Structural Properties of Semiconducting Nanostructures Prepared by DC Plasma Reactive Sputtering Method

In this work, semiconducting nickel oxide (NiO) nanostructures were prepared by reactive dc plasma sputtering method. Magnetron was employed at the cathode to prepare these nanostructures and show the advantage of such device in the production of highly pure nanostructures. The sputtered nickel atoms were sputtered and oxidized in presence of oxygen in the Ar:O₂ gas mixture of 4:1 ratio. Employment of magnetron results in formation of NiO only in the final samples according to the XRD analysis, increase the roughness and hence surface area of the produced NiO nanostructures, and finally decrease the particle size of NiO nanoparticles lower than 100nm. These improvements in the structural properties of the produced NiO make these nanostructures good candidates for specific applications, such as photodetectors, solar cells and electrochromic smart windows.

Keywords: Nickel oxide; Nanostructures; Magnetron sputtering; Reactive sputtering

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1. Introduction

Nickel Oxide is a semiconducting metal oxide of importance for use in device applications such as gas sensors, dye sensitized photocathodes and electrodes in alkaline batteries [1]. Also, two exciting novel applications based on nickel oxide have been developed recently. One is an electronic application as a resistive switching (RS) memory and the other is an energy-saving application as an electrochromic (EC) smart window [2-3]. Physical deposition of the NiO thin film can be achieved by sputtering, pulsed laser deposition, evaporation, atomic layer deposition and oxidation of metallic Ni [4].

NiO has a wide band gap of 3.6-4.0 eV and face-centered rombohedral crystal structure with lattice constants: a=4.1Å, α=90° 3.8′ at room temperature [3-4]. NiO can also exhibit small deviations from strict stoichiometry, as Ni₁₋ₓO, where 0<δ<5×10⁻³. At δ close to the upper boundary, the material is opaque, while with δ closer to zero, the material becomes translucent [3].

Chen et al. [5] have studied the dependencies of resistivity, carrier concentration, mobility and structural properties on the thickness of NiO films deposited onto glass substrates by magnetron sputtering in a pure oxygen atmosphere and observed that the crystallite size increases with the film thickness. Awais et al. [6] have deposited NiO coatings using DC magnetron sputtering from a nickel target in Ar:O₂ plasma. The influence of deposition parameters such as pressure, nickel target current and substrate bias voltage were correlated with the coating properties. Guziewicz et al. [7] have reported the properties of NiO films fabricated by magnetron sputtering where p-type conductivity of as-deposited films were annealed in O₂ or Ar at temperatures of 300-900°C. Reddy et al. [8] have reported NiO films deposited on glass substrates using DC reactive magnetron sputtering at different substrate temperatures in the range 30-400°C and concluded that higher substrate temperature induces larger grain size and more perfect crystalline structure, which lead to low resistivity.

In this work, reactive dc plasma sputtering system was used to prepare NiO nanoparticles on glass substrates by sputtering highly pure Ni target in argon-oxygen gas atmosphere and then study the structural properties of the prepared nanostructures.

2. Experiment

The magnetron sputtering system used in this work was designed to include vacuum chamber, discharge electrodes and magnetron assembly, vacuum unit, dc power supplies, gas supply system, cooling system and measuring instruments. The system is schematically shown in Fig. (1).

Discharge electrodes were constructed from stainless steel 304 hollow disks of 80mm in diameter and 8.5mm in thickness. The electrode was joined to holder of 295mm in length and outer and inner diameters of 16.2mm and 11.6mm, respectively, to include a stainless steel channel of 78.5mm in length and 5.6mm in diameter through which the cooling water was flowed to the inside volume of the electrode.

Two permanent ring magnets were placed at the back side of the cathode to form the magnetron with a separating distance of 1cm. The inner magnet was 12.5mm in height and 31.5mm in diameter with a central hole of 17.5mm in diameter, while the outer
magnet was 15.2 mm in height and 80 mm in diameter with a central hole of 40 mm in diameter.

A single-stage rotary pump (Leybold-Heraeus) of 9 m³/hr pumping speed was used to get pressure down to about 10⁻³ mbar inside the vacuum chamber. The flow rate of the argon gas used for preparation of NiO samples was ranging between 20-50 cm³/s. Sputtering target was Ni sheet of 99% purity for nickel oxide production. Nickel was selected as a target material because it is readily available material and has good electrical conductivity comparable to copper, gold, silver and platinum. Also, very uniform surfaces of nickel-based films are resulted when deposited on glass substrates due to very good adhesion [9].

Figure (1) Schematic diagram of the system used in the present work

Highly-pure argon and oxygen gases were mixed before supplied to the discharge chamber throughout flow meters and needle valves. Mixing ratio of 4:1 was used in this work and all experiments were carried out at working gas pressure of 0.7 mbar.

The transparent substrates used in this work were made of borosilicate glass. Before using them for sputtering experiments, they were first cleaned with ethanol to remove any oil layers or residuals may exist on their surfaces, rinsed and washed with distilled water to remove ethanol, and then dried completely before being kept in clean case or placed inside vacuum chamber.

Thickness of the prepared samples was measured by laser-fringes method where two semiconductor lasers of 1 mW output power and different wavelengths (532 and 632 nm) were used to produce the concentric fringes pattern and hence calculate film thickness (d) from the following relation [10]:

\[ d = \frac{L \cdot \lambda}{2 \cdot \Delta \lambda} \]  

(1)

where L and \( \Delta L \) are the widths of adjacent bright and dark fringes, respectively, and \( \lambda \) is the wavelength of laser beam.

The structures of the prepared samples were analyzed with a Bruker D2 PHASER XRD system (Cu-K\( \alpha \) x-ray tube with \( \lambda = 1.54 \AA \)). A proportional counter of 40 kV and current of 30 mA was used. The XRD patterns were recorded at a scanning rate of 0.08333° s⁻¹ in 20 ranges of 20-60°.

AFM and SPM measurements were performed on the prepared samples by an Angstrom AA-3000 apparatus in order to study the surfaces of nanostuctures prepared in this work as well as introduce the effects of some operating conditions on the surface of the prepared samples.

SEM measurements were performed using Tescan Vega EasyProbe instrument on samples prepared at the optimum conditions in order to confirm the formation of nanostructures as well as introduce the effects of some operating conditions on the fine structures of the prepared samples.

In order to determine the type of conductivity for the prepared samples, the four-point probe (F.P.P.) method was employed. The NiO nanostructures were found of p-type conductivity.

3. Results and Discussion

Figure (2) shows the effect of using magnetron at the cathode on the film thickness measured after different sputtering times. Due to the effect of confinement caused by the employment of magnetron at the cathode, the sputter yield is reasonably increased, i.e., much more Ni atoms are sputtered from the target to oxidize and form NiO molecules. Accordingly, the deposition rate and film thickness are increased too.

![Graph showing variation of film thickness with sputtering time for samples prepared without and with magnetron.](image)

The crystallinity of the prepared NiO nanostructures was examined by using powder x-ray diffraction (XRD), as shown in Fig. (3). Without magnetron (Fig. 3a), two peaks belonging to pure nickel appear due to the higher electric power transferred to the discharge volume that generates higher amount of heat inside the chamber. Such heat effect might induce to form these contaminations as the nickel oxide was forming too. As well, it can be seen that the diffraction peaks are low and broad due to the small size and incomplete inner structure of the NiO particle. The positions of peaks appearing at 20 of 37.125° and 43.156° can be readily indexed as...
(111) and (012) crystal planes of the NiO. Both diffraction peaks can be indexed to the face-centered cubic (f.c.c.) crystalline structure of NiO and corresponding with that of the standard spectrum [11].

The XRD pattern shows that the samples are single phase and no any other distinct diffraction peaks belonging to pure Ni atoms were detected, as shown in Fig. (3b). This result shows that the physical phases of the NiO nanostructures, prepared in this work, have higher purity. The acceleration effect of magnetic field accelerating sputtered Ni atoms might be disappeared then these atoms would have enough time to be oxidized and deposited as highly pure NiO particles.

The XRD results give an indication that all nickel atoms sputtered from the target are oxidized and then deposited on the substrate as NiO. In table (1), a comparison between experimental x-ray peaks for the NiO samples and standard peaks are presented. The lattice constant and grain size of the NiO nanostructures were calculated from the XRD data and tabulated in table (1). As only two crystal planes were recognized, the average value of the lattice constant can be estimated from them to be 4.04Å with a deviation of about 3% lesser than the standard value (4.17Å). Using Scherer formula, the average grain size can be estimated to be 18.335 nm.

Figure (4) shows the results of AFM test for the NiO samples prepared with and without magnetron at the cathode. As shown in Fig. (4a), the surface of the prepared sample is not highly uniform and the average and root mean square roughness are 1.08nm and 1.167nm, respectively. This figure indicates the formation of fine agglomerations consisting of compact nanoparticles with non-uniform grain size.

<table>
<thead>
<tr>
<th>2θ (deg)</th>
<th>d_{hkl} Exp. (Å)</th>
<th>a (Å) Exp.</th>
<th>FWHM (deg)</th>
<th>G.S. (nm)</th>
<th>d_{hkl}, Std. (Å) [111]</th>
<th>hkl</th>
</tr>
</thead>
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<tr>
<td>37.125</td>
<td>2.419</td>
<td>3.42</td>
<td>0.5625</td>
<td>18.83</td>
<td>2.412</td>
<td>(111)</td>
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<tr>
<td>43.156</td>
<td>2.094</td>
<td>4.68</td>
<td>0.59375</td>
<td>17.84</td>
<td>2.088</td>
<td>(012)</td>
</tr>
</tbody>
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Table (1) Comparison between experimental x-ray peaks for the NiO film and standard peaks.
In Fig. (4b), significantly homogeneous distribution of the NiO nanoparticles was produced with average roughness of 1.24nm and root mean square value of 1.49nm. The increase of the crystallite size may be caused by columnar grain growth in the structure.

The SEM micrographs show that preparation of NiO samples without magnetron at the cathode results in formation of big particles with sizes larger than 100nm (Fig. 5a). Using magnetron at the cathode causes to reduce the particle size by 50% (~70nm), as shown in Fig. (5b), as the collisional ionization rate is increased due to the confinement effect caused by the magnetron. However, particle size smaller than 40nm were observed.

Decreasing the particle size and increasing the roughness (and hence the surface area), homogeneity and surface density of the prepared NiO nanostructures are preferred for some optical, photonic and electrochromic applications. These characteristics can be easily obtained by the effective employment of magnetron at the cathode.

Fig. (5) SEM micrographs of the NiO samples prepared without (a) and with (b) magnetron

4. Conclusion
According to the results obtained from this work, using the magnetron at the cathode of discharge system causes to increase the deposition rate and improve the structural properties of nickel oxide nanostructures prepared by reactive dc plasma sputtering method. The structural measurements show that the prepared NiO samples with magnetron mostly contain two crystal planes, large surface area and the nanoparticles lower than 100nm in size as compared with those prepared without magnetron.

References
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