Dependence of the optical properties of NiO thin films on film thickness and nano-structure

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Abstract

NiO films of different thickness ranging from 285 to 645 nm were deposited, using the electron beam physical vapor method at room temperature on glass substrates. Nano-structures of the films were obtained using X-ray diffraction (XRD) and atomic force microscopy (AFM). It was observed that NiO thin films grow with (200) preferred orientation that increases with film thickness. In addition crystallite size obtained from XRD results and grain size obtained from AFM analysis increased with film thickness. Transmittance spectra of NiO films were collected between 340 and 850 nm wavelength. Refractive indices and the thickness of these films obtained using Swanepoel method. Optical functions of these films showed that films were of homogenous structure and the results agree with reported data obtained using different methods of film deposition.

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1. Introduction

Nickel oxide (NiO) thin films adopt the NaCl structure, with octahedral (Ni)(II) and (O²⁻) sites, are recently drawn considerable attention because they are important in several scientific and technological applications. They are attractive materials which have lots of special properties such as optical, electrical and magnetic properties. They have been employed as an antiferramagnetic material [1], p-type transparent conducting films [2], a material for electrochromic display devices [3] and a part of functional sensor layers in chemical sensors [4]. NiO films can be prepared by multiple physical and chemical methods such as: spray pyrolysis [5,6], electron beam evaporation [7] pulsed laser deposition [8], plasma-enhanced chemical vapor deposition [9] and reactive sputtering [10]. Also the theoretical and experimental researchers have investigated optical aspects of NiO for 3 decades. Powell and Spicer [11] presented the most important work in this topic. They reported optical reflectance spectra for the NiO single crystal over the wide energy range of 1 to 26 eV. However, interpretation of their optical constants and the corresponding electronic structure is difficult. Many other researchers have worked on this subject [12-14]. Recently Park and Kim [15] and Kamal et al. [16] by using spectroscopic ellipsometry and spectrophotometry obtained optical constants of NiO thin films.

In this work, the Swanepoel method of analysis of optical functions (i.e., transmittance spectrum) is used to obtain the optical constants and film thickness of NiO thin films of different thickness prepared by electron beam deposition method. The crystallographic and nano-structure of films are obtained by means of x-ray diffraction (XRD) and atomic force microscopy (AFM), respectively. A correlation between optical data and the nano-structure of the films is achieved. A brief description of Swanepoel method is given in Section 2. Experimental details are described in Section 3 and results are discussed in Section 4.

2. Theory

Let consider a thin homogeneous film with uniform thickness d and complex refractive index \( n = n + ik \) or absorption \( \alpha \), which is formed on a transparent substrate with refractive index S. The substrate surface is considered to be perfectly smooth and it is thick enough that the interference effects from substrate surfaces have no influence on the optical spectra measured for the thin film. The system is surrounded by air \( (n_0 = 1) \). Then the transmission for the normal incidence resulted from the interference from the three interfaces can be written as [11]:

\[
T = \frac{Ax}{B - Cx \cos \varphi + Dx^2}
\]

(1)

Where

\[
A = 16 \ n^2S,
\]

(2)

\[
B = (n + 1)^2(n + S^2),
\]

(3)
It is considered that the envelopes around the interference maxima \( T_M \) and minima \( T_m \) are continuous functions of \( \lambda \), where:

\[
T_M = \frac{Ax}{B - Cx + Dx^2},
\]

\[
T_m = \frac{Ax}{B + Cx + Dx^2}.
\]

Then the real part of the refractive index \( n \) can be obtained as:

\[
n = \left[ N + (N^2 - S^2)^{1/2} \right]^{1/2},
\]

where

\[
N = 2S \frac{T_M - T_m}{T_M T_m} + \frac{S^2 + 1}{2}.
\]

If \( n_1 \) and \( n_2 \) are the refractive indices of two consecutive maxima or minima related to two wavelengths of \( \lambda_1 \) and \( \lambda_2 \), then the film thickness can be obtained from:

\[
d = \frac{\lambda_1 \lambda_2}{2(\lambda_1 n_2 - \lambda_2 n_1)}.
\]

The thickness obtained from Eq. 13 is very sensitive to the uncertainty in the value of the refractive index which is driven from Eq. 11. As a general rule it is proposed that the two maxima and minima at the two ends of the spectrum be neglected. The normal equation for the interference fringes in normal light incidence is given by:

\[
2nd = m\lambda,
\]

where \( m \) is an integer number for the interference maxima and half integer for interference minima. Using the correct order for \( m \) for the maxima and minima in the spectrum one can recalculate the refractive index for the respective maxima and minima, hence obtaining more accurate results.

### 3. Experimental details

Nickel-oxide films of different thickness were produced by electron beam evaporation using a CE, SALTIS Vacuum Industries, SRA, Type: M6370 with a base pressure of \( 2 \times 10^{-6} \) mbar, at room temperature \( (300 \) K) with a deposition rate of 0.25 nm/s, on microscope slides substrates with a root mean square (rms) surface roughness, \( R_q \), of 0.3 nm, which was measured using a Rank Taylor Hobson Talysurf profilometer. Just before use all substrates were ultrasonically cleaned in heated acetone then ethanol. The film thickness was measured during deposition using a quartz crystal monitor (Sigma Instruments, SQM-160, USA), with nominal thicknesses of 285 to 645 nm. The distance between the evaporation crucible and substrate was 58 cm.

The deposition process was repeated several times and reproducibility of the results (i.e., transmission spectra) was confirmed. Nanostructure of these films was obtained using a Siemens D500 X-ray Diffractometer (Cu Ka radiation; 40 kV, 30 mA) with a step size of 0.02° and count time of 1 s per step, while the surface physical morphology and roughness was obtained by means of AFM (Digital Instruments, Nanoscope III, USA) analysis. The transmittance spectra of the samples were obtained using a double beam spectrophotometer (Hitachi U-3501, Japan) in the spectral range of \( 340–850 \) nm corresponding to the energy range of \( 3.65–1.46 \) eV. The details of samples produced for investigation in this work, surface roughness, peak position in the XRD pattern and related d-spacings obtained are given in Table 1.

### Table 1. Details and nano-structural results of NiO/glass thin film samples

<table>
<thead>
<tr>
<th>( d ) (nm)</th>
<th>( R_g ) (Å)</th>
<th>( R_{av} ) (Å)</th>
<th>( D ) (nm)</th>
<th>Crystallite Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>285</td>
<td>24.8</td>
<td>19.3</td>
<td>65</td>
<td>NiO(200) 77</td>
</tr>
<tr>
<td>515</td>
<td>50.9</td>
<td>40.2</td>
<td>67</td>
<td>NiO(111) 55</td>
</tr>
<tr>
<td>595</td>
<td>41.1</td>
<td>31.9</td>
<td>70</td>
<td>55</td>
</tr>
<tr>
<td>635</td>
<td>24.6</td>
<td>19.3</td>
<td>72</td>
<td>60</td>
</tr>
</tbody>
</table>

D) Film thickness; D) grain diameter

### 4. Results and discussion

#### 4.1. Nano-structure of NiO/glass thin films

Polycrystalline films deposited on substrates generally show preferred orientation, with a strength which depends on the deposition method, film material, and deposition conditions. Savaloni et al. [17,18] found a (002) preferred orientation in erbium (hcp, rare earth metal) thin films produced by electron gun evaporation, which reached its maximum at 575–775 K substrate temperature and was stronger for higher deposition rate of 2.5 nm/s compared with 0.55 nm/s. Huang et al.[19] in comparing an evaporated thin Ag (fcc, noble/transition metal) film with Ag film produced using Ar ion bombardment concluded that the latter
Dependence of the optical properties ...

shows much less (111) preferred orientation. Savaloni and Bagheri Najmi [20] also found a (002) preferred orientation for Zn (hcp, transition metal) films on glass and stainless steel substrates which reached a maximum at about 400 K for Zn/glass and a maximum at about 370 K for Zn/SS, while a (111) preferred orientation for Cu (fcc, noble/transition metal) on glass and SS films reached its maximum at about 590 K for Cu/glass and at about 560 K for Cu/SS. Both Zn and Cu films were produced by resistive evaporation technique and at a pressure of 10^-5 mbar. They also discussed the effect of residual gas and degassing of substrates (i.e., glass and SS) on the preferred orientation. Savaloni et al. [21] also observed strong (100) preferred orientation for Ti/glass sputtered films.

Fig. 1. X-ray diffraction patterns of NiO thin films of different thickness.

Fig. 1 shows the XRD patterns of the samples prepared at room temperature on glass substrate at different thicknesses and constant deposition rate of 0.25 nms^{-1}. The NiO film of 285 nm thickness showed NiO(111), (200), (220) and (311) diffraction lines. When the film thickness is increased to 515 nm, NiO(111) crystallinity decreased and NiO(311), (220) were disappeared, while the intensity of NiO(200) considerably increased. Further increase of film thickness clearly shows the development of the NiO(200) preferred orientation which reaches to almost single crystalline structure at 645 nm film thickness. The diffraction lines of NiO films discussed above were analyzed according to JCPDS Card No: 78-0249. It should be emphasized that the thicknesses mentioned here are those obtained from the quartz crystal monitor during deposition of the films. In Section 4, optical analyses of the films will give slightly different results. However, comparison of the two sets of thickness results will show that our quartz crystal monitor is a very reliable instrument. The crystallite size, D (coherently diffracting domains), is obtained using the Scherrer formula [22]:

\[ B = \frac{k\lambda}{D\cos \theta}, \]  

(15)

where, \( \lambda \) is the wavelength of X-ray, \( \theta \) is the Bragg angle in radian, and \( k \) is a dimensionless constant which is related to the shape and distribution of crystallites [23] (usually taken as unity). For obtaining the value of \( B \), we used the usual procedure of full width at half maximum (FWHM) measurement technique [19], therefore:

\[ B = (W_0^2 - W_i^2)^{1/2}, \]  

(16)

where, \( W_0 \) is the FWHM of the sample and \( W_i \) is the FWHM of stress free sample (single Si crystal in this work).

Typical 3D AFM images of NiO films of different thickness are shown in Figs. 2(a-d). The increase of physical grain size (obtained using JMicroVision Code) with film thickness is also obvious in Figs. 2(a-d), and are consistent with the modified structure zone model predictions [24] and the above discussion. Both root mean square roughness (Rq) and average roughness (Rave) obtained from the AFM analysis for all samples are also given in Table 1 and Fig. 3. It can be seen that the roughness increases with film thickness up to 515 nm film thickness then decreases and the thickest film of 634.5 nm thickness shows the lowest surface roughness. This is due to the evolution of the film structure as predicted by the modified structure zone model (MSZM) by Messier [24] and results reported by Savaloni and Player [18].

4.2. Optical properties

Fig. 4 shows the transmittance spectra of NiO/glass films of different thickness. Transmittance decreases with increasing film thickness due to increase of both reflection and absorption, while the number of oscillations in the transmittance spectra is increased with film thickness. The reduction of transmittance with increasing the film thickness can be related to the following parameters; a) film surface becomes more uniform with increasing the film thickness, b) surface roughness is decreased when the film thickness is
more than 515 nm (according to the AFM results given in Fig. 2).

Fig. 2. 3D AFM images of NiO/glass thin films of nominal different thickness. a) 285 nm; (b) 515 nm; (c) 595 nm; (d) 645 nm.

Hence reflection may increase and the scattering from uneven surface and grain boundaries may decrease, c) film structure may become more inhomogeneous with increasing the film thickness due to accumulation of different types of structural faults, hence increasing film absorption.

Fig. 3. Variation of surface roughness as a function of thickness.

The Swanepoel method as discussed in Section 2 was employed for the analysis of the transmittance curves. Fig. 5 shows as a typical example the $T_{\text{min}}$ and $T_{\text{max}}$ continuous functions (envelops) fitted to the thickest film of 635 nm film.

Fig. 4. Optical transmittance spectra of NiO thin films of different thickness.

Fig. 5. Fitted envelopes to maxima and minima of 634.5 nm thick NiO/glass, using Swanepoel method.

Tables 2 to 5 give the values of $n$ and $d$ obtained for NiO films of different thickness produced in this work. $n_1$ and $d_1$ are the results of initial calculation without taking into account the order of the maxima or minima (i.e., $m$ in Eq. 14) in the calculations, whereas $n_2$ and $d_2$ are the results obtained by using the $m$ value for each individual maximum or minimum. It can be observed that both $n_2$ and $d_2$ values obtained for different wavelengths are more consistent with each other and they do not show the fluctuations that is resulted for $n_1$ and $d_1$ values. In addition, it can be seen that the average values of $n_2$ obtained for NiO films of different thickness are reasonably close to
each other (between 2 and 2.1) which shows that the NiO films produced in this work are of homogeneous nature. The refractive indices obtained in this work are also in good agreement with the results of Vidal-Hurtado and Mendoza-Galvan [25] using chemical bath deposition method and Franta et al. [26] using pulsed laser deposition technique.

5. Conclusion

Influence of NiO film thickness on the optical properties of NiO thin films deposited using electron gun beam deposition is investigated and a correlation with the nano-structural changes by film thickness is achieved. XRD and AFM analysis were performed to obtain nano-structural information. A preferred orientation of NiO(200) is grown with increasing the film thickness and the thickest film of 645 nm shows almost a single crystal structure. The crystallite sizes obtained from XRD results and the grain sizes obtained from AFM analysis increased with film thickness. Optical functions of these films obtained from their transmittance spectra and Swanepoel analysis showed that films were of homogenous structure and the results agree with reported data obtained using different methods of film deposition.

References