Reactive DC magnetron sputter deposition and structural properties of NiO thin films

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Dr. Ibrahim R. Agool
Al- Mustansiriyah University / Baghdad.
Dr. Mohammed K. Khalaf
Ministry of Sciences and Technology / Baghdad.
Dr. Shaimaa H. Abd Muslim
Al- Mustansiriyah University / Baghdad.
Riyadh N. Talaq
Al- Mustansiriyah University / Baghdad

Abstract
Nickel oxide (NiO) films were deposited by using a homemade DC reactive magnetron sputtering system at different working pressure in the range (0.05-0.14)mbar. The effect of working pressure on the structure, surface morphology, optical of NiO films was investigated. X-ray diffraction (XRD) results suggested that the deposited films were formed by nanoparticles with average particle size in the range of (8.145-29.195) nm. And the films are identified to be polycrystalline nature with a cubic structure along (111) and (101) orientation also Ni_2O_3 was found by XRD. The texture of the films was observed using SEM and AFM, it was observed that the grain size was increased with working pressure. The energy band gap was found to be in the range of (4.1 eV to 3.9 eV) When the film thickness varying from 73 nm to 146.9 nm.
Keywords: Nickel oxide, magnetron, sputtering.

الترسيب بالترذيذ التفاعلي لل DC ماكنترون والخواص التركيبية لاغشية اوكسيد النيكل

الخلاصة
تم ترسيب اغشية اوكسيد النيكل (NiO) بأستخدام منظومة بلازما الماكنترون للتيارات المستمرة المحلية الصنع وبطريقة الترذيذ التفاعلي وبضغوط عمل مختلفة ضمن المدى (0.05-0.14) ملي بار. وقد تم دراسة تأثير ضغط العمل على تركيب ومورفولوجية السطح والخواص البصرية لاغشية اوكسيد النيكل .واقد اظهرت نتائج حيود الاشعة السينية ان الاغشية المترسبة ذات تركيب نانوي وبمعدل حجم حبيبي بين (8.145-29.195) نانومتر.بالاضافة لكون الاغشية ذات طابع متعدد التبلور مع بنية مكعبة على طول (111) و(101) التوجه. وعلاوة على ذلك تم العثور على Ni_2O_3 بواسطة حيود الاشعة السينية. كما تم دراسة تركيب الاغشية باستخدام SEM وAFM ، وقد لوحظ زيادة حجم الحبوب مع زيادة ضغط العمل.وقد وجد ان فجوة الطاقة في حدود (4.1 الكترون-فولت الى 3.9 الكترون-فولت) عندما يكون سمك الغشاء يتراوح بين 73 نانومتر إلى 146.9 نانومتر.
الكلمات المرشدة: اوكسيد النيكل ، الماكنترون، الترذيذ

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2412-0758/University of Technology-Iraq, Baghdad, Iraq

INTRODUCTION

NiO a semiconducting metal oxide, usually taken as a model for p-type material. NiO is having wide band gap of 3.6 to 4.0 eV [1], exhibit rhombohedral or cubic structure, but the most prominent structure was cubic structure [2]. NiO thin films have been studied for applications in electrochromic devices, electrode material for Li-ion batteries [3]. Recent works have shown that NiO is also a promising functional material for applications in resistive type gas sensors implementing thin NiO films [4]. In addition, two exciting novel applications based on NiO have been developed recently. One is an electronic application as a resistive switching (RS) memory[5] and the other is an energy-saving application as an electrochromic (EC) smart window[6].Most attractive features of NiO are: (i) excellent durability and electrochemical stability , (ii) Low materials cost (iii) Promising ion storage material in terms of cyclic stability ,(iv) Possibility of manufacturing by variety of techniques. NiO films can be prepared by physical and chemical methods such as: spray pyrolysis [7], electron beam evaporation [8], pulsed laser deposition [9], plasma enhanced chemical vapor deposition [10] and reactive sputtering [11]. In this studied magnetron sputter deposition had been used to prepare NiO thin films. The phenomenon of sputtering has several advantages in film deposition. There is no direct heating of the material as in evaporation methods. Therefore, there is no reaction between the source and crucible place. The average arrival energy at the substrate is higher for sputtered atoms (about 10 eV) than for evaporated atoms (about 0.25 eV at 300 K) and this is usually the reason for enhanced adhesion .The deposition rate in evaporation is an exponential dependence of rate on source temperature., whereas, The deposition rate in sputtering is linearly dependent upon the bombarding ion flux [12]. When sputtering is used with a transverse magnetic field, , the electron will move in helices around the magnetic field lines, and they will travel a much longer path-length in the plasma than in conventional glow discharge, giving rise to more ionization collisions, and consequently, higher ion fluxes [13] so several advantages should be produced high rate of sputtering is obtained due to the confinement of the plasma close to the target surface [12]

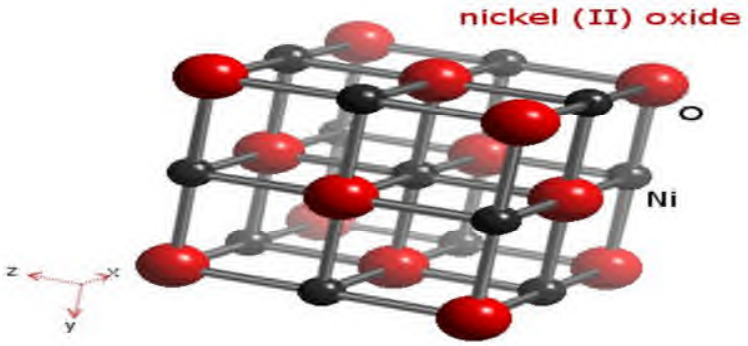


Figure (1) Structure of Nickel Oxide.

The Experimental Setup

NiO thin films were prepared by a home-made DC magnetron sputtering system. Figure 1 shows the schematic diagram of the sputtering system,Ni with high purity (99.9%) has been used as a sputtering target. The diameter of the target is 10 cm and 1mm thick sheet and the distance between the top electrode and the target is 4.5 cm.

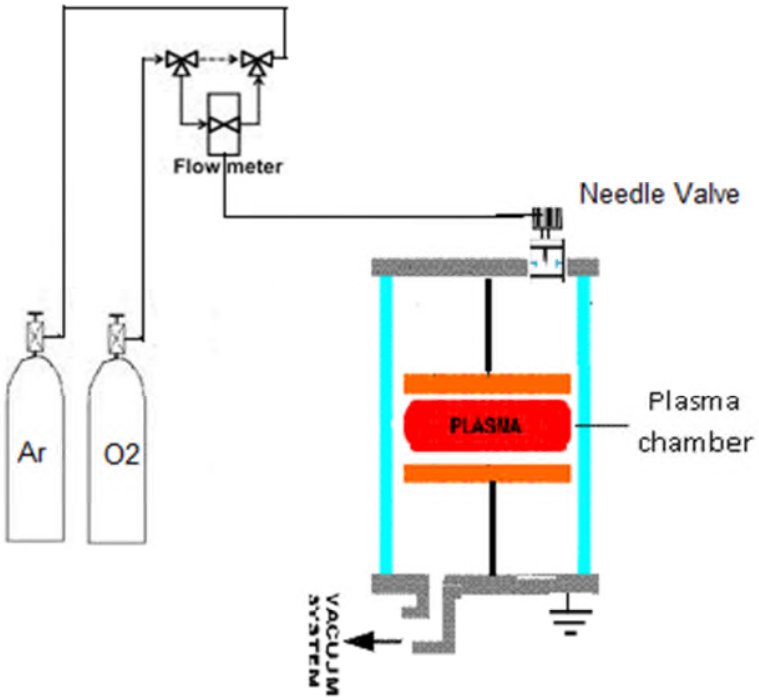


Figure (2) Schematic diagram of the DC magnetron sputtering system.

After loading the system with clean substrates (thin films are deposited on glass substrate, which is cleaned with alcohol, distilled water and dried in air). The system was pumped down to the base pressure, The base pressure of about $1x10^{-4}$ mbar is attained before each deposition. Argon is introduced into the chamber as precursor to ignite the plasma by applying a negative voltage to the cathode. Before deposition of each film, the targets are pre-sputtered in Ar for a minimum of 15 minutes to remove any surface oxide, in front of the target. Oxygen flow rate is a prerequisite in sample preparation so as to determine the appropriate stoichiometry and thickness. Sputtering is done at constant applied voltage. Prior to exposing a substrate the target is conditioned with the reactive gases at the chosen deposition condition. The cathode voltage as reflected by DC power supply and Ar/O_2 ratio determined by flow meter ,Ar/O2 mixture is introduced into the chamber at a specified pressure by using a needle valve. Deposition time is 60 minutes for all the experiments. These parameters identify the various sputtering deposition.The

crystalline properties of the NiO films were analyzed by Shimadzu X-ray Diffractometer XRD-6000. Using Cu Kα radiations (λ=0. 15406 nm) . The surface morphology of the films was characterized by scanning electron microscopy (SEM) of model Hitachi (S-4160), and atomic force microscopy (AFM) of model ntegra spm. In order to study optical properties of the films, the transmittance measurements were carried out by using a UV/Visible 2601 lambda spectrophotometer.

Result and discussion

X- Ray Diffraction Analysis

X-ray diffraction (XRD) measurements are used to determine the film crystallinity and estimate the average grain size. The X-ray diffraction patterns of the deposited NiO films on glass substrate at various partial pressures are shown in Figure(3) The XRD pattern shows a significant amount of line broadening which is a characteristic of nanoparticles.
The films are identified to be polycrystalline nature with a cubic structure along (111) and (101)orientation (JCPDS card no. 04-0835 and 44-1159).also Ni_2O_3 was found by XRD. The diffraction peak at around 27.593.4o is attributed to (101) plane. Based on the Joint Committee for Powder Diffraction Standards (JCPDS No.14-0481) data for Ni_2O_3, In general, for all samples materials, as the pressure increased, the intensity of the peaks was increased and becomes sharper. The increased intensity of the peak may be due to an increase in the crystallite size mention previously. The crystallite size of the films increased from 5.6 to 8.2 nm with increase of oxygen partial pressure from 0.05 to 0.14mbar,
An estimate of the crystallite sizes were obtained from the most intense XRD peak using Scherrer's equation [14]

$$D = K\lambda / \beta COS\theta \qquad \text{... (1)}$$

D: is the grain size (G.S), K: is a constant (0.94) ,λ: is the wavelength of Cu Kα, θ: is the Bragg's angle and β is full width half maximum (FWHM) of the preferential plane.

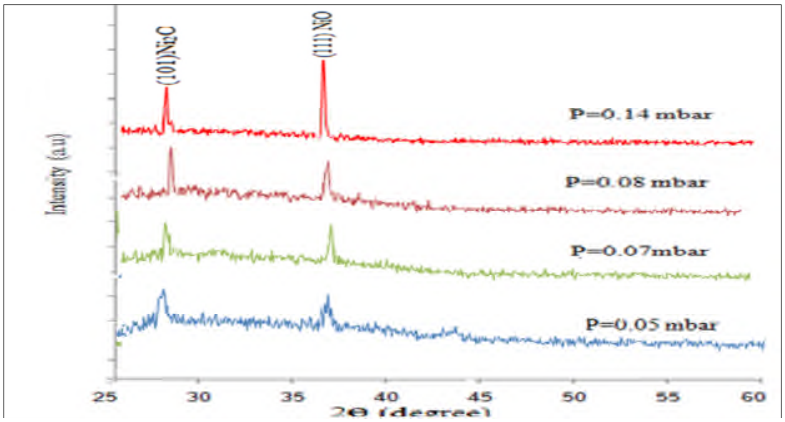


Figure (3) XRD of sputtered NiO thin films on glass substrate for different working pressure.

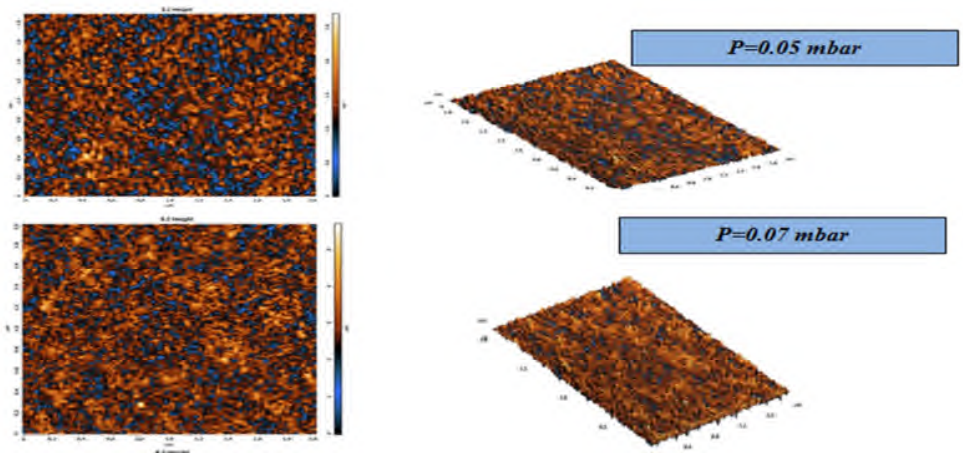
Table (1): Comparison between the Exp. and Std. value of dhkl for the NiO peaks showed in XRD for different gas pressure.

P (mbar)	2θ (Deg.)	FWHM (Deg)	dhkl Exp.(Å)	dhkl Std.(Å)	hkl	Type	G.S (nm)
0.05	27.85	1.05	3.202485	3.231517	(101)	Ni_2O_3	8.145403
	37.4	0.75	2.40376	2.411065	(111)	NiO	11.685
0.07	27.87	0.6	3.200232	3.231517	(101)	Ni_2O_3	14.25507
	37.35	0.7	2.406863	2.411065	(111)	NiO	12.51779
0.08	27.9	0.415	3.196859	3.231517	(101)	Ni_2O_3	20.61108
	37.32	0.5	2.408729	2.411065	(111)	NiO	17.52336
0.14	27.8	0.45	3.208131	3.231517	(101)	Ni_2O_3	19.00389
	37.2	0.114	2.416223	2.413063	(101)	NiO	29.19531

Atomic Force Microscope (AFM)

Figure (4) shows the two-dimensional (2D) and three- dimensional (3D) AFM images of (NiO) deposited at different working pressure on glass substrate .The 2D images show that the films are uniform and the substrate surface is well covered with grains that are nearly uniformly distributed over the surface. The surface morphology reveals the nano-crystalline (NiO) grains, which combine to make denser films markedly with the increased pressure. As shown in the figures, the images have light and dark regions. The

Color intensity shows the vertical profile of the thin film surface, with light regions representing the highest points and the dark points being the depressions. The 3D images reveal that there is a large sharp island or particle formation observed in depositing film microstructure. From the images, it is observed that the surfaces of the films exhibited a certain degree of roughness .The surface roughness are given further information about the surface morphology of thin films. The variation in surface roughness of thin film plays an important role in optical coatings. It improves the optical absorbance and influences the optical properties of thin films. The average grain size and root mean square roughness (RMS) of these films are shown in table (2).



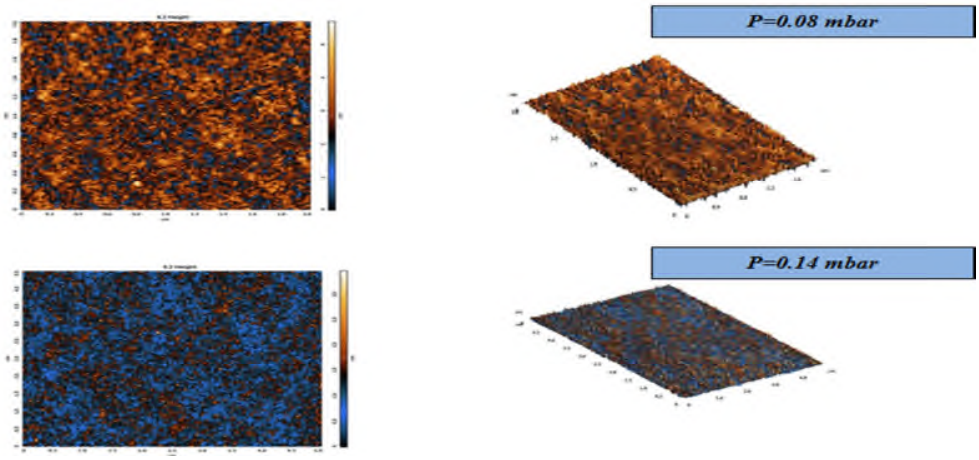


Figure (4) Two-dimensional (2D) and three-dimensional (3D) AFM images of NiO thin films deposited on glass substrate for different gas pressure.

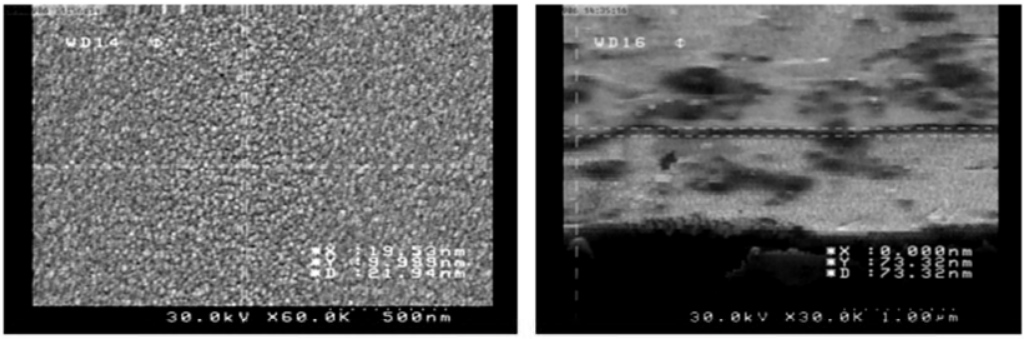
Table (2): The AFM data images of (NiO) thin films deposited on glass substrate for different pressure.

Pressure(mbar)	Average Roughness (nm)	Average Grain Size (nm)
0.05	0.3	27.1
0.07	0.463	32.6
0.08	0.914	40.7
0.14	0.832	49

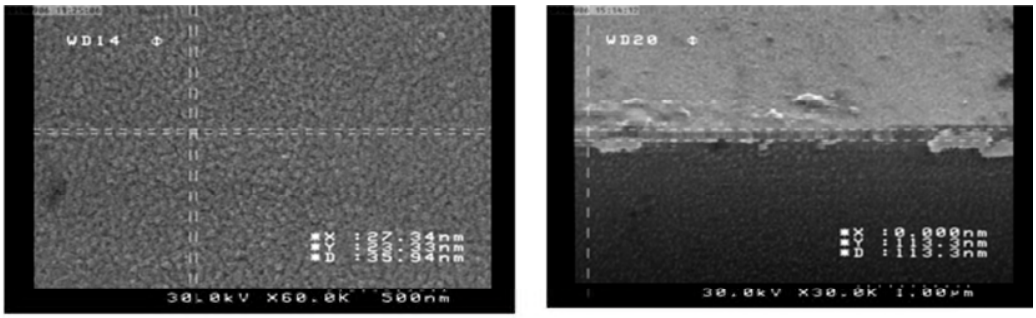
Scanning Electron Microscope (SEM)

The scanning electron microscopy (SEM) images of (NiO) films deposited on glass substrate at various pressures are shown in Figure (5).generally, all films consists of nanostructures . The grain size of the films markedly varied with pressure since it increases as pressure increased (as shown in images on the top left side) and surface shown some rougher at pressure increased . As small size of nanostructures increases surface area to volume ratio, the reactivity of the material increases, which in turn, will enhance the sensitivity of the sensing film. In addition to this, the grain boundaries between these nanostructures provide the resistance barrier for the charge carriers, hence increases the resistance of the film[15] . The right hand side of the figures shows images of the cross section of such films. It shows that the film thickness was also increased with pressure. That related to higher plasma density at higher pressures, marks dominant nucleation of (NiO) grains on the substrate. NiO Films composed of tiny grains with uniform distribution And consists of closely packed nanoparticles indicating good adhesiveness of film with the substrate. The most compact coating of samples makes its

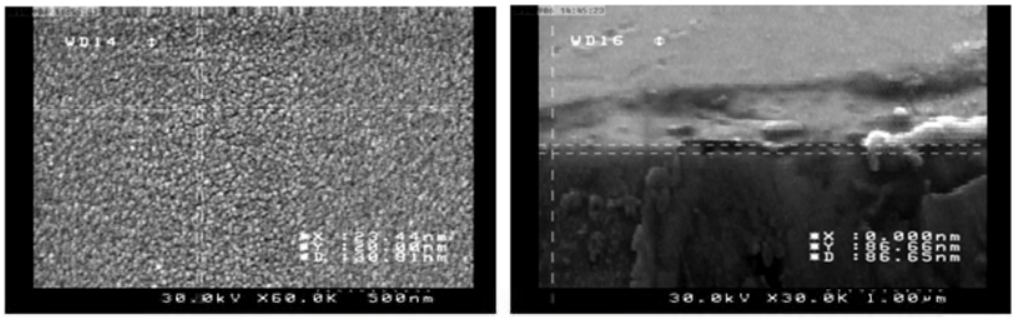
characteristics inconspicuous, but little granules can be observed in samples. The differences in deposition pressure cause the diversities the granule microstructure of the sample surface.



P=0.05mbar



P=0.08mbar



P=0.07mbar

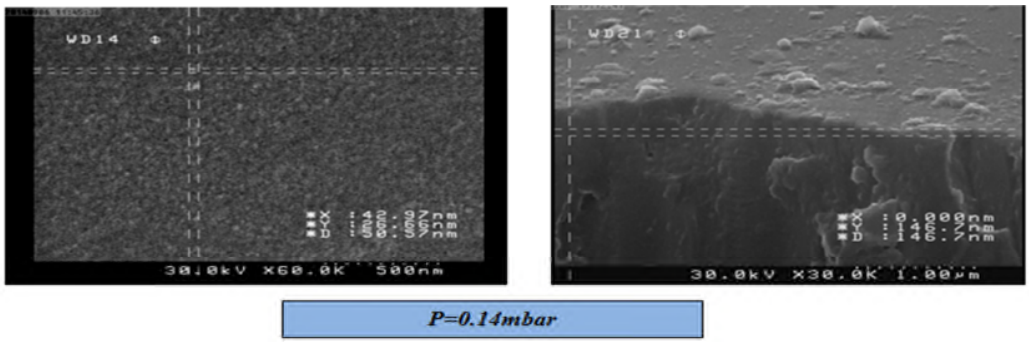
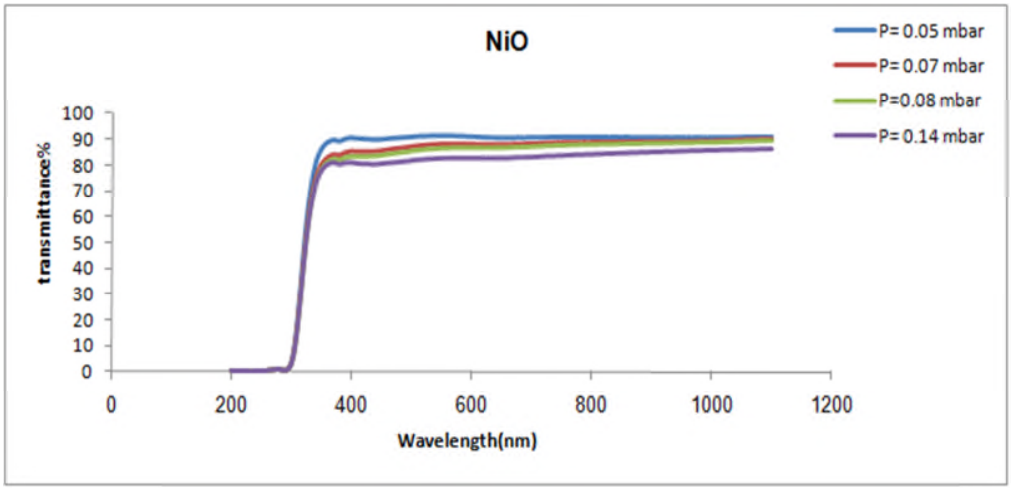


Figure (5) The SEM images of NiO thin films deposited on glass substrate at different gas working pressures.

Optical Properties

Optical experiments equip a good way of investigating the properties of energies provides knowledge about the band gaps of the material. Information of these band gaps is essential for understanding the electrical properties of a material, and is therefore of considerable empirical interest.Figure (5)shows the transmission of nickel oxide thin films prepared at defferent working pressure in dependence of the wavelength. for all samples films deposited at same conditions(d=4.5cm, applied voltage= 1200 volt, and deposition time=60min), at different working pressure for (9/1) argon to oxygen mixed flow; From this figure it is clear that there is for short wavelength there is no transmission because all the light is absorbed. For high wavelength however there are not enough electronic transitions possible so transmission is very high in this range.

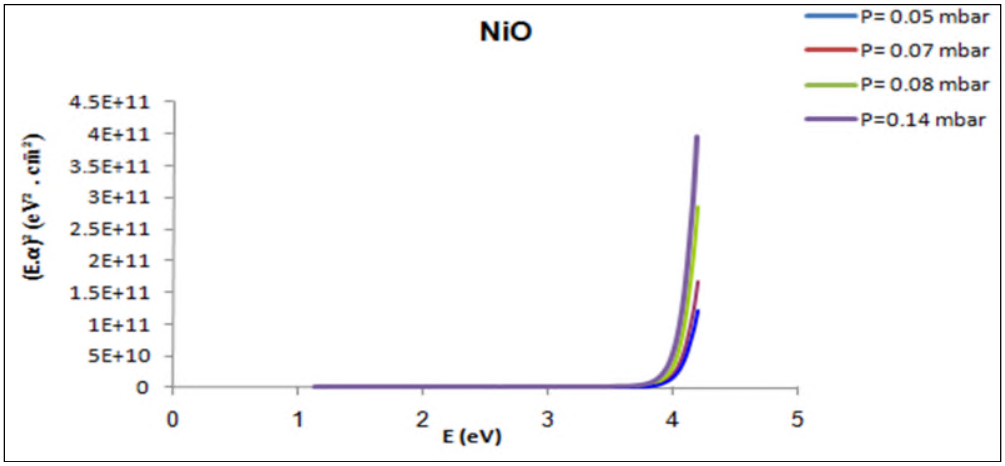


Figure(5)Transmission spectrum as a function of wavelength for sputtering (NiO) films at different working pressure.

In fig. (5) It has been clearly seen that, the transmittance go on increasing with wavelength. It is also found that, the optical transmittance of the films showed dependence on the pressure during deposition; the optical transmittance decreased with an increase working pressure, this decreased transmission can be due to increase film thickness since the increased thickness led to increased absorption. It was also found that, the NiO thin films showed transmittance in 86-90% range .The energy gap can be calculated from equation [14]:

$$(\alpha h\nu)^{1/2} = A\,(h\nu - Eg)^{1/2} \qquad ...(2)$$

Where : (α) Absorption coefficient, (h) Planck's constant, (ν) the frequency of the photon, (hν) photon energy,(A)Absorbance. The relation is drawn between $(\alpha h\nu)^2$ and photon Energy (hν), as shown in figure (6) which illustrate the allowed direct transition electronic



Figure(6) :(E.α)^2 as a function of (E=hυ) for sputtering (NiO) films at different working pressure.

The value of band gaps decreased slightly with increased working pressure since the film thickness increased at working pressure increase largely, thickness dependence of band gap can be referred to (i)an increment in barrier according to change in grain size in polycrystalline films, since when the grain size increases the wideness of the electronic levels and the band gap increases This is because the pairs of electron hole are much nearer together and the Coulombic interaction between them can no longer be neglected giving an overall higher kinetic energy[16]. (ii) Reduction in strain and dislocation density. Table (3) summarizes the optical band gap for (NiO) films with different thickness.

Table (3) optical band gap of(NiO)films of different working pressure and thickness.

Pressure(mbar)	Thickness(nm)	E_g(eV)
0.05	73	4.1
0.07	86.66	4
0.08	113.3	3.95
0.14	146.7	3.9

Conclusions

Nickel oxide (NiO) thin films were deposited by homemade DC reactive magnetron sputtering process at different working pressure (0.05-0.14 mbar). The films crystallinity and the grain size exhibited increased with increasing working pressure. AFM and SEM images also support the slow growth of crystallite sizes for the as-grown films .Contrary the optical pand gap decreased slightly with increased working pressure since the film thickness increased at working pressure increase.

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