A Study on the Structural, Optical and Electrical Properties of Tungsten TrioxideWO_3Thin Film for Gas Sensing Applications

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ABSTRACT

The pulsed laser deposition method, PLD, has been used in this project to deposit the pure Wo_3 The aim was to study the influence of temperature on surface morphology of the deposits materials using Atomic Force Microscope measurements at different temperatures of (RT,300 ,400)$^{\circ}$C . The structural characteristics of the films prepared on glass substrates have been studied by using X-ray diffraction and AFM. These tests show that there is a direct relationship between the grain sizes of the nanoparticles observed at the surface and influence of temperature which means as temperature increases there will be a similar enhancement in the grain size as well. Additionally, we were able to find that the best of temperature was 400^{o}C. Furthermore, the characterizations of the gas sensing of these thin films were strongly influenced by the surface morphology. It has been also found that nanocrystalline Wo_3 gas sensing material was presented a better sensitivity as temperature increases

Keywords: Pulsed Laser Deposition (PLD), thin films, nanocrystalline.

دراسة الخصائص التركيبية والبصرية والكهربائية لاغشية اوكسيد التنكستن الرقيقة لتطبيقات متحسسات الغاز

الخلاصة

في هذا العمل استخدمت طريقه الترسيب بالليزر النبضي لترسب ثلاثي اوكسيد التنكستن وتهدف لدراسه تأثير درجه الحراره الترسيب على مورفولوجيه السطح للمواد المترسبه باستعمال المجهر القوة الذرية و النتائج بينت ان هنالك علاقه مباشر بين الحجم الحبيبي للتراكيب الملاحظه عند السطح وتأثر درجه الحرارة وهذا يعني عند زيادة درجه الحراره يزداد الحجم الحبيبي وكانت افضل درجه حراره هي 400 سليزي . كما ان مورفولوجه السطح لها تاثير على الخصائص التحسسيه لهذه الاغشية وأيضا وجدالتحسسيه ثلاثي اوكسيد التنكستن تزداد مع زياده درجه الحراره .

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INTRODUCTION

Over the last few years, interest in tungsten trioxide (WO_3) has increased rapidly and significantly due to the material's potential applications in photo voltaic and photo catalytic processes[1].Tungsten trioxide (WO_3) is a cheap material , with excellent chemical stability, nontoxicity, good mechanical properties and is one of the most efficient semiconductor photo catalyst for extensive environmental applications because of its strong oxidizing power, high photochemical corrosive resistance and cost effectiveness[2,3 However, anatase is a wide band gap semiconductor (3.2-3.5 e**v**)[7 ,8]. Anatase possesses a higher photocatalytic activity than rutile due to the difference in the optical band gap[10].There are many techniques to synthesize WO_3 thin films, including sol–gel ,sputtering , anodic oxidation, pulsed laser deposition (PLD) , electron-beam evaporation and spray pyrolysis [8]. Among available techniques is pulsed laser deposition (PLD) which is a cheap deposition procedure, allowing the growth of rough-surface films at atmospheric pressure and on large area [11].

PLD plays a great roll in reducing the chemical contamination due to: the use of laser light, controlling of the composition of deposited structure, and in situ doping. Moreover, it is a versatile and powerful tool for production of nanoparticles with desired size and composition by only manipulating the deposition conditions. [3,4] It has been always applied as a gas sensing material to detect combustible, toxic and pollutant gases due to its high sensitivity, simple design and its low cost[5].

We report here the deposition of Tungsten trioxide thin film substrate at oxygen pressure of (2×10^{-1} mbar) and 1.2 J/cm^2 laser fluence and different substrate temperature. We also investigated the influence of different substrate temperature on structural ,morphological and sensing properties of the films.

Experimental Work

The deposition was carried out using a Q switched Nd:YAG laser at 532 nm (pulse width 7 n sec and laser fluence 1.2 J/cm^2). Nd:YAG laser (HuafeiTongdaTechnology—DIAMOND-288 pattern EPLS) was used for the deposition of WO_3 on different substrates . Tungsten trioxide powder was taken from Fluka Company with high purity (99.99%) and pressed under a 10 tons to form a pellet with 2.5 cm diameter and 0.4 cm thickness. X-ray diffraction measurements (Philips PW 1050 X-ray diffractometer**)** have been conducted according the ASTM (American Society of Testing Materials) cards, using 1.54 Å from Cu-k_α. In order to study the surface morphology atomic force microscopy (AFM) (Digital Instruments Nanoscope II). A double–beam UV-VIS (210A Spectrophotometer) was used to measure the transmittance of WO_3 film deposited under different

conditions. Finally, film thickness was measured by using an optical interferometer and found to be around 153 nm.

Results and discussion

The X-ray diffraction of TrioxideWO_3Thin Film:

WO_3 films formed at substrate temperatures of($25^{\circ}C$,300° C, 400 $^{\circ}C$) on glass substrate with a laser fluence of $1.2J/cm^2$ and Oxygen pressure of 2×10^{-1} mbar were used . Fig (1) shows the XRD measurements results for different peaks on $2\theta=23^{\circ}$,2θ

=29.3765°, 2θ =33.02°, 2θ =50 °, 2θ =53.75° and 2θ=54.11° corresponding to the (001), (101), (111), (102), (112) peaks respectively with low intensity. Fig (1) shows dominant peaks on 2θ =23.652° .

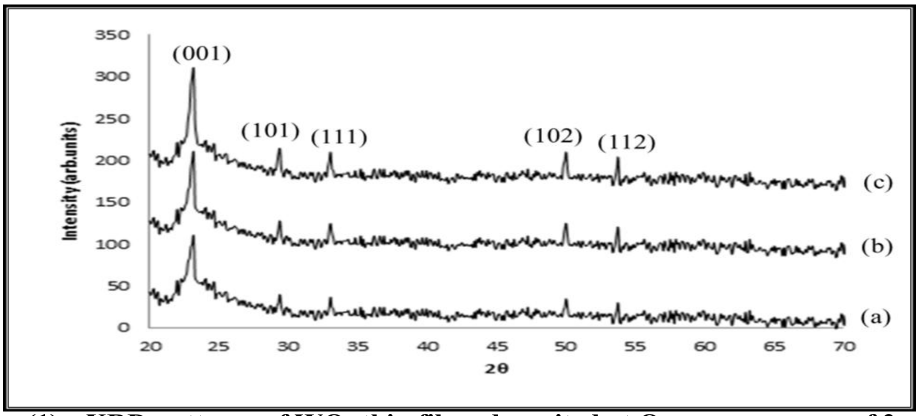


Figure (1):- XRD patterns of WO_3 thin films deposited at Oxygen pressure of 2 ×10^{-1}mbar (a) RT(b) 300 °C,(c)400 °C.

Fig (2) shows The doped tungsten trioxide films become less crystalline than undoped samples. The peaks in the X- Ray diffraction shift into the region of higher θ, indicating stress in the grains. XRD analysis also did not detect the dopant phase [13].

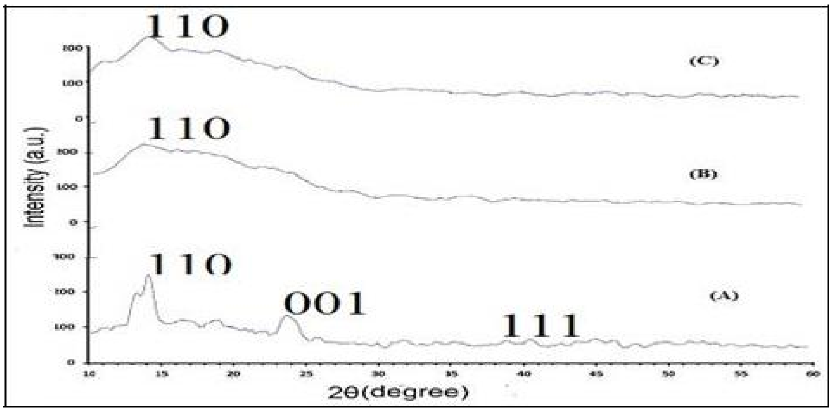


Figure (2):- XRD patterns of WO_3:PT thin films deposited at Oxygen pressure of 2 ×10^{-1}mbar and at different concentrations a) 1% b) 3%, c)5%.

Atomic Force Microscopy (AFM)

Figure (3) shows the granularity accumulation distribution chart of WO_3 for WO_3 pure and doped with Pt films deposited at temperature of 400°C and on glass substrate by using PLD technique .The average grain size was found to be 115-140 nm from AFM. The average grain size was obtained by using Scherrers- Debye formula[13] it was smaller than that estimated from AFM measurement indicating that grains are probably an aggregate of many crystallites**.**

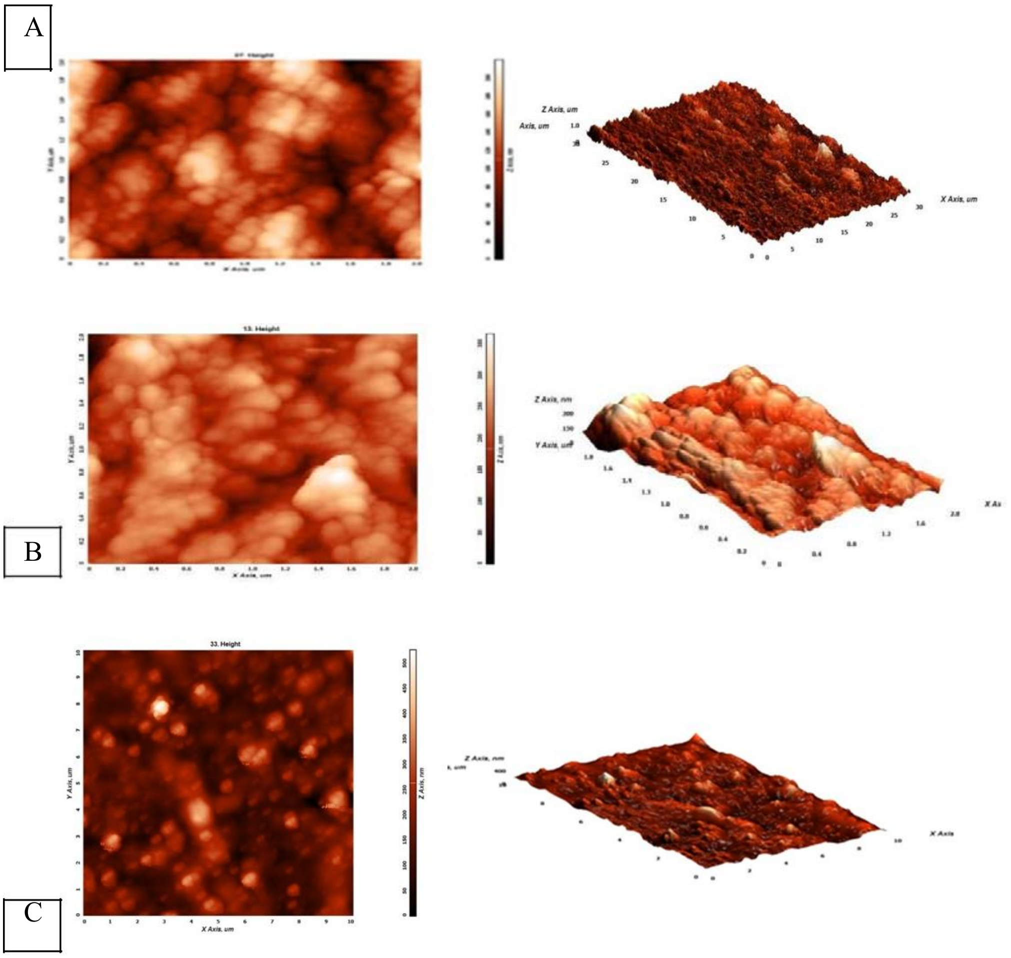


Figure (3): AFM images at 400˚C: (A) WO_3doped Pt at 1% (B) WO_3 doped Pt at 3%(c) WO_3 doped Pt at 5%

From Fig (4) shows the optical transmittance of the undoped WO_3 films deposited on glass substrate at different temperatures. From all the films analyzed it is observed that the optical transmittance increases with increasing the temperatures.

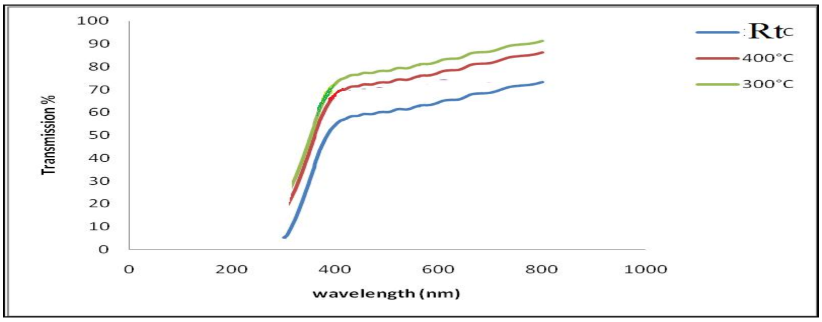
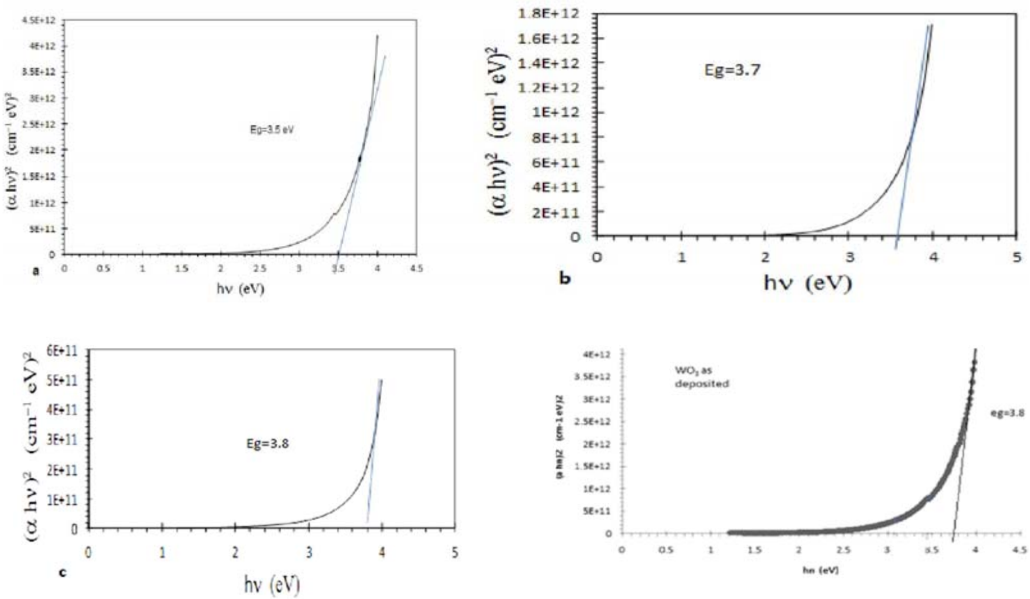


Figure (4): Transmittance spectra of WO_3 thin films at different temperatures with fixed Oxygen pressure of 2 $\times 10^{-1}$mbar

From Fig (5a,b,c,d) shows The direct band gap values for WO_3:Pt thin film doping at different Pt concentrations(1,3,5)% at substrate temperature of 400°C. The results show an increase in the Pt content resulted in a decrease in the band gap to about (3.8-3.5) eV. This decrease in energy gap can be due to the prohibited impurities that led to the formation of donor levels within the energy gap near the conduction band



Figure(5): A plot of $(\alpha h\upsilon)^2$ versus $(h\upsilon)$ of Wo_3 thin films at400 ^{o}C 400 at different doping concentrations with Pt a- as deposited, b-WO_3 at (1%) , c- WO_3:pt (3%) and d- WO_3:pt (5%)

The Electrical Properties

Figure (6) shows the resistivity decreases as the temperature is increased, with different thicknesses. This agrees with semiconductor behavior.

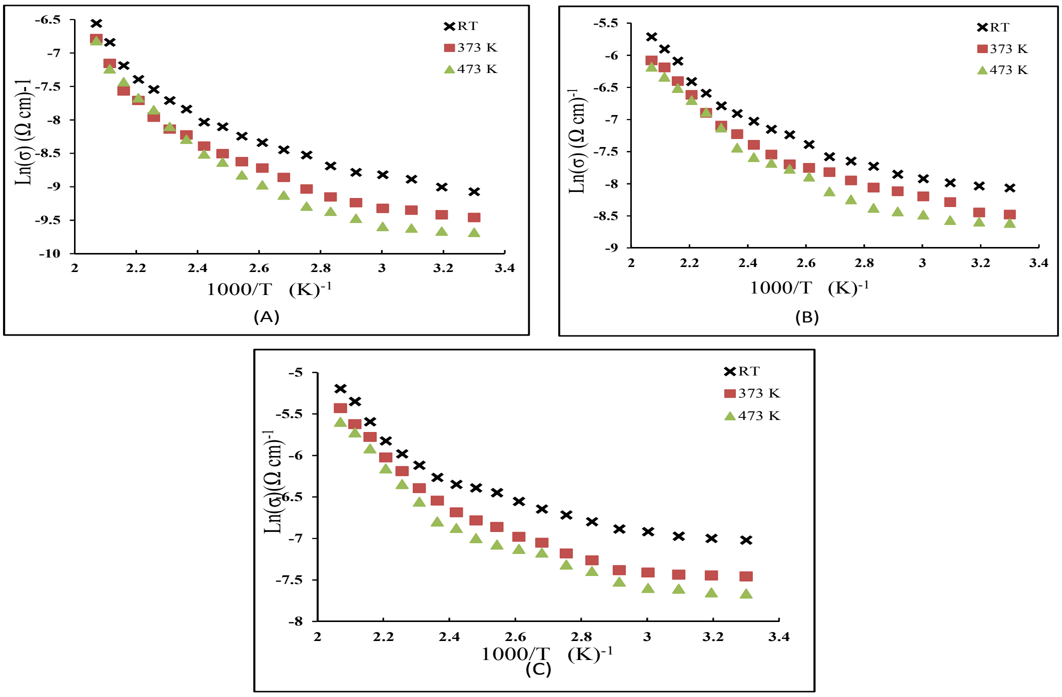


Figure (6) Ln σ versus 1000/T for WO_3 films at different thicknesses (a): 135nm, (b): 145nm, (c): 153nm, with different Substrate temperatures.

Table (1): D.C conductivity parameters for WO_3 films at different thicknesses and temperatures.

Thickness(nm)	T_a (K)	(303 – 363)K	(363 – 433)K	(403 – 483)K	$\sigma_{R.T} \times 10^{-3}$ $(\Omega.cm)^{-1}$
		E_{a1} (eV)	E_{a2} (eV)	E_{a3}(eV)	
135	R.T	0.069	0.159	0.346	0.115
	373	0.075	0.179	0.376	0.077
	473	0.089	0.215	0.411	0.062
145	R.T	0.055	0.143	0.335	0.314
	373	0.064	0.161	0.361	0. 208
	473	0.0755	0.172	0.386	0.182
153	RT	0.0466	0.1	0.321	0.894
	373	0.061	0.125	0.332	0.577
	473	0.067	0.132	0.358	0.496

electrical resistivity was found to be a function of doping concentration as shown in Fig (7).

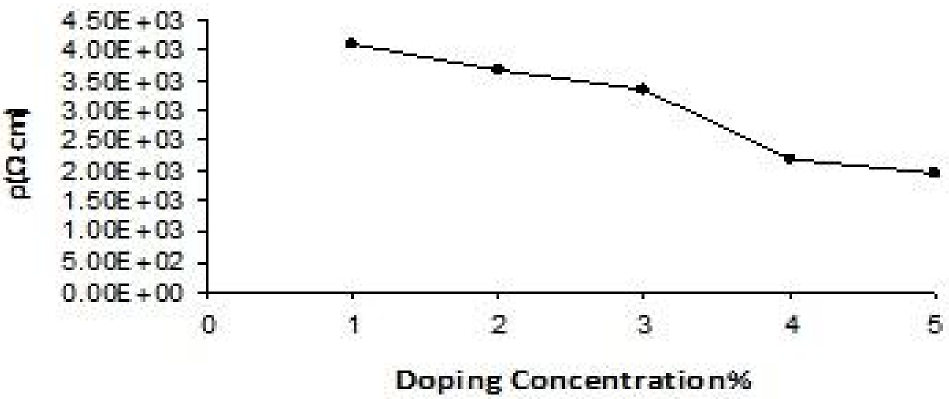


Figure (7): The electrical resistivity as a function of different doping concentrations with Platinum

Figure (8) shows that the electrical resistivity decreases with increasing doping concentration of Pt in WO$_3$ thin films. The results may be attributed to the increasing concentration (n).

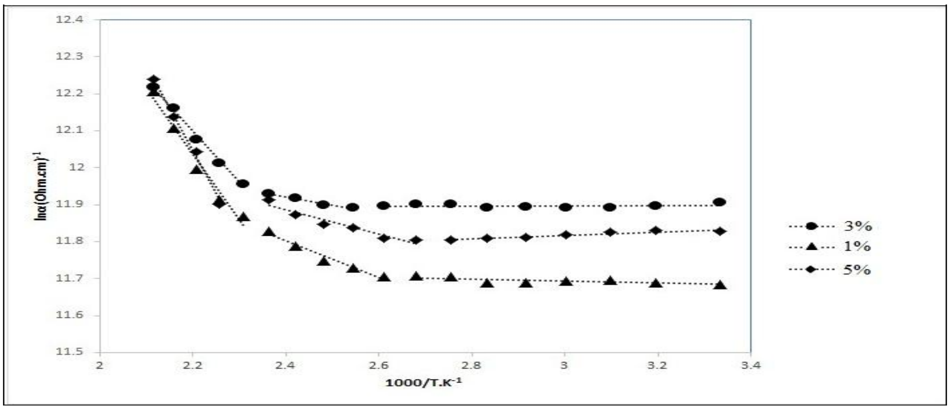


Figure (8): Ln ρ as a function of 1000/T(K) $^{-1}$ for WO3 films at different doping concentrations with Platinum(wo$_3$:1%pt,wo $_3$:3%pt wo $_3$:5%pt)

Table (2): Activation energies Ea$_1$ and Ea$_2$ for WO3$_2$ thin films for different doping concentrations with Platinum(wo$_3$:1%pt,wo$_3$:3%pt wo $_3$:5%pt)

Doping with Cr	E$_{a1}$(ev)	E$_{a2}$(ev)
wo$_3$:1%pt	0.0957	0.11388
wo$_3$:3%pt	0.10383	0.1175
wo $_3$:5%pt	0.1279	0.13383

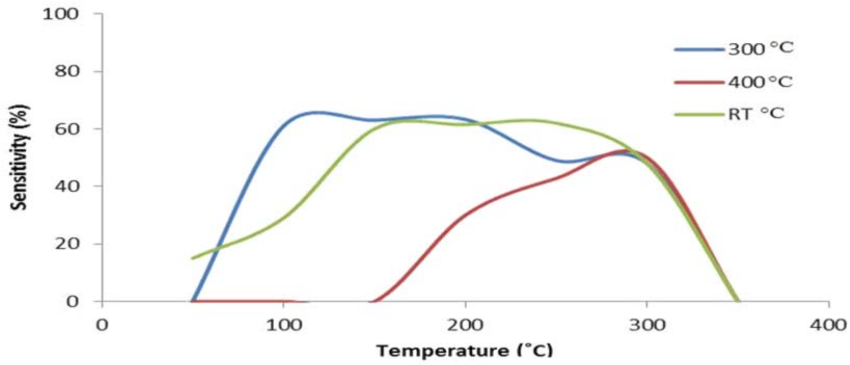


Figure (9): sensitivity of WO_3 films to NO_2 gas at different operation temperatures (RT,300,400) ^{0}C at laser fluence of 1.2 J/cm^2.

Fig (9) shows the sensitivity as a function of operation temperature in the range of (50-400 °C) for WO_3 pure and doped with noble metal at different concentrations of (1 , 3 and 5%) . All the films increases with the increasing in the operating temperature ,reaching a maximum value corresponding to an optimum operating temperature which is 350°C for all the samples. The response of the undoped sensor to NO_2 gas is relatively low.

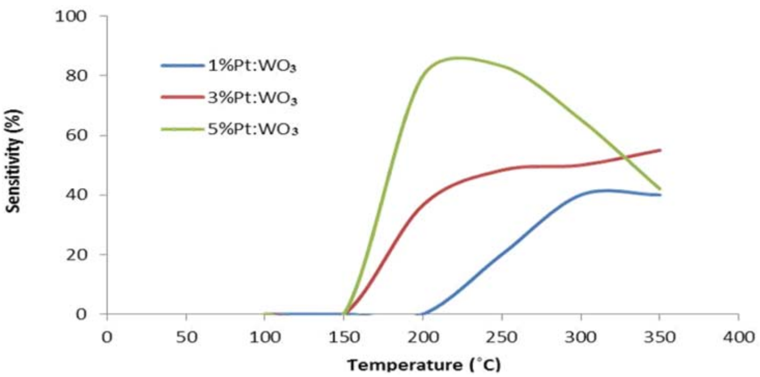


Figure (10): Sensitivity of WO_3: Pt films to NO_2 gas at different operation temperatures at laser fluence of 1.2 J/cm^2.

Fig (10) shows Noble metal doping (Pt) increases the sensitivity of WO_3:PT sensors to NO_2 gas and improves the sensor response at which the sensor response is maximized at 250°C for WO_3 doping 5% Pt.

CONCLUSION

From this work ,it can be concluded that best conditions of WO_3 pure and doping with noble metal for gas sensing prepared by PLD the substrate temperature deposition is $400^{\circ}C$. The oxygen pressure is 2×10^{-1}mbar. The laser fluence energy density is 1.2 J/cm^2. The doping at percent (5 wt %)

Thus for sensing performance of WO_3 pure and dopant with noble metals modified sensors; it is clear that pure WO_3 showed poor response to NO_2 gas. 5 % wt Pt doped WO_3 thin film was the most sensitive element to NO_2 gas. The optimum operating temperature for NO_2 gas sensing was (250) $^{\circ}C$

Pt doped WO_3 thin film would be suitable for fabricating the NO_2 gas sensors showed good selectivity to NO_2 gas.

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