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Impact of the thickness of Nickel oxide film for nitrogen dioxide gas sensing Applications

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Abstract: ***Nickel oxide (NiO) thin films were formed by RF reactive magnetron sputtering onto glass substrates. The Argon and Oxygen partial pressure were (3.2×10^{-3} torr) and (2.12×10^{-2} torr) respectively at room temperature. The thickness of the films deposited was in the range of 50-150 nm. The thickness necessity structural, electrical and sensing properties of (NiO) films were methodically examined. X-ray diffraction method which shows polycrystalline landscape with preferred reflection peak at (200) plane. Scanning electron microscope analysis revealed that the growth of nanorods in all the films. The gas sensitivity of nitrogen dioxide gas was (67 %). It was observed that the gas sensitivity for (NiO) films was increased as film thickness increases.***

Keywords: magnetron sputtering, Nickel oxide, Nitrogen dioxide, Dynamic resistance, Sensitivity.

1. INTRODUCTION

Nickel oxide (NiO) is the most exhaustively investigated transitional Metal oxide. It is a NaCl P-type antiferromagnetic oxide semiconductor. It offers promising candidature for many applications such as solar thermal absorber [1], catalyst for O_2 evolution [2], photoelectrolysis [3], electrochromic device [4], and functional sensor layers for chemical sensors [5] These films have been fabricated using various physical and chemical vapor deposition techniques such as thermal oxidation of nickel [6], chemical bath deposition [7], spray pyrolysis [8], sol-gel process [9], electron beam evaporation [10], atomic layer deposition [11], pulsed laser deposition [12], metal organic chemical vapor deposition [13], molecular beam epitaxial [14], and DC [15] and RF magnetron sputtering and electrodeposition [16], Among these methods, reactive sputtering is the most extensively used. Researchers [17] have been carried out on the dependence of film properties on sputtering parameters. Numerous reference data and previous studies [18] have demonstrated that superior electric and optical properties of NiO films can be obtained by reactive sputtering with a sputtering pressure in the range 0.1–1 Pa and in a pure oxygen atmosphere using a heated substrate. The increase in surface area and the quantum confinement effects have made nanostructured materials are quite distinct from their bulk form in both electrical and optical properties various one-dimensional structures of NiO, such as nanowires, nanorods, and Nanobelts, have attracted much attention [19]. Among these deposition techniques, magnetron sputtering is industrially adopted thin films preparation method because of the advantages in the generation of uniform and large area films. The physical properties of the sputtering films depend mainly on the process parameters such as oxygen partial pressure, sputter power, substrate temperature, substrate bias, thickness and post deposition annealing The influences of film thickness on the structural, optical, and electrical properties of thin films are very important. Many reports on the effect of size on thin films of various materials have been published [20]. However, only a few works on the dependence of the properties nickel oxide films on film thickness have been published [21].

2.METHODS AND MATERIALS

Thin films of nickel oxide were formed onto well-cleaned glass substrates (Super River w. Germany) held at temperature range 40°C – 50°C which is the sputter chamber temperature by RF magnetron sputtering method. Metallic nickel target (99.99 % pure supplied by Nuclear Fuel Complex, India) with 50 mm diameter and 3mm thickness was used as sputter target for deposition of the films in the sputter dawn configuration. The deposition rate kept at (0.1 – 0.2) Å/sec by the deposition rate and thickness controlled by crystal sensor (FTM-2000). The distance between the target and the substrate was (100 mm). The sputter chamber was evacuated to the base pressure of $4.1x10^{-6}$ torr employing molecular devotion and turbo combination. The pressure in the sputter chamber was measured with digital Pirani - Penning gauge (adixen ACS 2000) combination. Argon and oxygen (99.999 % purity) were used as sputter and reactive gasses for deposition of the films. Individual Argon and Oxygen gasses penetrate to the chamber with gas mass flue controller (Ailcat scientific) controllers were employed to admit these gasses in required quantities in the sputter chamber. The Argon and Oxygen partial pressure were (3.2×10^{-3} torr) and (2.12×10^{-2} torr) respectively. Radio frequency (13.5 KHz) RF power (TORR INTERNATIONAL, INC.CRC600) used to feed the sputter target of 200 W. The crystal structure of deposited films was identified by the X-ray diffraction (XRD) (shimadzo 6-2000, with cuk_α radiation having wavelength λ=0.15406 nm) technique. The surface microstructure was studied by (S-4160) Hitachi (college of engineering and communications, iran-Tehran) scanning electron microscopy (SEM).

3.RESULTS AND DISCUSSIONS

Structural reading of Nickel Oxide Films:

X-ray diffraction pattern of NiO films prepared by RF reactive magnetron sputtering with different thickness (50, 100 and 150) nm at (50- 60) °C is shown in figure (1) which illustrate that all sample deposited were polycrystalline nature [22] consisting nickel oxide cubic phase with sharp and very fine peaks indicate a good crystallization and the

major peak is along (200) plane at 2 θ = 42.98 °. This is for cubic crystal structure according to ASTM card [No.00-047-1049][23]. Minor small peaks along (111) and (220) planes corresponding to the angles 2θ = 37.23° and 2θ = 62.34° respectively for thickness 50 nm, and only (111) reflection for both thickness 100 nm and 150 nm. It's observed that the higher intensity in the direction of (200) plane is for the thickness 150 that indicates that enhanced the crystallinity [24].

The lattice constant (a) was calculated by equation (2).

$$a = d/(h^2+k^2+l^2)1/2 \quad (1)$$

a = lattice constant (nm).
d= inter planer distance (nm).
(hkl) = miller indices.

Table (1) shows lattice constant values that measured from XRD pattern for nanostructure NiO films and theoretical lattice constant values of ASTM standard card which shows good agreement with those reported earlier by [25]. The peak intensity increase as the film thickness increase, this due to the peak intensity and crystalline are associated with the crystallinity of the deposited films [26]. According to crystal growth mechanism, the crystal orientation of the film is determined by the growth of the nuclei in the deposition of the oxide film, the film initially nucleated in a random orientation. When the film grows from the initial nuclei, the crystal plane of the nuclei with minimum surface free energy may remain parallel to the film surface because of the growth rate of the crystal plane with a minimum surface free energy another crystal plan [27]. The deposition controls processes that including controlling the deposition rate to limits close to 0.1- 0.3 (Å\sec.) Advantages to controlling the amount of the thickness of the film which is a key parameter, especially in the Field of nanotechnology. Also reaching necessary vacuum to 10-6 torr and high purity of used materials leading to achieve high crystalline materials [28]. The Crystallite size (D) has been calculated by Schere's equation (2):

$$D = K\lambda / \beta \cos\Theta \quad (2)$$

λ = wavelength of the copper X-ray source which was equal to (1.5406 Å)
β = FWHM in radian.
Θ = Bragg's diffraction angle

It was found in nanoscale and estimated about 22nm-25nm, as the film thickness increase from (50 – 150) nm. The enhancement of the crystallinity, which gives Crystallite size with nanoscale, through controlling sputter power and deposition rate with small values led to decreases the FWHM value [29]. Figure (2) shows the Crystallite size and FWHM values varieties with a thickness of NiO film the results are shown in Table (1). Microstrain (ε) which has been valued from equation (3):

$$\varepsilon = \beta \cos\Theta / 4 \quad (3)$$

is caused during the growth of the film and will be raised from stretching or compression in the lattice. The Microstrain (ε) reduction caused by varying displacement of the atom with respect to their reference lattice position [30]. Figure (2) shows the Microstrain in the films decreases with the increases in the film thickness, which may cause the increases in the crystallinity of the film [25]. Dislocation density (δ) is an imperfection in the crystal associated with the registry of the lattice in one part of the crystal with another part. The dislocation density (δ) has been calculated by using the equation (4)

$$\delta = 1 / D2 \quad (4)$$

Figure (2) shows the dislocation density decreases as the thickness increases [31]. The results of Microstrain and dislocation density values are shown in Table (1).

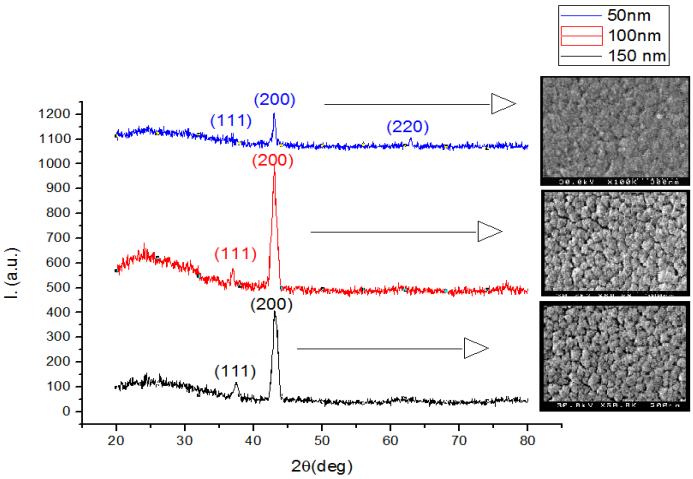


Figure 1: XRD Pattern of Nickel Oxide Films Deposited by RF Reactive Magnetron Sputtering

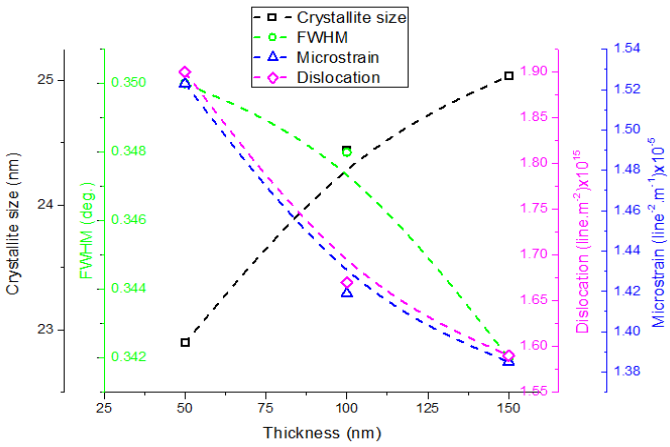


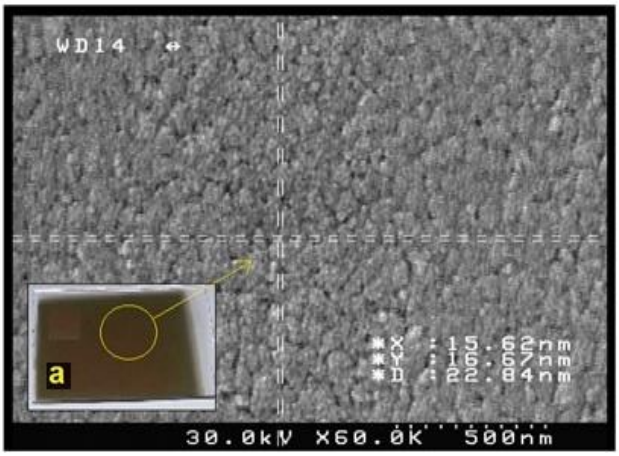
Figure 2: Crystallite, FWHM, Microstrain and Dislocation Density Variation With thickness for NiO Deposited by RF Reactive Magnetron Sputtering.

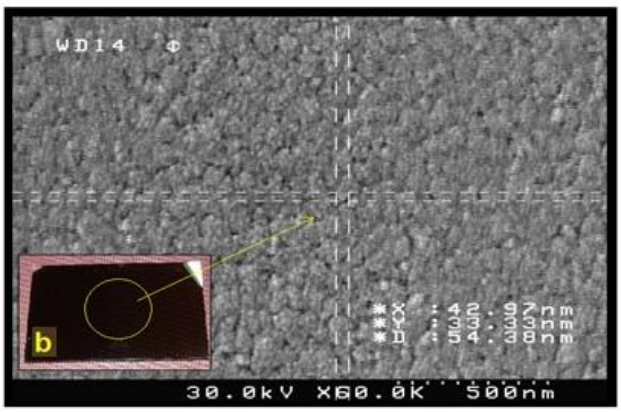
Table 1: Structural Parameters of NiO Thin Films Prepared RF. Sputtering .

Thickness (nm)	*(hkl) plane*	*FWHM (deg.)*	*2θ*		*XRD d(A⁰)*	*I/I₀*	*Crystallite size D (nm)*	*Lattice Constant (nm)*	*Microstrain (line⁻².m⁻⁴)× 10⁻⁵*	*Dislocation density(δ) (line.m⁻²)×10¹⁵*
			XRD	*ASTM*						
50	*(200)*	*0.374*	*42. 98*	*43.27*	*0.208*	*100*	*22.894*	*0.4174*	*1.523*	*1.90*
	(111)	*0.300*	*37.40*	*37.42*	*0.213*	*6*	-	-	-	-
	(220)	*0.482*	*62.85*	*62.78*	*0.408*	*5*	-	-	-	-
100	*(200)*	*0.350*	*43.31*	*43.27*	*0.210*	*100*	*24.438*	*0.4204*	*1.419*	*1.67*
	(111)	*0.421*	*37.23*	*37.42*	*0.242*	*12*	-	-	-	-
150	*(200)*	*0.342*	*42.35*	*43.27*	*0.208*	*100*	*25.036*	*0.4170*	*1.385*	*1.59*
	(111)	*0.300*	*37.04*	*37.42*	*0.356*	*5*	-	-	-	-

Scanning Electron Microscope (SEM)

The morphology of NiO nanostructures film prepared by RF-reactive magnetron sputtering method is characterizes by SEM images. Figures (3) show the typical SEM images of the prepared NiO nanostructures films at a different thickness (50,100 and 150) nm respectively, homogeneous distribution, very smooth and the crystallites are very fine. No large particles can be found from SEM image. Particle size increases from 45 nm to 60 nm when the thickness rose from 50 nm to 100 nm and nanorods growth perpendicularly with diameter 85 nm and the surface becomes more porous. When the thickness is further increased to 150 nm the Nano grains size increases to 70 nm. That is good agreement with XRD measurement for undoped nickel oxide nanostructure films.





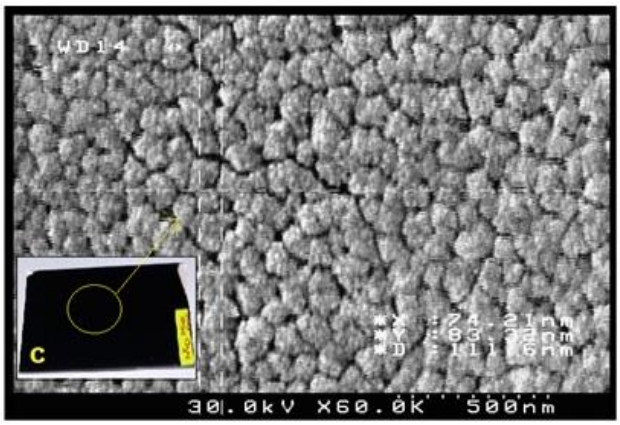


Figure 3 :SE M pattern for nanostructure NiO prepared by RF sputtering (a) 50 nm, (b) 100 nm and (c) 150 nm).

Gas Sensing Properties:

Nitrogen dioxide, NO_2, is one of the most dangerous gasses emitted from burning of the exhaust of cars engines, home heaters, furnaces, plants [32].

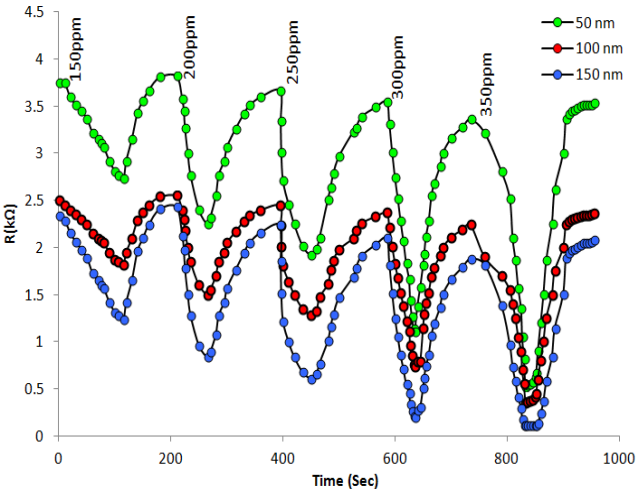


Figure 4: A Dynamic Resistance Change of NiO Films for Different Concentrations of NO_2 Gas and Different Thicknesses at an Operating Temperature of 150 °C.

Therefore the development of sensors that are tough small size, long lifetime, and quick in response and with sufficient sensitivity for the detection of nitrogen dioxide in low concentrations, in the environment is so important and needed. The surface morphology and particle size is the key variables in the sensing properties of Metal oxide gas sensors and are mostly organized by the adsorbed oxygen molecules, obviously increasing the surface-to-volume ratio or enhancing the surface adsorption which will increase the resistance change and improve the sensitivity [33]. It is known for many years that the adsorption-dependent electrical properties of metal oxide semiconductors are often sensitive to much gaseous ambient. The gas sensing properties of copper-doped and pure NiO nanostructures for NO_2 as oxidizing gas and hydrogen as reduced gas were studied as a function of the operation time at operation temperature 150°C. Figure (4) show the dynamic resistance change of NiO films prepared by RF reactive magnetron sputtering method with different thickness (50, 100 and 150) nm, exposure to different concentrations of NO_2 gas (150, 200, 250, 300 and 350) ppm. It's obvious that lowest resistance was for the samples of 150 nm. Which can be related to the highest roughness obtained from AFM analysis and also due to the high surface area and porosity confirmed from data obtained from the SEM image and also from the electrical resistance that shows the lowest resistance for the film of 150 nm thickness. All the samples showed p-type semiconductor performance (decreasing in resistance when exposing to oxidize gas) and the resistance of the films decrease with increasing of NO_2 concentration inside the chamber [34, 35], this can explain as the electrons are taken from ionized donors through conduction band and the density of majority charge carriers (holes) at the gas–solid interface is increased. This leads to the decreases of a potential barrier for electrons with increasing of the oxygen ions density on the surface. The depletion layer and potential barrier lead to the decreasing of the electrical resistivity value this value is strongly dependent on the concentration of adsorbed oxygen ions of the surface [36]. Introducing the NO_2 ambient will change the concentration of these ions and decrease the resistance. The sensitivity can be calculated from equation (5)**:**

$$\text{Sensitivity} = \Delta R/ R_a = (R_a - R_g/R_a) \times 100\% \qquad (5)$$

R_a = resistance of the film sensor in air presence.

R_g = resistance of the film sensor in gas presence. And plotted as a function of gas concentration (ppm) as shown in figure (5). The sensitivity percentage value for NiO films to nitrogen dioxide gas with different thickness, found to increases with the increasing of film thickness and the highest sensitivity value, is 67% for 350 ppm gas concentration of NO_2 is obtained for the film of 150 nm thickness at operation temperature 150°C. The sensitivity of the metal oxide semiconductor sensor is mainly determined by the interaction between the target gas and the surface of the sensor. The greater surface area of the materials that showed in AFM measurements becomes a stronger interaction between the adsorbed gasses and the sensor surface, i.e. higher gas sensing sensitivity.

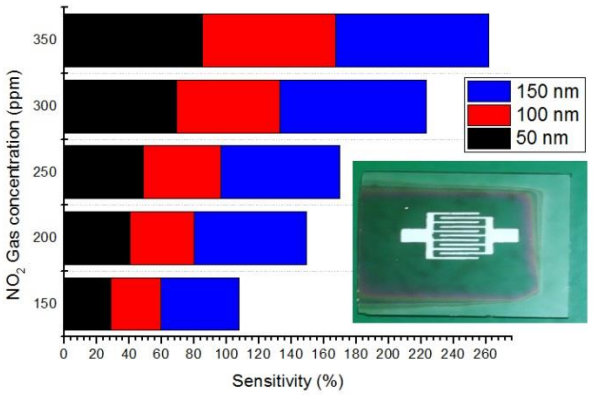


Figure 5: Percentage Sensitivity of NiO Films for Different Concentrations of NO_2 Gas and Different Thicknesses at 150°C Operating Temperature.

Figure (6) shows the response time, which is found to decrease from (140 to about 60) sec. as the gas concentration increasing, the decreasing in response time may be due to the large availability of vacant sites on thin films for gas adsorption [37]. The response time values are found convergent for all NiO films to NO_2 gas, while, figure (7) shows the increasing in recovery time from (70 to 140) sec. as the NO_2 gas concentration increases, this increasing due to the saturation of the sensor by the target gas furthermore the change in the structural properties that could take place by the operating temperature.

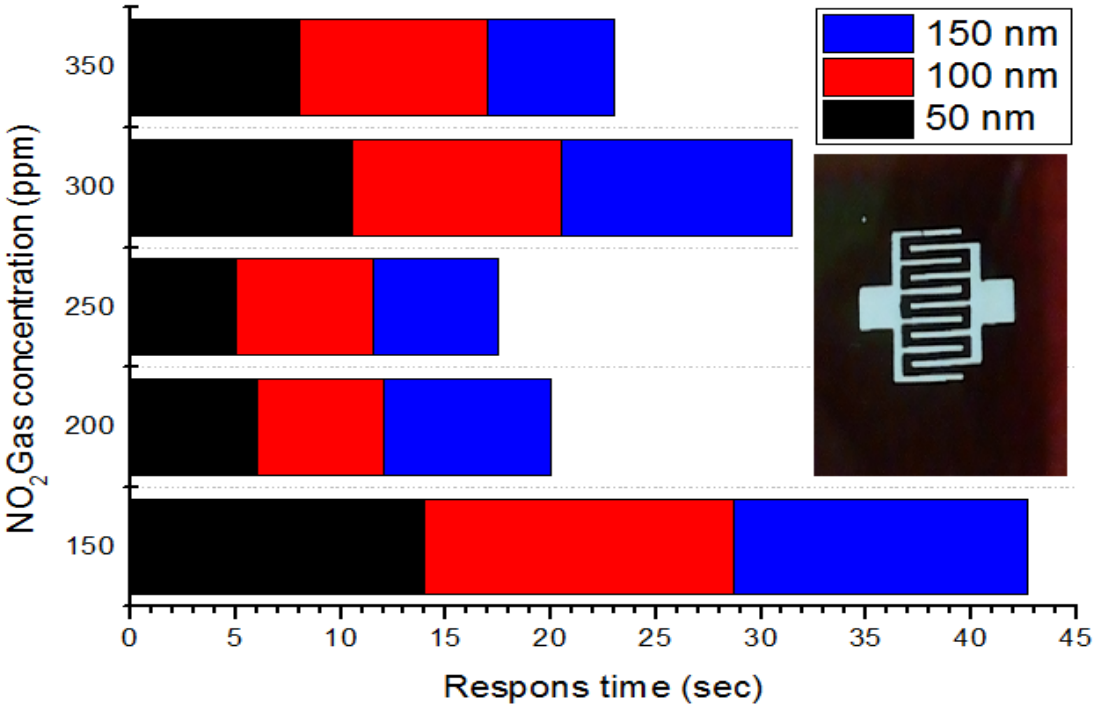


Figure 6: Response Time of NiO Films for Different Concentrations of NO_2 Gas and Different Thicknesses at 150°C Operating Temperature.

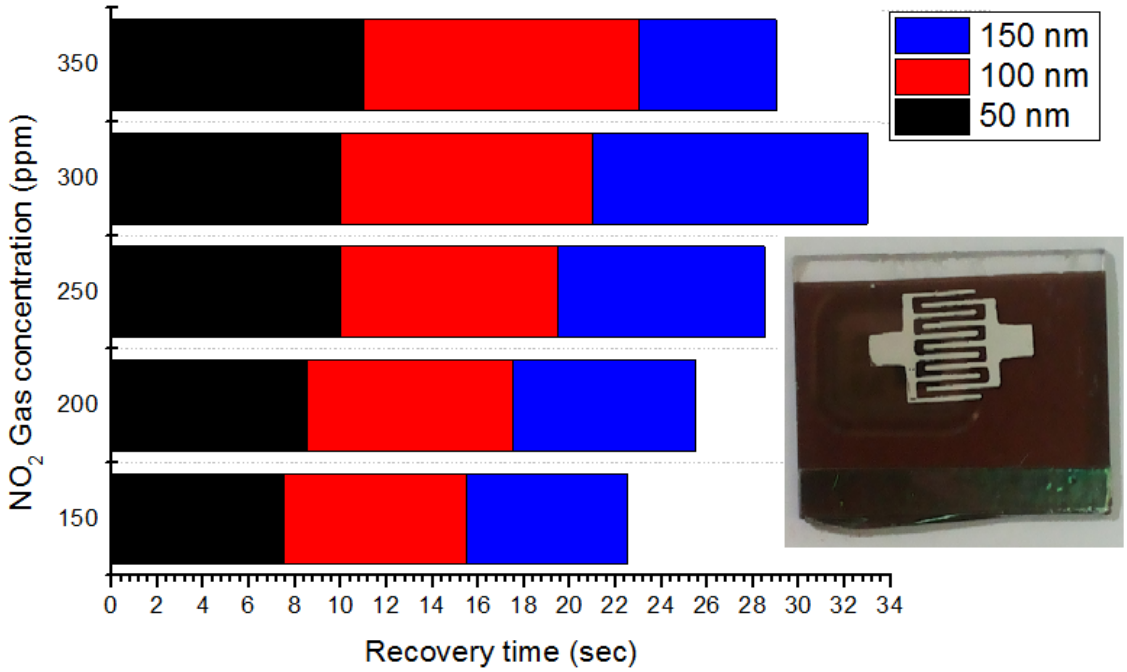


Figure 7: Recovery Time of NiO Films for Different Concentrations of NO_2 Gas and Different Thicknesses at 150◦C Operating Temperature

4. CONCLUSIONS:

Different thickness of NiO nano structures films are successfully prepared using RF reactive magnetron sputtering. The polycrystalline structure film with cubic structure of NiO film is formed and the films show growth along the (200) direction for all prepared films with Rod like nano structure growth. The transmittance in the UV and VIS regions results the value of optical Eg decreasing with thickness increases. The NiO films of 150 nm thickness show the maximum sensitivity is 67% for NO_2 gas of 350 ppm gas concentration obtained at operation temperature 150^{o}C.

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