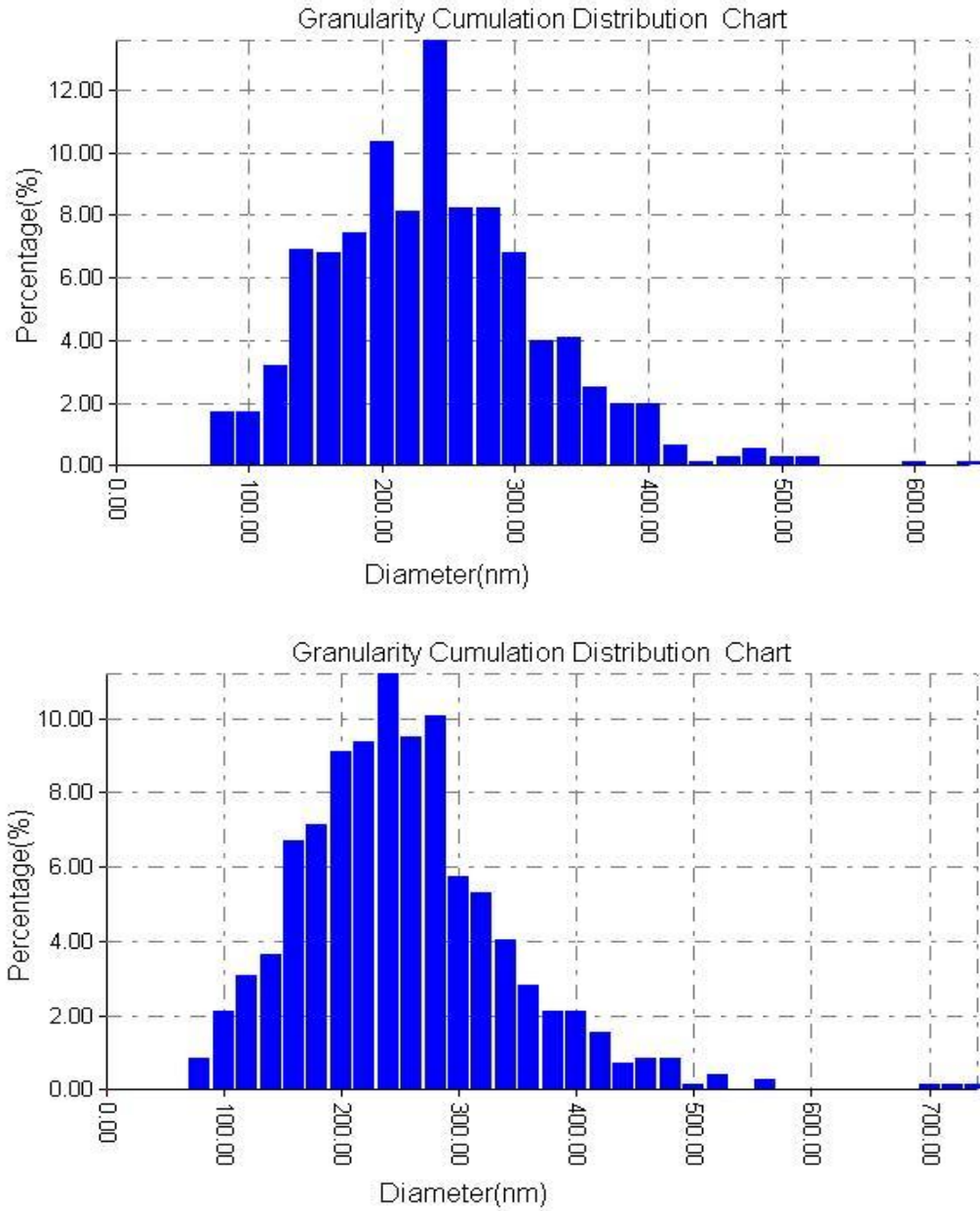


Figure (5): AFM particle size of the TiO₂/glass thin films at different laser energy a) 800 mJ

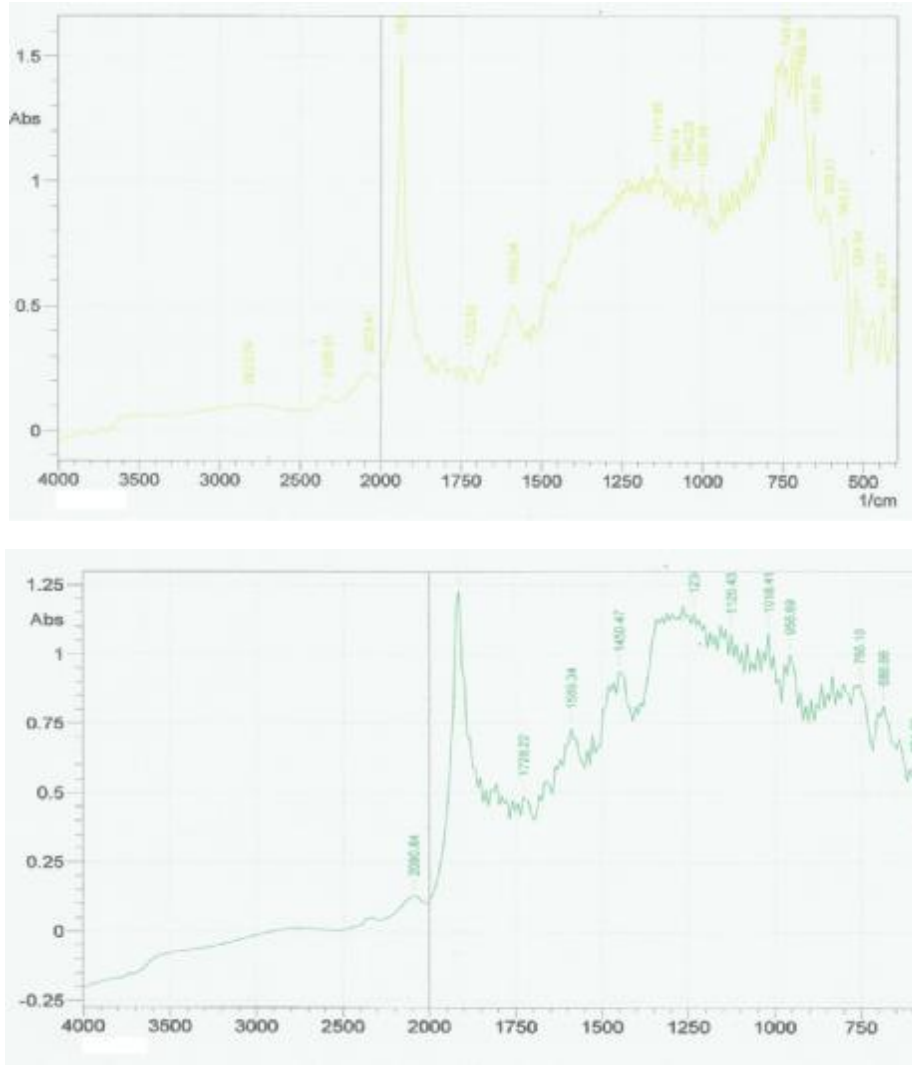


Figure (6): FTIR structure of the TiO₂/glass thin films at different laser energy a) 800 mJ, b) 1000 mJ respectively.

REFERENCES

- [1]. Misra, A. R. K., Thareja, J. Appl. Phys. 86 (1999) 3438.
- [2]. ZHANG S K, WANG T M, XIANG G, WANG C. "Photocatalytic activity of nanostructured TiO₂ thin films prepared by dc magnetron sputtering method", Vacuum, 2001(62): 361–366.
- [3]. PAILY R, DASGUPTA A, DASGUPTA N, GANGULI T, KUKREJA M L. "Effect of oxygen pressure and laser fluence during pulsed laser deposition of TiO₂ on MTOS (Metal-TiO₂-SiO₂-Si) capacitor characteristics", Thin Solid Films, 2004, 462/463: 57–62.
- [4]. YAMAMOTO S, SUMITA T, SUGIHARUTO, MIYASHITA A, NARAMOTO H. "Preparation of epitaxial TiO₂ films by pulsed laser deposition technique", Thin Solid Films, 2001, pp(88–93).
- [5]. LINSEBIGLER A L, LU G, YATES J T Jr. "Photocatalysis on TiO₂ surfaces: Principles, mechanisms, and selected results", Chemistry Review, 1995, 95: 735–758.
- [6]. XAGAS A P, ANDROULAKI E, HISKIA A, FALARAS P. "Preparation, fractal surface morphology and photocatalytic properties of TiO₂ films", Thin Solid Films, 1999, 357: 173–178.
- [7]. FOTOU G P, PRATSINIS S E. "A model of particle re-entrainment in electrostatic precipitators", Journal of Aerosol Science, 1995 (26): 227–239.
- [8]. BEMS B, JENTOFT F C, SCHLOGL R. "Photoinduced decomposition of nitrate in drinking water in the presence of titania and humic acids", Applied Catalysis: B Environmental, 1999, 20: 155–163.
- [9]. Dr. Evan T. Salem, Mukkaram. A Fakhry, Frhan A. Mohammed, "Oxygen pressure effect on optical and FTIR measurement of MgO thin films prepared by reactive PLD technique using for optoelectronic application", Almustansria University.j.ci, 2010, Vol. 21, No. 5.
- [10]. Raid A. Ismail, Bassam G. Rasheed, Evan T. Salm, Mukram Al-Hadethy, "High transmittance–low resistivity cadmium oxide films grown by reactive pulsed laser deposition" J Mater Sci: Mater Electron (2007) 18:1027–1030, DOI 10.1007/s10854-007-9129-4.
- [11]. Merouani, A. H. Amardjia-Adnani, "SPECTROSCOPIC FT-IR STUDY OF TiO₂ FILMS PREPARED BY SOL-GEL METHOD", International Scientific Journal for Alternative Energy and Ecology, NO. 6 (62) 2008, pp (151-154).
- [12]. Fusi, M. E. Maccallini, T. Caruso, C.S. Casari, A. Li Bassi, "Surface electronic and structural properties of nanostructured titanium oxide grown by pulsed laser deposition", Surface Science 605 (2011) 333–340.