Research Article

A Study on the Thermodynamics of Grain Growth in R.F. Magnetron Sputtered NiO Thin Films

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Postdeposition annealing of thin nickel films synthesized using R.F. magnetron sputtering technique is carried in this study. The XRD analysis indicates that annealing of the nickel films leads to the formation of nickel oxide with a preferential growth along (200) plane. The oxidation mechanism is observed with a phase transformation and results in polycrystalline NiO films. The surface morphology of the thin films was investigated by scanning electron microscopy (SEM) and atomic force microscopy (AFM) as a function of annealing temperature. The studies indicate the formation of well-defined grain boundaries due to agglomeration of nanocrystallites. The films annealed in the range 573–773 K are found to be porous. The optical transmission spectra of the films annealed at 773 K exhibit interference effects for photon energies below the fundamental absorption edge. The optical studies indicate the existence of direct interband transition across a bandgap of 3.7 eV in confirmation with earlier band structure calculations.

1. Introduction

Nickel oxide (NiO) is considered as a model p-type semiconductor. It is a wide bandgap ($E_g \sim 4$ eV) transition metal oxide, with a cubic rock-salt structure and antiferromagnetic properties below its Neel temperature 523 K. Transparent conducting nickel oxide films have potential advantages for use as active layers in flat panel displays and gas sensor devices. There has been an increasing interest in developing nanostructured films due to their broad range of applications as catalysts, electrochromic display devices, and fuel cells [1–5]. P-type conducting thin films are required for the fabrication of many optoelectronic devices, which make use of hole injection [6]. Nickel oxide, as one of the relatively few p-type metal oxides, has got considerable attention because of its stable wide bandgap and excellent chemical stability [7]. Recent studies have shown that NiO thin films can make attractive sensing materials in gas like hydrogen and humidity detection devices [8]. There are several reports on nickel oxide thin film preparation by physical vapor deposition [9], electron beam evaporation [10], dip coating [11], sputtering [12–14], spray pyrolysis, chemical vapor deposition, sol gel,

and pulsed laser deposition [15]. R.F. magnetron sputtering has been used extensively to fabricate high surface area thin films, having large potential in the region of gas sensing [16]. Attempt has been made in this study to prepare NiO films by postdeposition annealing of R.F. magnetron sputtered thin nickel films and to understand the influence of postdeposition heat treatment on the crystalline phase formation, surface morphology, and optical properties of the film using different structural, optical, and electrical characterization tools.

2. Experimental Details

Thin nickel films are prepared by R.F. magnetron sputtering in a plasma focusing magnetic field using 99.99% pure nickel powder as the target, purchased from Sigma-Aldrich company. Clean soda lime glass slides are used as substrate material and kept perpendicular to the target surface at a distance of 4.5 cm. The sputter deposition is performed using R.F. magnetron sputtering equipment (Hind Hivac. Planar magnetron sputtering, model-12" MSPT) with a frequency of 13.56 MHz and an R.F. sputtering power of 200 W.

TABLE 1: Sample codes with preparation conditions.

Sample code	S1	S2	S3	S4	S5	S6	S7	S8	S9
Dep. time (Minutes)	45	45	45	45	45	15	15	15	15
Annealing temp. (K)	413	473	573	773	773	413	473	573	773
Annealing time (h)	0	3	3	3	5	0	3	3	3

Before sputtering, the chamber is evacuated to a base pressure of 10^{-6} mbar. The reflected power is minimized to 0 W and the argon inlet is adjusted to get a work pressure of 4×10^{-2} mbar in the chamber during deposition. The films are then deposited for time durations of 45 and 15 minutes [17]. In order to study the oxidation process, the films prepared are thermally annealed in air at constant temperatures within the range of 473 to 773 K for 3 hours in a programmable muffle furnace. One sample is annealed to 773 K for a longer period of 5 hours. The thin film samples prepared under different conditions together with sample codes assigned for convenience are listed in Table 1.

The crystalline structural changes of the sputtered films were determined by X-ray diffraction (XRD) in reflection geometry with a Philips P W 1710 diffractometer using $\text{Cu } K_{\alpha}$ radiation (0.15406 nm). The XRD patterns were recorded at a scanning rate of 0.05 deg s^{-1} in the angular (2θ) ranges from 15° to 65° . Film structure and surface morphology were investigated using atomic force microscopy (AFM) in contact mode with digital instruments Nanoscope III and scanning electron microscopy (SEM) using the system Quanta 200, fitted with an energy dispersive X-ray spectroscope (EDX). The stoichiometric composition of the film was evaluated by energy dispersive X-ray analysis. Optical measurements were performed in the wavelength ranging from 300 to 900 nm using a double beam UV-Visible spectrophotometer, JASCO-V550. The thickness of films was determined from the oscillations in the transmission spectra. The resistivity of the samples is measured by the two probe method employed with a Keithley digital source meter model 6430.

3. Results and Discussion

3.1. XRD Studies. In order to investigate the dependence of crystalline structural changes on annealing, the X-ray diffractograms of the samples annealed at different conditions are taken and are shown in Figure 1.

Only the crystalline phases of the fcc structure of Ni and the rock salt of NiO were identified. The peaks are consistent with the respective ASTM data and indicate the formation of NiO with a preferential growth along (200) plane. The peaks obtained at 2θ equals to 44.55° and 51.91° represent diffractions corresponding to (111) and (200) planes of nickel. These results do not show any formation of the Ni_2O_3 phase as that has been reported to appear in the temperature range of 573–773 K for evaporated nickel films [9]. It can be seen that the intensity of (200) peak corresponding to NiO increases with increasing annealing temperature. This is due to enhanced oxidation kinetics and improvements

FIGURE 1: XRD pattern of Ni powder (S0), Ni/NiO thin film samples (S1, S2, S3, S4, and S5) peak positions for S0Ni powder, and Ni thin film at Ni (111) and Ni (200). For NiO thin films S2, S3, S4, and S5 at NiO (111), NiO (200), and NiO (220).

in crystallinity. The better crystallinity of films at higher temperature is in agreement with previous studies [18–20]. The full width at half maximum (FWHM) of the peak is found to decrease, and the peaks become sharp with increase of annealing temperature. This indicates that the NiO average grain size increases with heat treatment. For lower annealing temperatures, the samples obtained are of imperfect lattice structure and have smaller grain size.

The crystallite size can be calculated using Scherrer's equation as follows:

$$D = \frac{K\lambda}{B \cos \theta}, \quad (1)$$

where D is the diameter of the nanoparticles, $K = 0.9$, λ is the wavelength of X-rays, θ is the Bragg's angle of XRD peak, and B is the FWHM for the peak [15].

The crystallite size determined from the (200) diffraction peak for the samples as a function of annealing temperature and time is given in Table 2. It must be mentioned that for the deposited film, it was not possible to obtain a reliable value of NiO grain size.

TABLE 2: Lattice parameters of annealed NiO thin films with respect to Ni powder.

Parameter	Ni powder	S2	S3	S4	S5
a_{111}	4.174	4.183	4.1829	4.161	4.160
a_{200}	4.176	4.166	4.162	4.168	4.168
a_{220}	—	4.186	4.178	4.179	4.170
$\Delta a_{(220-200)}$	—	0.002	0.016	0.011	0.010
$\Delta a_{(200-111)}$	0.002	0.017	0.12	0.0073	0.006
Grain size (nm)	80	14	15	16	15

The lattice parameter can be calculated using the following:

$$a_{(hkl)} = d_{(hkl)} \left(\sqrt{h^2 + k^2 + l^2} \right), \quad (2)$$

where h , k , and l are all integers, (hkl) is the lattice plane index, and $a_{(hkl)}$ is the corresponding lattice constant [21]. The lattice constants of oxidized nickel samples obtained are listed in Table 2. Even though NiO is of rock salt structure, the presence of large number of vacant lattice sites and local lattice disorders may lead to obvious lattice distortions and reduction in intensities or even the disappearance of XRD peaks of some lattice planes [22].

The lattice parameter “ a ” and change in lattice parameter “ Δa ” along the planes of S2, S3, and S4 are found using the relation following:

$$\Delta a = a_{111} - a_{200} \cong a_{200} - a_{220}. \quad (3)$$

It is found that there are changes in lattice parameters of the annealed NiO thin film samples when compared with that of NiO powder. The slit difference in peaks of Ni powder with respect to annealed NiO thin films is due to the film preparation conditions and annealing effects [23]. This implies that the prepared nanocrystalline NiO thin film samples contain a large number of vacant lattice sites, vacancy clusters, and local lattice disorders. The change in unit cell parameters Δa along (111), (200), and (220) plane, for different low-temperature samples is almost the same and collectively leads to the cubic crystalline nature of NiO. The variation of lattice parameters with temperature is shown in Figure 2.

The study of texture grade (Tc) for different planes is helpful in determining the crystalline nature of samples under different preparation conditions. The theoretical intensities for texture grade are taken from JCPDS file 4-835 of cubic NiO. The texture grade of samples is given by

$$Tc_{I(hkl)} = \frac{I_{(hkl)}/I_{(hkl)}^0}{1/k \sum_{i=1}^k I_{(hkl)}/I_{(hkl)}^0}. \quad (4)$$

XRD patterns of different samples in Figure 1 shows prominent peaks along (200), (111), and (220) planes; thus, the value of reflection number K is taken as 3. Among the peaks, prominent one is that of 200 plane having $I_{(hkl)}^0 = 100\%$, with (111) of 91% and (220) of 57% from JCPDS file, and $I_{(hkl)}$ represents the intensities of the corresponding peaks,

FIGURE 2: Variation of lattice parameters with temperature.

FIGURE 3: Annealing effect on texture grade of a_{200} , a_{220} , and a_{111} plane.

in the diffraction patterns for different samples. The texture grade for NiO peak along (200) plane shows a polycrystalline nature. For annealed samples, the texture grade shows a deviation from unity as shown in Figure 3.

The annealed samples with preferential orientation along (200) plane show values greater than one which implies the texture nature as well. The same annealed samples with peak orientations along (111) and (220) plane indicate “Tc” values smaller than unity, which means there is a depletion of grains in this direction [24].

FIGURE 4: SEM micrographs of NiO thin film samples (a) S1, (b) S3, (c) S5.

FIGURE 5: AFM image of NiO thin film sample (S4).

3.2. SEM and AFM Studies. The SEM micrographs of nickel films deposited for 45 minutes (S1) and subjected to annealing temperatures of 573 K for 3 h (S3), and 773 K for 5 h (S5) are shown in Figure 4. The surface morphology of a deposited film in Figure 4(a) consists of closely packed nanocrystals of Ni/NiO. Further increase of annealing temperature and time gives rise to porous film with voids between the grains (Figure 4(c)). The AFM image of nickel oxide film (sample S3) is shown in Figure 5.

The AFM image of sample annealed at 773 K for 3 hours (S4) indicates the agglomeration of nanocrystals and the voids in between the grains. The peaks in between vacant sites in the AFM image account for the high concentration of nucleation centers while annealing the film. The characteristics of height profile indicate the smooth and uniform nature of the film surface on annealing.

3.3. X-Ray Energy Dispersive Analysis. Energy dispersive spectroscopy was done for the elemental analysis of the film

FIGURE 6: Energy dispersive spectroscopy of Ni film coated for 45 minutes and annealed at 773 K for 5 hours.

surface. The EDX spectrum of the film annealed at 773 K for 5 h is shown in Figure 6.

There are no other prominent peaks besides those corresponding to nickel and oxygen detected in the spectrum. The nonstoichiometric atomic ratio (Ni/O-70/30) shows the effect of controlled oxygen mechanism on annealing.

3.3.1. Optical and Electrical Studies. The transmission spectra of samples S4, S5, S8, and S9 in the wavelength range 300–900 nm are shown in Figure 7. The color of the film in the deposited state is opaque, dark brown, and has negligible transmittance. On other hand, samples on annealing in air showed a color change and an increase in transmittance depending on annealing temperature. Similar reports of color change in NiO films with preparation conditions are found in literature [5, 9, 25]. The optical transmission spectra of the films annealed at 773 K exhibit interference effects for photon energies below the fundamental absorption edge. This arises due to difference of refractive index of the film with the substrate and interference of multiple reflections originated from films and substrate surfaces.

The optical bandgap E_g of the films can be determined from the transmission spectra by the Tauc plot [26] using the following relation

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \quad (5)$$

where A is a constant and $h\nu$ is the incident photon energy. The variation of $(\alpha h\nu)^2$ versus $h\nu$ for the NiO samples is

FIGURE 7: Transmission spectra of different thin film samples.

FIGURE 8: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for NiO thin film samples S4 and S8.

shown in Figure 8. The nature of the plots indicates the existence of direct interband transition in these NiO films [27]. The bandgap of the films is determined by extrapolating the linear portion of the plot to the energy axis. It is observed that the band gap energy gets shifted towards lower energy values and the slope of the plot decreases with increase in deposition time and annealing. The values of E_g for nickel film annealed at 773 K for 3 h with a sputter deposition of 45 and 15 minutes are estimated to be 3.1 and 3.8 eV, respectively. The values indicate that the optical bandgap of the films are sensitive to deposition time. Reported bandgap energies for NiO films are in the range of 3.6 to 4.0 eV [28]. The electrical conductivity of NiO films depends on their structure, composition, and deposition environment. The sample S6 is opaque, is dark brown, and shows a sheet resistance of 825 K $\Omega/\square$.

The conductivity is found to increase with sputter deposition time (for S1, sheet resistance is 387 K $\Omega/\square$) and indicate the presence of a large number of Ni^{3+} ions in film which in turn enhanced the p-type conductivity. The film annealed at 773 K for 5 h (S5) is found to have a sheet resistance of 125 M $\Omega/\square$ and shows a maximum transmittance of 80% in the visible region.

4. Conclusions

Thin nickel films are prepared at room temperature by R.F. magnetron sputtering technique from pure nickel powder source. The effect of annealing temperature and deposition time on the properties of these films has been investigated. The NiO films obtained showed enhanced transparency and high surface uniformity. The structural analysis using X-rays reveals the formation of cubic NiO with a well-defined preferential growth along (200) plane. The decrease of full width at half maximum (FWHM) and sharpness of peaks with increase of annealing temperature show that average grain size of NiO thin films increase due to heat treatment. The average grain size decreases with annealing and it shows a microlevel nature on thin films with respect to nickel powder sample. Texture grade analysis on NiO thin films shows its deviation from unity that leads to polycrystalline nature in its prominent peak (200) and a depletion of grains along (220) and (111) peaks. Annealing effects on the SEM and AFM studies on thin film result in the increase of oxidation kinetics, grain rotations, and enhanced crystallization which in turn produces nanocrystalline NiO film with well-defined grain boundaries. AFM analysis on annealed thin nickel film results in an agglomeration of NiO nanocrystals with voids in between grains. The controlled oxidation mechanism is well explained by the nonstoichiometric composition rates of Ni and oxygen in EDX analysis. The fringes on the transmission spectra are a measure of the thickness uniformity and high optical quality of the film. The annealed sample S5 shows a high transparency of 80% with appreciable sheet resistance. The bandgap energies for NiO samples S4 and S8 have comparable values with the reported ones. The conductivity was found to increase more with sputter deposition time than annealing.

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