

Preparation and characterization of NiO thin films by PLD

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ABSTRACT

In this work, NiO thin films have synthesized by pulsed laser deposition on glass substrates with different substrate temperature (100, 200, 300) °C, using Q-switching Nd:YAG laser. Structure and optical properties have carried out by using FTIR, AFM and UV- Vis spectroscopy. FTIR spectra conformed of NiO bonding and AFM images show the increase in grain size with temperature. The optical transmission results show that the transparency of the NiO films is greater than 85% in the visible region which increases with the increasing substrate temperature, While the energy band gap was decreased with increasing substrate temperature.

Keywords: NiO thin film, pulsed laser deposition.

خصائص أغشية اوكسيد النيكل المحضرة بطريقة الترسيب بالليزر النبضي

الخلاصة

في هذا البحث, تم تحضير أغشية رقيقة من اوكسيد النيكل بواسطة الترسيب بالليزر النبضي على قواعد زجاجية بدرجات حرارة مختلفة (100, 200, 300) درجة مئوية باستخدام ليزر النديميوم ياك بتقنية عامل النوعية. درست الخصائص التركيبية والبصرية باستخدام تحليلات فورير للأشعة تحت الحمراء (FTIR) والتحليل الطيفي للأشعة المرئية وفوق البنفسجية. اظهرت نتائج طيف (FTIR) وجود اصرة اوكسيد النيكل وبينت صور مجهر القوى الذرية زيادة الحجم الحبيبي بزيادة الحرارة, واظهرت الاغشية نفاذية عالية اكبر من 85% للمنطقة المرئية والتي تزداد بزيادة درجة حرارة القاعدة بينما تقل فجوة الطاقة بزيادة درجة حرارة القاعدة.

INTRODUCTION

Nickel oxide (NiO) films has a cubic rock salt (NaCl)P structure with a lattice constants of (4.178 Å) and a wide band gap energy from (3.5 to 4) eV^[1-3]. The p-type semiconducting behavior can be produced by the creation of native defects, nickel cation vacancies and or interstitial oxygen in NiO crystallites formed in non-stoichiometric NiO_x. In spite of, this behavior NiO is an insulator at room temperature with resistivity of the order (10¹³Ωcm)^[4-6].

It is an attractive material due to their excellent chemical stability, optical, electrical and magnetic properties. NiO was used as an antiferromagnetic material, chemical sensors, electrochromic devices, catalysts and fuel cell electrodes^[7-10]. NiO thin films can be fabricated by different physical and chemical techniques such as: pulsed laser deposition^[6], reactive sputtering^[10], electron beam evaporation^[5], spray pyrolysis^[11], and sol-gel deposition^[9,12].

In this work, pulsed laser deposition (PLD) was used for the deposition of NiO thin films on glass substrates at different substrate temperatures. The effect of substrate heating during deposition on optical and structural properties was studied.

Experiments details

The focused Nd:YAG Q-switching laser beam at 532nm (pulse width 7nsec, repetition frequency 6 Hz) were used to prepared NiO thin films. The films were deposited at energy density (1.6 J/cm²), and at oxygen pressure (2*10⁻¹ mbar). Each film was subjected to 40 laser pulse with different substrate temperature (100, 200, 300) C°. High purity (99.99%)NiO powder supplied from Fluka company, was pressed hydraulically with 5 ton pressure to form a target with 2.5 cm diameter and 0.4 cm thickness. Films thickness is measured by optical interferometer (Fizeau method). The method based on interference of the light beam reflected from thin film surface and substrate bottom. The thickness wasdetermined using the formula^[13]:

$$t = \frac{\Delta x}{x} \cdot \frac{\lambda}{2} \quad \dots(1)$$

Where

(x) is fringe width, Δx is the displacement in fringe position, and λ is wavelength of using source light.

The structure of thin films was diagnostic with FTIR and AFM (Atomic Force Microscope). FTIR spectra were recorded with(8400S,Shimadzu) spectrometer. The surface morphology of thin films was investigated by AFM with (Digital Instruments Nanoscope II, AA3000). A double-beam (UV-VIS) spectrophotometer was used to measure optical transmittance of films in range (200-900) nm.

Results and discussion

Figure (1) shows the FTIR spectra of NiO thin films deposited at different substrate temperature. The bonds at ≈2800 cm⁻¹ and at≈ 2700 cm⁻¹ can be assigned to CH₂ vibration. The peaks at≈ (1600, 1500, and 1400) cm⁻¹ corresponds to O-H bonding

vibration at water due to absorbed moisture^[12,13]. The peaks at (418.55, 437.84, 497.63, 426.27, 634.58, and 644.22) cm⁻¹ corresponds to the stretching vibration of Ni-O bond of nickel oxide nanoparticles. These results are in a good agreement with K.K. Purushothaman et al. & M.N. Rifayat al.^[14-16].

Surface morphology image of synthesised thin films with different temperature was studied by AFM spectroscopy as shown in figure (2). These figures demonstrate the homogeneity in grain distribution and will be more spherical shape at temperature (300 C°). The relation between the grain size calculated from AFM image at the deposited temperatures was shown in table (1). which increased with increasing temperature due to the nucleation which enhanced with rising temperature, these result agreed with I. Fasaki et al.^[1].

The optical transmission of NiO thin films on glass substrate is shown in figure (3) as a function of the wavelength for different substrate temperatures. The figure shows that the transmission decrease with increasing substrate temperature, which notice that the films deposited at substrate temperature (300C°) have transmittance about 60%, this is due to the absorptivity dependence on crystalline state, the absorption coefficient (α) determined from transmittance data using the relation^[10]:

$$\alpha = \frac{1}{d} \ln \frac{1}{T} \quad \dots(2)$$

Where

(d) is the thickness of thin films (0.25 μm), and (T) is transmittance. Figure (4) shows the variation of absorption coefficient as a function of wavelength for different substrate temperatures. The highest absorption coefficient was for the film prepared at (300C°), this is due to the strong influence of optical properties by the structure of thin film.

The absorption coefficient (α) was used to calculate the band gap of NiO films using the equation^[9,14]:

$$\alpha h\nu = A (h\nu - E_g)^m \quad \dots(3)$$

Where

(A) is a constant, E_g is energy band gap of NiO film, $h\nu$ is the incident photon energy, where (m=1/2) for direct allowed transitions and (m=2) for indirect allowed transition for NiO films.

Figure (5) shows the variation of $(\alpha h\nu)^2$ versus the photon energy ($h\nu$) for the films. The extrapolation of the linear part to $\alpha=0$ gives the band gap width as shown in table (1). The band gap decrease with increasing substrate temperature, and this result agreement with I. Fasaki et al.^[1].

The attenuation value of electromagnetic wave was determined from the extinction coefficient k by the following relation^[15]:

$$K = \frac{\alpha \lambda}{4 \pi} \dots(4)$$

Figure (6) represent the relation between the extinction coefficient (k) and wavelength (λ).

Conclusion

NiO thin films were deposited by PLD on glass substrates at different deposition temperatures (100, 200, 300) C°. All the films deposited at energy density 1.6 J/ cm². FTIR and AFM results shows that the formation of NiO, the surface structure and grain size depend on substrate deposition temperature ,while the optical properties reveal a high transmittance up to 85% in the visible region for film deposited at temperature =100 C°.

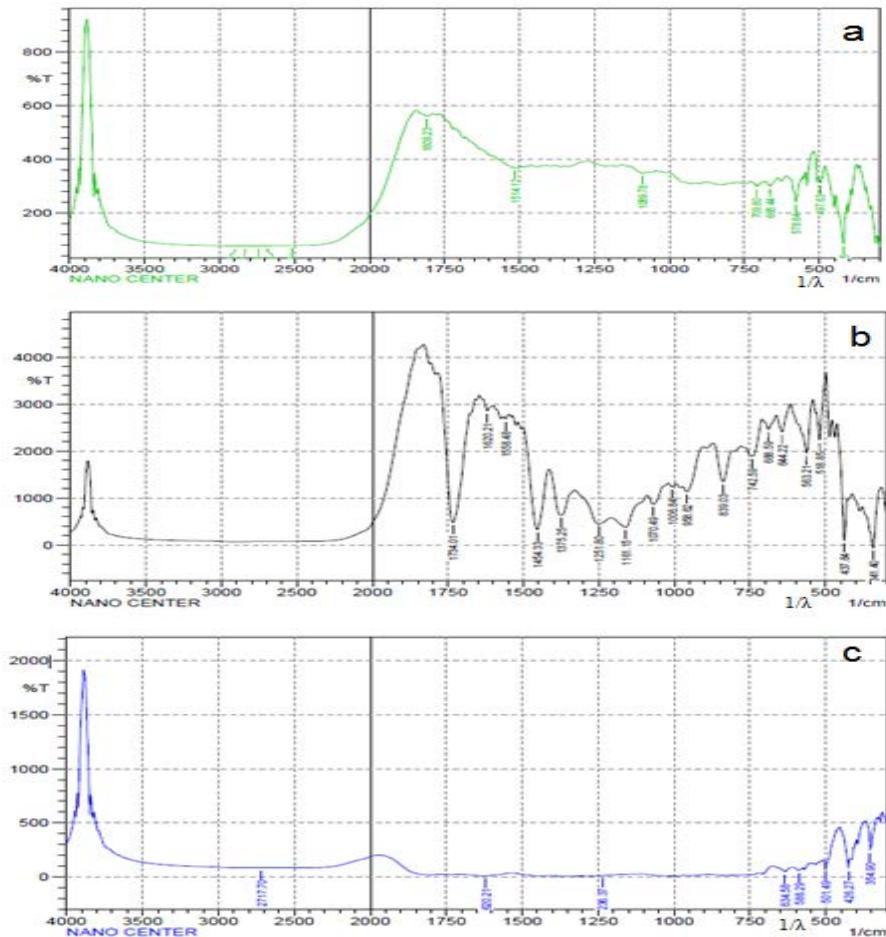


Figure (1): Transmittance v.s wavenumber by FTIR of NiO films deposit at different substrate temperatures. a)100C°, b)200C°, and c)300C°.

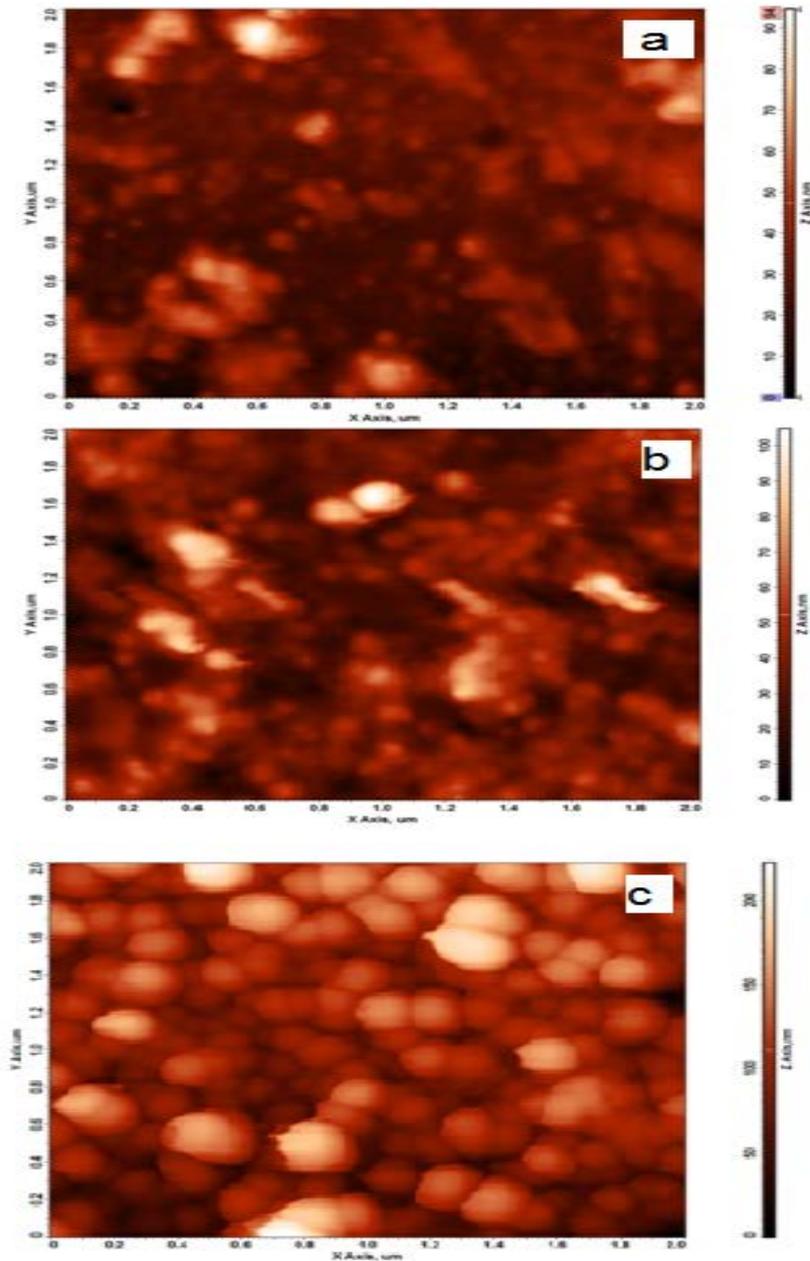


Figure (2): Grain size pictures of NiO thin films at different temperatures by AFM a) 100°C, b) 200°C, and c) 300°C.

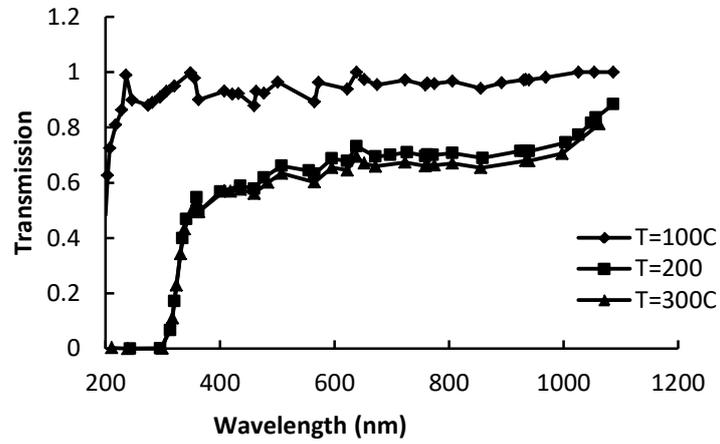


Figure (3): Optical transmission spectra of NiO films grown on glass substrate for different substrate temperatures: a) $T_s=100C^\circ$, b) $T_s=200C^\circ$, c) $T_s=300C^\circ$.

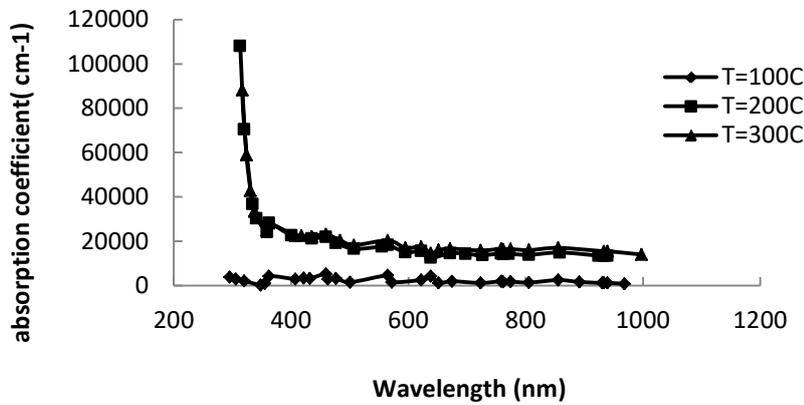


Figure (4): The absorption coefficient as a function of wavelength for different substrate temperatures.

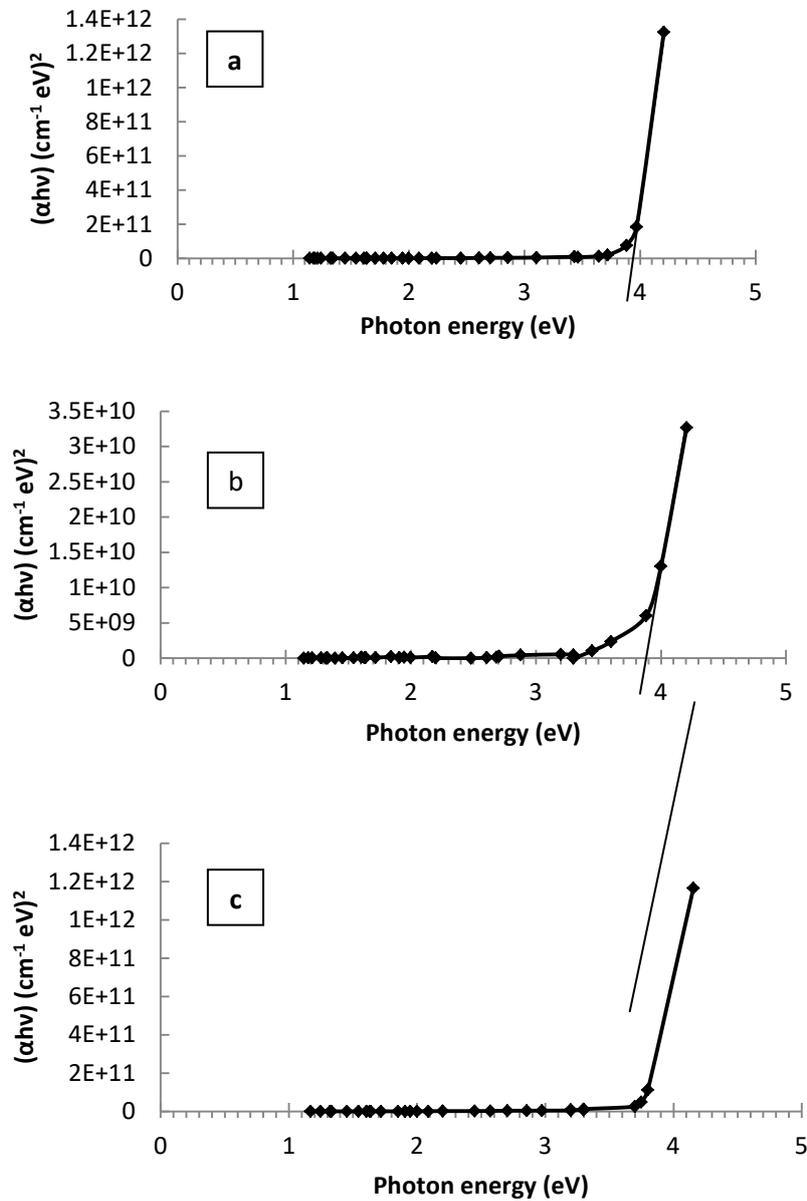


Figure (5): The variation of $(\alpha h\nu)^2$ with photon energy for NiO thin films prepared at different substrate temperatures a) $T_s=100^\circ\text{C}$, b) $T_s=200^\circ\text{C}$, c) $T_s=300^\circ\text{C}$

Table (1): The values of band gap energy

Substrate Temperature(C ^o)	Energy gap (eV)	Grain size (nm)
100	3.94	64.6
200	3.85	66.8
300	3.8	83.8

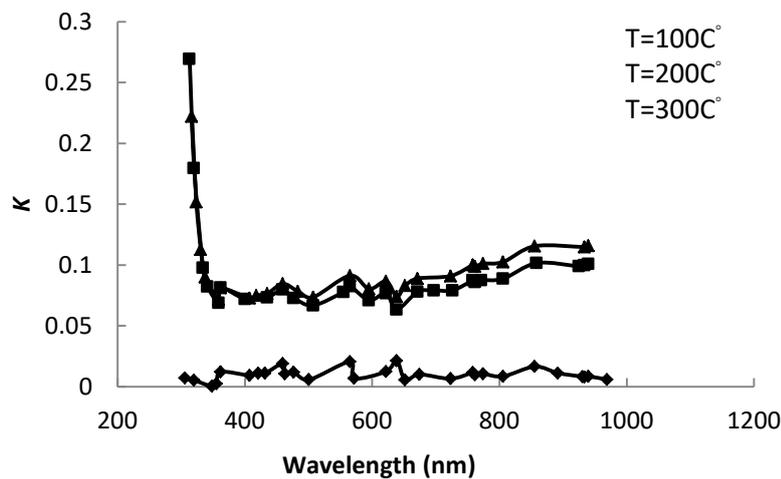


Figure (6): The absorption coefficient as a function of wavelength for different substrate temperatures.

Reference

[1]. I. Fasaki, A. Giannoudakos, M. Stamataki, M. Kompitsas, E. György, I. N. Mihailescu, F. R. Kalantzopoulou, A. Lagoyannis, S. Harissopoulos "Nickel oxide thin films synthesized by reactive pulsed laser deposition: characterization and application to hydrogen sensing" Appl. Phys. A 91, (2008) 487–492.
 [2]. T. Dutta "Nanostructured Transparent Conducting Oxides for Device Applications" Doctor thesis (2011).

- [3]. A. F.Saleh "Structural and morphological studies of NiO thin films prepared by Rapid thermal oxidation method" International Journal of Application or Innovation in Engineering & Management (IJAIEM) Volume 2, Issue 1, January (2013) 16-21.
- [4]. V. Verma, M.Katlyar "Effect of the deposition parameters on the structural and magnetic properties of pulsed laser ablated NiO thin films" Thin Solid Films 527 (2013) 369–376.
- [5]. B. Subramanian, M. M. Ibrahim, K. R. Murali, V. S. Vidhya, C. Sanjeeviraja, M. Jayachandran "Structural, optoelectronic and electrochemical properties of nickel oxide films" J Mater Sci: Mater Electron 20: (2009) 953–957.
- [6]. I. Fasaki, A. Koutoulaki, M. Kompitsas, C. Charitidis " Structural, electrical and mechanical properties of NiO thin films grown by pulsed laser deposition" Applied Surface Science 257 (2010) 429–433.
- [7]. Y.M. Lua, W.S. Hwang, J.S. Yang, H.C. Chuang "Properties of nickel oxide thin films deposited by RF reactive magnetron sputtering" Thin Solid Films 420 –421 (2002) 54–61.
- [8]. F. Saadati, A. R. Grayeli, H. Savaloni "Dependence of the optical properties of NiO thin films on film thickness and nano-structure" Journal of Theoretical and Applied Physics 4-1(2010) 22-26.
- [9]. H. Aydın, S. A. Mansour, C. Aydın, A. A. Al-Ghamdi, O. A. Al-Hartomy, F. El-Tantawy, F. Yakuphanoglu "Optical properties of nanostructure boron doped NiO thin films" J. Sol-Gel Sci. Technol. 64: (2012) 728-733.
- [10]. A. Karpinski, N. Ouldhamadouche, A. Ferrec, L. Cattin, M. Richard-Plouet, L. Brohan, M.A. Djouadi, P-Y. Jouan "Optical characterization of transparent nickel oxide films deposited by DC current reactive sputtering" Thin Solid Films 519 (2011) 5767–5770.
- [11]. R. Romero, F. Martin, J.R. Ramos-Barrado, D. Leinen "Synthesis and characterization of nanostructured nickel oxide thin films prepared with chemical spray pyrolysis" Thin Solid Films 518 (2010) 4499–4502.
- [12]. M. Alagiri, S. Ponnusamy, C. Muthamizhchelvan "Synthesis and characterization of NiO nanoparticles by sol–gel method" J Mater Sci: Mater Electron 23: (2012) 728–732.
- [13]. M. Hernández, A. Juárez, R. Hernández, "Interferometric thickness determination of thin metallic films", Superficies y Vacío 9,(1999) Diciembre 283-285.
- [14]. K.K. Purushothaman, S. J. Antony, G. Muralidharan "Optical, structural and electrochromic properties of nickel oxide films produced by sol–gel technique" Solar Energy 85 (2011) 978–984.
- [15]. S. R. Nalage, S. T. Navale, V. B. Patil "Polypyrrole-NiO hybrid nanocomposite: Structural, morphological, optical and electrical transport studies" Measurement 46 (2013) 3268–3275.
- [16]. M. N. Rifaya, T. Theivasanthi, M. Alagar "Chemical Capping Synthesis Of Nickel Oxide Nanoparticles and Their Characterizations Studies" Nanoscience and nanotechnology, 2(5) (2012) 134-138.