Materials Science in Semiconductor Processing 21 (2014) 7–13

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

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

Optical and electrical properties of nickel oxide thin films synthesized by sol–gel spin coating

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ARTICLE INFO

Available online 1 February 2014

Keywords:
Thin films
Nickel oxide
Sol–gel
Spin coating
Structural analysis
Electrical and optical properties

ABSTRACT

Nickel oxide thin films were prepared by the sol–gel technique combined with spin coating onto glass substrates. The as-deposited films were pre-heated at 275 °C for 15 min and then annealed in air at different temperatures. The effects of the annealing temperature on the structural and optical properties of the films are studied. The results show that 600 °C is the optimum annealing temperature for preparation of NiO films with p-type conductivity and high optical transparency. Then, by using these optimized deposition parameters, NiO thin films of various thicknesses were deposited at the same experimental conditions and annealed under different atmospheres. Surface morphology of the films was investigated by atomic force microscopy. The surface morphology of the films varies with the annealing atmosphere. Optical transmission was studied by UV–vis spectrophotometer. The transmittance of films decreased as the thickness of films increased. The electrical resistivity, obtained by four-point probe measurements, was improved when NiO layers were annealed in N_2 atmosphere at 600 °C.

1. Introduction

Research and development on thin films has led to the conclusion that different classes of materials are of particular interest for different applications. Nickel oxide thin films have been widely studied as optically active layers in electrochromic devices [1]. Literature reports indicate that thin films of NiO have been produced by a number of techniques. Among various deposition techniques the sol–gel method combined with spin-coating deposition is important because the final properties of the films can be tailored using various precursors and annealing temperatures, and it is a low cost method [2]. Most of the reports address the structural aspects of the films [3], emphasizing the effect of substrate temperature on electrochromic properties, cyclic durability, surface morphology, sensing properties [4], electronic response during potential switching and the degree of coloration [5], as well as their practical use in electrochemical, photovoltaic, and heterojunction solar cells [6]. NiO has a wide band gap [7] and is a promising ion storage material in terms of cyclic stability [8]. It has an excellent durability and electrochemical stability with a large range of optical densities and the possibility to be manufactured by a variety of techniques.

In the present paper, the fabrication and characterization of optically transparent NiO films are presented, where up to five layers have been deposited on glass substrates, applying treatment in different atmospheres. The structural and optical properties of the NiO thin films are characterized by X-ray diffraction (XRD), atomic force microscopy (AFM) and UV–visible spectroscopy. Electrical resistivity has been studied with a four-point probe.

2. Experimental procedure

NiO thin films were prepared by the sol–gel method. First, the nickel acetate tetrahydrate $Ni(Ac)_2 \cdot H_2O$ precursor

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http://dx.doi.org/10.1016/j.mssp.2014.01.018

was dissolved in 2-methoxyethanol and monoethanolamine (MEA) was added as catalyst. The molar ratio of MEA to nickel acetate was maintained at 1.0 and the concentration of nickel acetate was 0.5 M. The resulting solution was stirred for 2 h at 60 °C to yield a clear and homogeneous solution, and then aged for 24 h at room temperature. Before deposition, glass substrates were cleaned with acetone, ethanol, and deionized water successively in an ultrasonic bath. The films were deposited on ordinary glass substrates by spin coating at room temperature, with a rate of 3000 rpm for 30 s. After each coating, the as-deposited films were dried at 275 °C in air for 15 min using a hot plate to evaporate organic residuals. The coating and drying procedures were repeated five times to increase the film thickness. Finally, all the films were annealed in air or in N_2 atmosphere for 1 h in order to enhance their physical properties.

The crystallographic structure was studied by XRD using a Bruker D 8 advance X-ray diffractometer with Cu K_α (k=1.5418 Å) radiation for 2θ values in the range of 20–90°. The surface morphology of the prepared films was characterized via atomic force microscopy (AFM) (Nanoscope III) in tapping configuration (Veeco AFM head RTESP silicon pur) to a scanning area of 1 μm × 1 μm. The optical transmittance $T(\lambda)$ of the films was measured by a UV–vis–NIR (Lambda 950) spectrophotometer, equipped with an integrating sphere, in the wavelength range 300–2500 nm. The electrical resistivity was measured at room temperature by a S302-X stand-alone four-point head. All measurements were carried out at room temperature.

3. Results and discussions

3.1. Effect of annealing temperature on physical properties

In this study, we examined the effect of annealing temperature on the structural and optical properties of thin NiO films. First, we develop a monolayer NiO films deposited on a glass substrate. Then, the as deposited films were dried at 275 °C in air for 15 min. Finally, the samples were annealed in a controlled temperature oven. Once the desired temperature is reached, annealing proceeds for 1 h. The XRD spectra shown in Fig. 1 reveal the effect of post-annealing treatment in the temperature range of 300–600 °C on the structure of the NiO thin films. When the films were dried at 275 °C in air for 15 min, the results present a single broad unstructured XRD line. The XRD patterns show that all annealed films have polycrystalline structures. After annealing at 300 °C, a small peak appears at around 2θ=43.3° assigned to (200) crystallographic plane of simple cubic NiO showing partial crystallization of the film. The intensity of the (200) peak increases as the annealing temperature increases. For annealing temperatures higher than 400 °C, the crystallites undergo a reorientation and secondary peaks such as (111) and (220) emerge. By further increasing the annealing temperature to 500 °C, the intensity of the (200) diffraction peak increases in the XRD pattern. Increasing the annealing temperature to 600 °C, a strong orientation along (200) is observed. Other peaks, such as (111), (220), (311), and (222) are also present, but their intensity is very small compared to the (200) peak. When the annealing

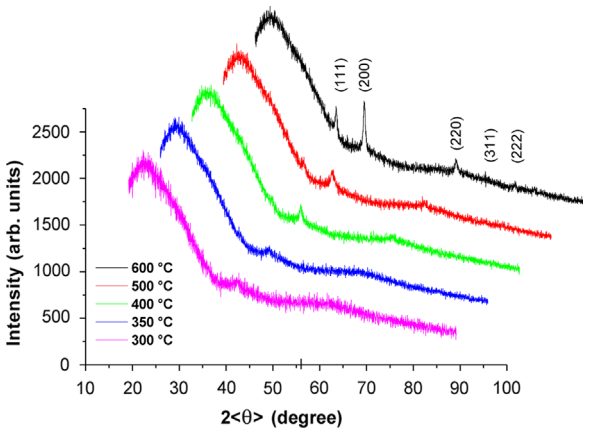

Fig. 1. X-ray diffraction patterns of NiO thin films for different annealing temperatures.

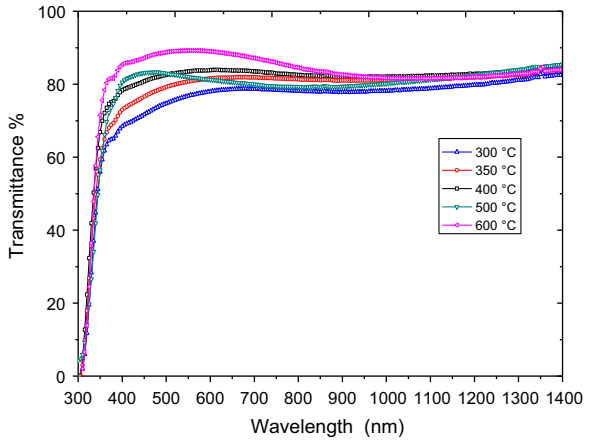

Fig. 2. Optical transmission spectra for NiO thin films annealed at various temperatures.

temperature was increased, the intensity of NiO peaks increased while the full width at half maximum values decreased. From these results, it is obvious that the effect of annealing temperature on the orientation of NiO is the key factor, which demonstrates that the orientation along the (200) direction is the most suitable direction for ion exchange. Fig. 2 shows the effect of thermal annealing in the range of 300–600 °C for 1 h on the optical transmittance of NiO thin films. It is clear that the films exhibit high transparencies in the visible and the NIR spectral regions when the annealing temperature increases. The variation of the transmission in the visible region ranges from 80 to 92%, depending on the annealing temperature. The annealing temperature of 600 °C seems to be the best, resulting in films with excellent transmittance. We observed that, for the temperature range of 300–400 °C, the transmission spectra show no interference oscillations in the region of low absorption. Indeed, there are no multiple reflections inside the substrate for these wavelengths because the thickness is much greater than the wavelength of the incident light. The interference oscillations appear at the annealing temperature of 500 °C. The interference fringes are due to multiple reflections at the