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Effect of cobalt doping on microstructural and optical properties of nickel oxide thin films

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ABSTRACT

In this study, transparent thin films of cobalt-doped nickel oxide ($Co_xNi_{1-x}O$; $x=0$, 0.005, 0.01, 0.05, 0.075 and 0.15) were deposited on to microscopic glass substrates using a spray pyrolysis technique. The effect of cobalt doping on structural, morphological and optical properties was investigated. XRD studies reveal that all the films are polycrystalline with cubic structure and exhibit (111) preferential orientation. Co is well incorporated in the host lattice, i.e. octahedrally coordinated on the Ni site without altering the structure. The effect of Co doping was observed to have a strong influence on the surface morphology of NiO films. An interesting correlation between the optical transmittance and the RMS roughness was observed. All the coatings retain high transparency throughout the visible spectral regime. The optical band gap varies from 3.44 eV to 3.26 eV due to the presence of Ni vacancies and/or oxygen defects. The optical reflectance spectra along with refractive index and extinction coefficients of the prepared films have also been discussed. Among all the Co-doped NiO thin films in this study, films doped with 1 at% Co concentration exhibited the best properties, namely improved crystallinity, smooth and compact surface morphology, lowest RMS roughness value of 2.26 nm and highest transmittance of ~85% in the visible region.

1. Introduction

Transparent semiconducting oxide thin films are attractive due to their good optical characteristics, high stability and excellent electrical properties. Transparent conducting oxides are basically metal oxide semiconductors that can be classified as either n-type or p-type. Currently, transparent conducting thin film coatings of p-type semiconductors are required in a variety of optoelectronic applications. In particular, NiO, the most exhaustively investigated p-type transition metal oxide, is a promising candidate for many applications such as positive electrode in batteries [1], solar thermal absorbers [2], in electrochromic display devices [3], in hetrojunction solar cells [4] and in gas sensing applications [5]. NiO is a wide band gap, low cost, promising ion storage material in terms of cyclic stability [6]. In recent years several studies have been carried out to modify the properties of NiO thin films by doping with various elements [7–9]. Das et al. studied phosphorous doped nanocrystalline NiO thin films prepared using the radio frequency sputtering method [7]. They found that the optical band gap increases from 3.66 eV for undoped NiO to 3.81 eV for 10% phosphorous doped NiO thin films. Optical properties of NiMgO thin films were studied by Boutwell et al. [9]. The Mg-doped

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NiO films were prepared by a sol–gel spin coating method. The optical transmission was found to increase in the UV–visible spectral region to as high as 90%. In another study Marco et al. [10] prepared Ni_xCo_{3-x} films using the spray pyrolysis deposition technique. In the films with $x=1.3$ and 1.8 the preparation leads to the formation of significant amounts of NiO and CoO which are segregated at the surface of sprayed films. Recently the functional properties of nickel cobalt oxide thin films have been reported by Iacomi et al. [11]. They have deposited nanocrystalline nickel–cobalt oxide thin films by a spin coating method on glass substrates. They found that 100 nm thin films were transparent with the phase composition depending on $x=$ Ni/(Ni+Co). The literature survey suggested that the Ni–Co binary oxide system could be developed for specific applications such as supercapacitors, switches and sensors or optical limiters [11–14]. However the amount of available information on nickel–cobalt oxide system is still limited and the detailed optical transition mechanisms have not been fully investigated yet.

It would be interesting to investigate the effect of Co doping on the microstructural and optical properties of NiO thin films. This has been in fact the objective of the present work. Thus we have prepared the $Co_xNi_{1-x}O$ thin films by the chemical spray pyrolysis technique. The structural properties have been studied by the X-ray diffraction method (XRD), the morphological studies have been done using an atomic force microscope (AFM) and the optical properties have been studied using a UV–visible spectrophotometer.

2. Experimental details

$Co_xNi_{1-x}O$ ($x=0$, 0.005, 0.01, 0.05, 0.075 and 0.15) thin films were prepared onto microscope glass substrates using the well known spray pyrolysis technique. The apparatus used for deposition is described and schematized elsewhere [15]. The precursor solution was prepared from a mixture of 0.1 M nickel chloride ($NiCl_2\cdot 6H_2O$) and de-ionized water. The solution was stirred at room temperature for few minutes to yield a clear and homogeneous solution. For uniform deposition of thin films the solution was sprayed through a linearly moving glass nozzle. The nozzle to substrate distance was 28 cm. The spray rate of 1 ml/min was maintained by using air as a carrier gas. The substrate temperature was kept constant at 573 K during deposition by means of an electronic temperature controller. Nickel chloride solution was sprayed onto the preheated glass substrates, which undergoes evaporation, solute precipitation and pyrolytic decomposition, thereby resulting in the formation of nickel oxide thin films according to the following reaction:

$$NiCl_2\cdot 6H_2O \rightarrow NiO + 2HCl\uparrow + 5H_2O\uparrow \quad (1)$$

Cobalt doping was achieved by the addition of cobalt chloride ($CoCl_2$) to the precursor solution. The doping concentration of films for a particular precursor in grams has been measured by the weight percentile method with the help of the molarity equation, i.e. [16]

$$\frac{Molarity \times Molecular\ \ weight \times Volume}{1000} \quad (2)$$

The glass substrates were chemically and ultrasonically cleaned before coating. In the first step the substrates were washed with a detergent solution 'Labolene' and then washed with water. In the next step substrates were immersed in concentrated nitric acid for 15 min. These substrates were further dipped in 4 M NaOH solutions for 15 min to remove any acidic contamination. Finally these substrates were washed with distilled water and then treated in an ultrasonic bath of distilled water for 15 min, prior to deposition. Several initial trials were made to optimize the deposition conditions before final sample preparation. The thickness of the prepared films was determined by a weight difference method using a sensitive microbalance and was found to be approximately 350 nm. $Ni_{1-x}Co_xO$ films of the same thickness were used for further characterization. To study the structural properties X-ray diffraction analysis was performed on Bruker D8 ADVANCE with CuKα radiation ($\lambda=1.5418$ Å). The surface morphological study of deposited films was carried out by the atomic force microscope (AFM) (Digital instruments nanoscope E with Si_3N_4 100 μm cantilever, 20 nm resolution and 0.58 N/m force constant) in contact mode at room temperature. Optical measurements were done in transmittance mode as well as in reflectance mode within the wavelength range 300–900 nm using the UV–vis spectrophotometer (Perkin-Elmer Lambda 950). The major focus was confined to the investigation of the optical properties of $Ni_{1-x}Co_xO$ thin films.

3. X-ray diffraction study

The XRD patterns of $Co_xNi_{1-x}O$ thin films deposited with $x=0$, 0.005, 0.01, 0.05, 0.075 and 0.15 are shown in Fig. 1. All the patterns exhibit a cubic crystal structure having a preferential growth along (111) plane. The other lower intensity peaks (200) and (220) have also been assigned to NiO cubic phase. A small variation in the peak position (111) between $2\theta=37.34°$ and $2\theta=37.27°$ has been observed in X-ray ω-rocking curve measurement (Fig. 2a). The unit cell volume corresponding to different

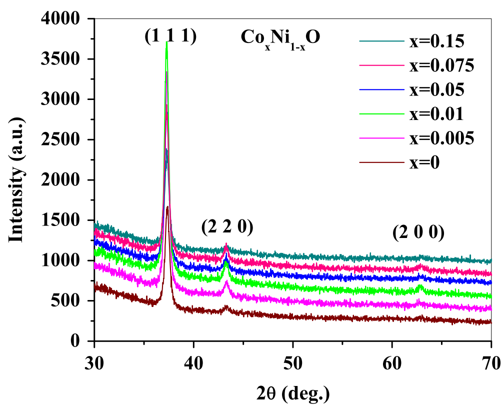

Fig. 1. XRD patterns of NiO and $Co_xNi_{1-x}O$ thin films.