

Short Communication

Effect of Annealing in Physical Properties of NiO Nanostructure Thin Film

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Nickel oxide was deposited on highly cleaned glass substrates using spray pneumatic technique. The effect of precursor molarity on structural, optical and electrical properties has been studied. The XRD lines of the deposited NiO were enhanced with increasing precursor molarity due to the improvement of the films crystallinity. It was shown that the average of the crystalline size of the deposited thin films was calculated using Debye–Scherer formula and found 46.62 for as-deposited sample and 119.89 nm for the annealed one. The optical properties have been discussed in this work. The absorbance (A), the transmittance (T) and the reflectance (R) were measured and calculated. Band gap energy is considered one of the most important optical parameter, therefore measured and found ranging ranging 3.64 for as-deposited sample and 2.98 eV for the annealed one. The NiO thin film reduces the light reflection for visible range light. The increase of the electrical conductivity to maximum value of $0.09241 (\Omega \text{ cm})^{-1}$ can be explained by the increase in carrier concentration of the films. A good electrical conductivity of the NiO thin film is obtained due to the electrically low sheet resistance. NiO can be applied in different electronic and optoelectronic applications due to its high band gap, high transparency and good electrical conductivity.

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1. INTRODUCTION

Nickel oxide (NiO) is the most investigated metal oxide and it has attracted considerable attention because of its low cost material, and also for its applications in several fields such as a catalyst, transparent conducting oxide, photodetectors, electrochromic, gas sensors, photovoltaic devices, electrochemical supercapacitors, heat reflectors, photo-electrochemical cell, solar cells and many opto- electronic devices [1–11]. NiO is an IV group and it can be used as a transparent p-type semi-conductor layers, it has a band gap energy ranging from 3.45 eV to 3.85 eV [12]. Band gap energy is significant to adjust the energy level state of NiO.

The reduction in particle size to nanometer scale results more interesting prosperities in compared with their bulk properties [13]. Therefore, there are several techniques have been used for synthesis and manipulation of nanostructures NiO such as the thermal evaporation, sputtering, pulse laser ablation, thermal decomposition, electrochemical deposition and spray methods etc. Among of these techniques, spray has some advantages such as high purity of raw materials and a homogeneous solution hence easy control over the composition of the deposited films.

In this work, a low cost spray pneumatic technique was used to prepare pure NiO nanoparticles thin films with 0.15 mol L^{-1} precursor molarity. The structural properties of the produced nickel oxide thin films have been examined. The absorption, transmittance and reflectance spectra of the produced thin films for the NiO are also measured in range between 300-900 nm.

Moreover, the optical band gap is determined as a function of the precursor concentrations.

2. EXPERIMENTAL DETAILS

2.1 Preparation of Samples

NiO thin films were prepared onto a highly cleaned glass substrates using sol-gel spray pneumatic technique. Nickel nitrate was dissolved in 50 ml of water as a solvent and chloride acid was used as a stabilizer for the all samples in this work. The produced mixture was stirred at 60°C for 2 h in order to obtain a clear and homogenous solution then the mixture was cooled down at room temperature and placed at dark environment for 48 h. The glass substrates were cleaned by detergent and by alcohol mixed with deionized water.

2.2 Deposition of Thin Films

The coating was dropped into glass substrates at 480°C that sprayed during 2 min by pneumatic nebulizer system which transforms the liquid to a stream formed with uniform and fine droplets, followed by the films dried on hot plate at 120°C for 10 min in order to evaporate the solvent.

2.3 Devices and Measurements

The X-ray diffraction (XRD) spectra of the NiO were measured to verify the structure. (XRD) was measured by using BRUKER-AXS-8D diffractometer with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 KV and 40 mA

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in the scanning range of (2θ) between 20° and 80° . The spectral dependence of the NiO transmittance (T) and the absorbance (A), on the wavelength ranging 300-1100 nm are measured using an ultraviolet-visible spectrophotometer (Perkin-Elmer Lambda 25). The reflectance (R) was calculated by the well-known equation as ($T + R + A = 1$). Whereas the electrical conductivity of the films was measured in a coplanar structure of four golden stripes on the deposited film surface; the measurements were performed with Keithley model 2400 low voltage source meter instrument.

3. RESULTS AND DISCUSSIONS

3.1 Structural Properties

Fig. 1 shows the spectra of the grown NiO nanoparticles with 2 XRD lines, showing the broadening of the peak which is a characteristic of the formation of nanoparticles. The X-ray diffraction was used in this work in order to understand the structure of the as-deposited and the annealed NiO thin.

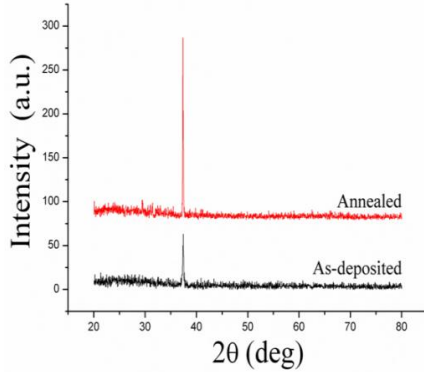


Fig. 1 – XRD patterns of the as-deposited and annealed NiO thin films

The indexed peak (111) at $2\theta = 37.1^\circ$ correspond to the cubic structure of NiO nanoparticles which are consistent with the JCPDS (No.47-1049). Fig. 1 shows that the diffraction intensity increased for annealed sample; it shows that the best crystalline quality of the film is achieved for this annealed sample. The crystalline size was calculated using the well-known Debye-Scherrer for(1)

$$D = \frac{0.9}{\beta \cos \theta}$$

where λ is the wavelength of the X-rays used (1.5406 Å), β is the full width at half maximum (FWHM) and θ is the diffraction angle.

The increasing of the diffraction peaks may indicate to the resulted of the NiO in good crystallinity [15]. The crystalline size is found in the range of 46.62 nm for as-deposited sample and 119.89 nm for annealed one. The changing in the crystallites size leads to the changes in optical properties i.e. band gap energy increased with decreasing crystallites size as shown in Fig. 2.

3.2 Optical Properties

Fig. 2 shows the optical absorption spectra of NiO

nanoparticles. The absorption spectra of as-deposited sample show that the absorption edge is slightly shifted towards shorter wavelength when compared to the annealed one. The absorption edge of annealed sample is shifted to longer wave-lengths. This shift predicts that there is a decrease in band gap value ($E_g = 2.98$ eV), which is due to an enlargement in particle size ($D = 119.89$ nm). The fundamental absorption, which corresponds to the electron transition from the valance band to the conduction band, can be used to determine the nature and value of the optical band gap. The optical absorption study was used to determine the optical band gap of the nanoparticles, which is the most familiar and simplest method.

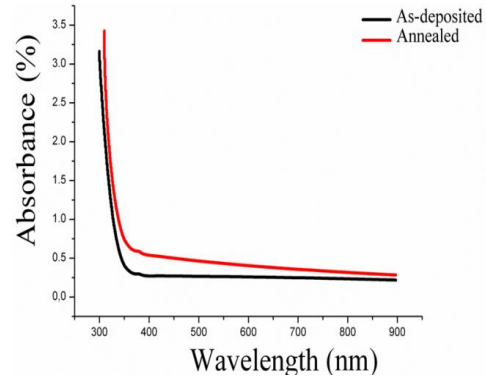


Fig. 2 – Absorbance spectra of the as-deposited and annealed NiO thin films $D = \frac{0.9}{\beta \cos \theta}$

The absorption coefficient (α) and the incident photon energy ($h\nu$) are related by the expression [16]:

$$(\alpha h\nu) = C(h\nu - E_g)^n \quad (2)$$

where α is the absorption coefficient, C is a constant, $h\nu$ is the photon energy, ν is the frequency of the incident radiation, h is the Planck's constant, exponent n is 0.5 for direct band allowed transition ($h\nu = 1239/\lambda(\text{nm})(\text{eV})$) and E_g the band gap energy of the semiconductor.

As it was shown in Fig. 3a typical variation of $(\alpha h\nu)^2$ as a function of photon energy ($h\nu$) of NiO nanoparticles Eq. (2), used for deducing optical band gap E_g . The optical band gap values have been determined by extrapolating the linear portion of the curve to meet the energy axis ($h\nu$) [17]. The band gap values were given in Table 1.

For a transmittance study (Fig. 4), the as-deposited NiO showed high transmittance, averaged in the wavelength (λ) of 300-900 nm. Suppression of light reflection at a surface is an important factor to absorb more photons in semiconductor materials.

The reflectance profiles of NiO coated as deposited and annealed are shown in Fig. 5. The averaged reflectance values were significantly lower than 0.203 %. Moreover, NiO coating drives a substantially suppressed reflectance under 0.20 % in $400 \text{ nm} < \lambda < 900$ nm. This notifies that the NiO coating is an efficient design scheme to intro-duce the incident light into substrate.

3.3 Electrical Properties

The electrical properties of the NiO films are summarized in Table 1. The as-deposited films have good conductivity $0.04125 (\Omega \text{ cm})^{-1}$, after annealing the conductivity increase at $0.09241 (\Omega \text{ cm})^{-1}$. The increase

Table 1 – Structural, optical and electrical parameters of as-deposited and annealed NiO thin film

Sample	Crystallite size (nm)	Band gap energy (eV)	Conductivity $(\Omega \text{ cm})^{-1}$
As-deposited	46.62	3.64	0.04125
Annealed	119.89	2.98	0.09241

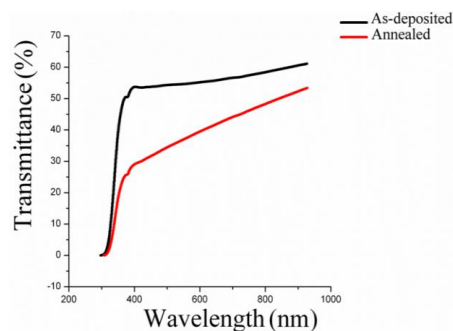


Fig. 3 – Transmission spectra of the as-deposited and annealed NiO thin films

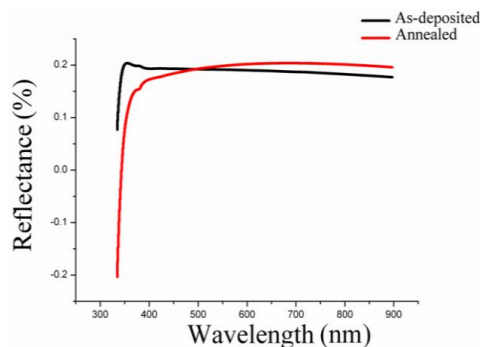


Fig. 4 – Reflectance profiles of the as-deposited and annealed NiO thin films

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of the electrical conductivity can be explained by the increase in the carrier concentration. Patil et. al. [18] have reported that the increase of the electrical conductivity is due to the increase in activation energy. This was explained by the crystal structure of the film which is increased, leading to a reduced concentration of structural defects such as dislocations and grain boundaries. Thus, the decrease of the concentration of crystal defects leads in the increase of free carrier concentration. The improvement of crystal quality

reduces the carrier scattering from structural defects, leading to higher mobility.

4. CONCLUSION

The spray pneumatic technique has been successfully employed to deposit NiO thin films with $0.15 \text{ mol} \cdot \text{L}^{-1}$ concentration precursor on glass substrates. The films showed cubic crystal structure with preferential orientation according to the direction (111). It has found that the crystallite size increase from 46.62 nm for the as-deposited sample to 119.89 nm for the annealed one. We have observed an improvement in the films crystallinity for the annealed sample where the peak at position 37.1° corresponding to the (111) plans is very sharp, the film obtained for the annealed sample has higher and sharper diffraction peak indicating an improvement in peak intensity compared to the as-deposited film. The band gap value of NiO films decreased from 3.64 eV for the as-deposited sample to 2.98 eV for the annealed one. The high transmittance, low reflectance under 0.20 %, widened band gap and good conductivity obtained for NiO thin films make them promising candidate for optoelectronic devices as well as window layer in solar cell applications.

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