Materials Research Bulletin 75 (2016) 71–77

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Structural, optical and photo-catalytic activity of nanocrystalline NiO thin films

Attieh A. Al-Ghamdi[a], M. Sh. Abdel-wahab[a,b,*], A.A. Farghali[b,c], P.M.Z. Hasan[a]

[a] Center of Nanotechnology, King Abdulaziz University, Jeddah, Saudi Arabia
[b] Materials Science and Nanotechnology Department, Faculty of Postgraduate Studies for Advanced Sciences, Beni-Suef University, Beni-Suef, Egypt
[c] Chemistry Department, Faculty of Science, Beni-Suef University, Beni-Suef, Egypt

ARTICLE INFO

Article history:
Received 6 June 2015
Received in revised form 3 November 2015
Accepted 17 November 2015
Available online 28 November 2015

Keywords:
Thin films
Oxides
Semiconductors
Nanostructures
Optical materials

ABSTRACT

Physical deposition of nanocrystalline nickel oxide (NiO) thin films with different thickness 30, 50 and 80 nm have been done on glass substrate by DC magnetron sputtering technique and varying the deposition time from 600, 900 to 1200 s. The results of surface morphology and optical characterization of these films obtained using different characterization techniques such as X-ray diffraction (XRD), field emission scanning electron microscope (FESEM), photoluminescence (PL) and UV–vis spectrophotometry provide important information like formation of distinct nanostructures in different films and its effect on their optical band gap which has decreased from 3.74 to 3.37 eV as the film thickness increases. Most importantly these films have shown very high stability and a specialty to be recycled without much loss of their photo-catalytic activity, when tested as photo-catalysts for the degradation of methyl green dye (MG) from the wastewater under the exposure of 18 W energy of UV lamp.

1. Introduction

NiO is a p-type semitransparent semiconductor with a broad band gap of ~(3.2–3.8 eV) [1]. Its cubic rock salt-like crystal structure combined with its wide band gap, transparency and p-type conducting ability makes it a very suitable material for various applications such as antiferomagnetic material [2], photoelectrolysis [3], electrochromic device [4], gas sensor [5] and the anode buffer layer in organic solar cells [6] are reported in the literature. The combination of NiO and other metal oxides like NiO–ZnO [7], NiO–SiO_2 [8] and nanoporous NiO–folic acid [9] etc. have also been studied as a sensitizer. Recently the scientific community all over the word has started considering semiconducting oxides as a potential photocatalyst for degradation of pollutants. After going through the literature it can be found that while TiO_2 and ZnO have been widely investigated for their photo-catalytic performance, very few reports are available regarding photocatalytic activities of NiO and other metal oxides. In particular the photo-catalytic behavior of NiO thin films has hardly been reported. There are different routes for the synthesis of NiO thin films such as, electron beam evaporation [10], spray pyrolysis [11–13], chemical path deposition [14,15], sol–gel [16–18], pulsed laser deposition [19,20] and DC/RF magnetron sputtering [21–23]. Out of these techniques, DC magnetron sputtering is preferred for the deposition of NiO thin films because of its various advantageous features mainly low substrate temperatures, transfer of exact chemical composition and its universality. This report presents the study of physical, optical and chemical properties of nanocrystalline NiO thin films deposited over glass substrate through DC magnetron sputtering technique. The effect of thickness variation on the photo-catalytic performance of NiO thin films has been especially taken into account. In this regard, the degradation of methyl green as a water pollutant was investigated under different operating conditions such as pollutant concentration, pH and reuse cycle for all the three films and noticeable results were found.

2. Experimental

2.1. Sample preparation and characterization

Three different nanocrystalline NiO thin films, with deposition times 600, 900 and 1200 s respectively, were grown on glass substrates at room temperature. Special attention was paid to clean the glass substrate surface before deposition. Acetone cleaning of the substrates surfaces was done which were finally dried with pressurized nitrogen gas. Afterward, thin films of NiO were deposited on these substrates using DC magnetron sputtering (DC/RF Magnetron Sputter System, Syskey Technologies, Taiwan).

* Corresponding author at: Center of Nanotechnology, King Abdulaziz University, Jeddah, Saudi Arabia. Fax: +966 0126951449.
E-mail address: mshabaan90@yahoo.com (M. S. Abdel-wahab).

http://dx.doi.org/10.1016/j.materresbull.2015.11.027
0025-5408/

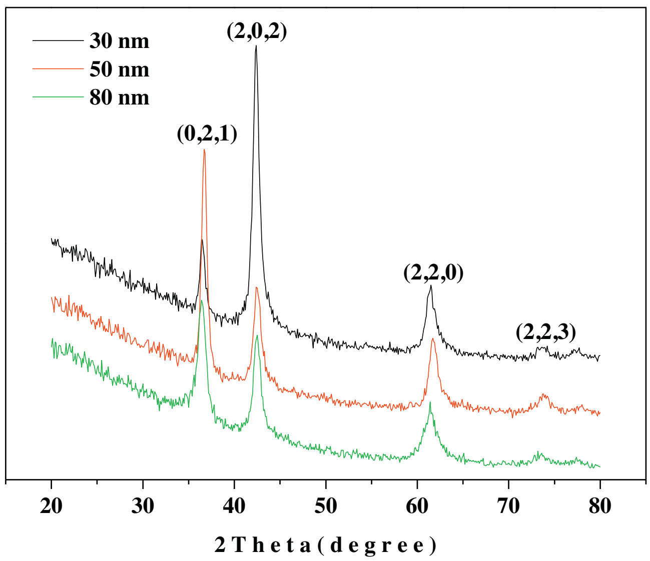

Fig. 1. XRD spectra of NiO thin films deposited on glass substrate by RF sputtering.

For the deposition we have used high purity (99.999%) Ni (3×0.6 in.) metal target, while the distance between target and substrate was almost 14 cm. The values of other parameters of deposition like operating pressure, Argon flow, DC power and oxygen flow were kept 1×10^{-6} Torr, 20 sccm, 200 W and 40 sccm, respectively.

The analysis of surface, structural and optical properties of the deposited NiO thin films have been carried out by the relevant characterization systems like field emission scanning electron microscope (FESEM) (JSM—7600F; JEOL—Japan), X-ray diffractometer (Ultima-IV; Rigaku, Japan), UV–vis spectrophotometer (PerkinElmer, Lambda 750) and Fluorescence Spectrophotometer (RF—5301 PC, Shimadzu, Japan).

2.2. Photo-catalytic experiments

In order to observe the photo-catalytic performance of these films, we have studied the response of all NiO thin films of different thicknesses for the degradation of methyl green (MG) dye as a model for water pollutant. For each film, three concentrations, (5, 10 and 20 ppm) of the MG dye have been tested to investigate the effectiveness of a particular thickness for a specific concentration. 100 mL of MG aqueous solution was taken in a glass reactor for each experiment. The reactor was irradiated with 18 W UV lamp (λ_{max} = 254 nm) for 2 h, which was placed vertically on the top of reaction reactor at a distance of 10 cm. For evaluating the effect of pH value, the initial pH of the solution was adjusted using HCl solution. Using UV–vis spectrophotometer (PerkinElmer, Lambda 750), the variation in its characteristic absorption of the solution at around 630 nm of wavelength were studied to analyze the outcome of the photo-catalytic activity of NiO thin films. A sample of 3 mL of the MG solution was taken after each 30 min to analyze the outcome. Same procedure was adopted each concentration.

The degradation efficiency was calculated after analysis using the following equation:

$$\text{Degradation}\% = \frac{C_o - C_t}{C_o} \times 100 \quad (1)$$

where C_o is the initial concentration of MG (mg/L) and C_t is the concentration of MG at time t during the catalytic reaction (mg/L).

3. Results and discussion

3.1. XRD analysis

XRD results of all the three films of different thicknesses show peaks corresponding to pure nickel oxide phase (Fig. 1). For all the samples, (0 2 1), (2 0 2), (2 2 0), and (2 2 3) diffraction peaks (ICDD card no. 01-089-3080) were observed with C2/c space group, showing the growth of NiO crystallites along different directions. The effect of increase in deposition time, which results in a linear increase in the film thickness, is very much obvious in the XRD patterns. These XRD results also confirm that the NiO films are perfect crystalline with high purity level. By using the following Scherrer's equation [24], the average crystal size of all the deposited nanocrystalline NiO thin have been calculated

$$D = \frac{0.94\lambda}{\beta\cos\theta} \quad (2)$$

where D: crystal size, λ: X-ray wave length, β: the broadening of the diffraction peak and θ is the diffraction angle. All the calculated structural parameters such as: average crystallite size, lattice parameter, cell volume are given in Table 1.

3.2. Morphology and compositional analysis

It is evident from FESEM images that the increase in deposition time affects the shape and size of particles of the films. Deposition times of 600, 900 and 1200 s results in the films of 30, 50 and 80 nm thicknesses respectively with particle size around 8, 10 and 12 nm, respectively but we can notice the agglomeration of the particles increases by increasing the deposition time as shown in Fig. 2(a–c). It can be observed from optical and photo catalytic properties that particle structures of these films also play an important role in their different applicability. The purity of the films is also verified by the EDS spectra of all the deposited NiO thin films. Peaks corresponding only to Ni and O elements can be easily seen in the spectra.

3.3. Optical properties

The UV–vis spectrophotometer absorbance and transmittance spectra in the range of 300–900 nm at room temperature, reveals the very obvious and expected decrease in the transmittance with increasing film thicknesses as shown in Fig. 3. The important point to note is the magnitude of this decrease which gives an insight

Table 1
Structural parameters of NiO thin films deposited by DC sputtering.

Sample (film thickness)	Average crystallite size (nm) by Scherrer's equation	Lattice parameters			Cell volume (Å^3)
		a (Å)	b (Å)	c (Å)	
30 nm	7.89	6	6	7.4	230.3
50 nm	8.7	6.019	6.019	7.39	231.8
80 nm	9.91	6.047	6.047	7.363	233.1