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Sol–gel derived nanostructured nickel oxide films: Effect of solvent on crystallographic orientations

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ABSTRACT

Nickel oxide films were deposited onto glass substrates by sol–gel dip coating method using solvents of different polarities without any catalysts, templates or surfactants. Methanol, 1,4-butanediol, ethanol, and 2-propanol were used as solvents. The structural, optical and electrical properties of NiO films were investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM), UV–visible spectroscopy and Hall effect measurements, respectively. Nickel oxide thin films with cubic phase crystal structure of various preferred orientations were obtained in the different solvents. The XRD results showed that films deposited from solution using higher polar solvents develop a (1 1 1) preferred orientation, while the (2 0 0)-orientated films were obtained using lower polar solvents. The average particle size increases with viscosity of solvents. Surface morphology of the nickel oxide film consisted of nanoparticles with uniform coverage of the substrate surface. The solvent of higher viscosity induced larger particle size. Band gap narrowing from 4.42 to 3.87 eV was observed using different solvents. The lower resistivity and Hall coefficient was obtained for prepared NiO films using higher polar solvents. The relationships between solvent physicochemical properties, preferred orientation, structural, optical and electrical properties of NiO films were investigated.

1. Introduction

There has been an increasing interest in developing nanostructured metal oxides with p-type conductivity due to their unique properties and potential applications. Thin films of p-type semiconductors are required in many optoelectronic device applications, which make use of hole injection [1]. Nickel oxide thin films with NaCl-type structure are considered to be a model semiconductor with p-type conductivity films due to its wide band-gap energy range from 3.6 to 4.0 eV [2]. It is an attractive material due to its excellent chemical stability, novel optical, electronic, magnetic, thermal, and mechanical properties. Nickel oxide is extensively used in electrochromic devices, smart windows, active optical fibers, gas sensors, solar thermal absorbers, alkaline batteries cathode, catalyst, magnetic materials, supercapacitors, and p-type transparent conducting electrodes, etc [3–6].

In these applications, it is still needed for synthesizing high-quality crystallite NiO films with required characteristics in terms of their size, morphology, microstructure, composition purity, crystallizability. These characteristics are closely related to the preparation techniques. Controlling the crystallographic orientation and surface roughness is very important in using NiO films.

The nickel oxide thin films have been prepared using various techniques including thermal evaporation [7], spray pyrolysis [8], chemical vapor deposition [9], electrochemical deposition [10], sputtering [11], sol–gel [12], thermal decomposition [13], electron-beam evaporation [14], chemical solution deposition [15], etc. However, some methods require high temperature, harsh growth conditions, expensive experimental setup and time consuming removal of the hard and soft templates or organic additives. Therefore, developing a simple approach for low cost, lower temperature, larger-scale production, and controlled growth without additives to prepare NiO nanostructures is a great challenge to material scientists. Among these, the sol–gel based dip-coating technique is now becoming popular for film deposition because of its inherent advantages. It requires low temperature for processing, ensures high purity and chemical homogeneity, allows easy doping at solution stage, offers a better composition control and makes possible deposition on a large area and on a variety of substances at a low cost [16]. For these

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reasons, sol–gel method is chosen here to prepare precursor for casting NiO thin films via dip coating techniques and to investigate their characteristics.

The morphology and size of the NiO nanostructures could greatly influence their optical, electronic, magnetic, and catalytic properties [5,6,17]. Chen et al. synthesized nickel oxide thin films of various preferred orientations by radio-frequency (RF) magnetron sputtering process in different gas ratios of oxygen atmosphere on unheated and heated substrates [18,19]. Wu et al. synthesized NiO nanoparticles of different shapes by four different methods using different amines and surfactants [20]. Tiwari and Rajeev prepared NiO nanoparticles of different sizes by sol–gel method using nickel nitrate as precursor [21]. To the best of our knowledge, few works are available in the literature on the sol–gel synthesis and characterization of NiO-based nanosystems [22–24] and there are no reports on solvent-dependent NiO nanostructures properties prepared by sol–gel method.

Since the solvent physico-chemical properties will strongly influence the solubility and transport behavior of the precursors, the solvent in a sol–gel process could be used as shape or size-controller of nanocrystallites. The control of stable crystalline size and phase obtained by the sol–gel method is one of the most versatile, reproducible procedures to obtain high reactivity, and improved crystallinity [25,26]. In the present study, we report a novel "solvent-dependent" approach of synthesis and characterization of nanocrystalline NiO thin films by simple and inexpensive sol–gel dip coating technique. The solvents including methanol, ethanol, 1,4-butanediol and 2-propanol of different polarities were chosen to study the interface–solvent interaction effect on the structural, optical and electrical properties of nickel oxide thin films.

2. Experimental details

2.1. NiO films preparation

Nanocrystalline NiO thin films have been synthesized by a sol–gel method using nickel acetate $Ni(CH_3COO)_2{\cdot}4H_2O$ as a source of Ni and methanol, 1,4-butanediol, ethanol, and 2-propanol as solvent. In a typical experiment, 3.322 g of nickel acetate was added to 40 ml of solvent and stirred vigorously at 60 °C for 1 h, leading to the formation of light green colored solution. Glass substrates were dipped in the starting solution and with drawn at a rate of 3 cm/min. The deposited layers were then dried in air at 150 °C for 30 min after each dipping. The process is repeated several times to get the film of desired thickness. After six coating cycles, the crystallization of the films was finally performed by thermal annealing in the air at temperature of 500 °C for 120 min. The film thickness (measured using spectroscopic ellipsometer) was found to vary in the range of 110–130 nm. After here for convenience, NiO films prepared in methanol, 1,4-butandiol, ethanol and 2-propanol as solvent would refer as NiO–M, NiO–B, NiO–E and NiO–P, respectively.

2.2. NiO films characterization

The structural, surface morphology and optical properties of NiO films were investigated using X-ray diffraction (XRD, Bruker, D8 ADVANCE with Cu Kα radiation), scanning electron microscopy (SEM, Philips, XL30 scanning electron microscope), and UV–visible spectroscopy (Shimadzu, MPC-2200), respectively. The electrical properties of nickel oxide films, including resistivity and Hall coefficient were measured by the Hall measurement system (Lake Shore model 7604 Hall Effect measurement systems).

3. Results and discussions

3.1. Structural characters

The purity and crystallinity of NiO films were examined by using XRD as shown in Fig. 1a. The XRD patterns of all films presented single-phase NiO with a cubic structure (bunsenite, NaCl type structure) [27,28]. The diffraction data were in good agreement with JCPDS card of NiO (JCPDS no. 44-1159), no impure peaks are observed in the XRD patterns. The average crystallite size 'D' and the strain 'η' have been determined from the intersection and slope of $\beta\cos(\theta)$ verses $\sin(\theta)$ plot as [29,30]:

$$\beta\cos\theta = \frac{k\lambda}{D} + 2\eta\sin\theta$$

where 'β' is the corrected full width at half maxima of diffraction peaks, 'θ' is the Bragg angle and 'λ' is the wavelength of X-rays. Accordingly, the average crystallite size (nm) increases as following order: NiO–B (87) > NiO–P (70) > NiO–E (56) > NiO–M (41). The solvents used in this study had widely varying polarities and viscosities. Table 1 shows some physical features of used solvents. The average particle size increases with viscosity of solvents. The highest viscosity for 1,4-butanediol may depress the diffusion of all ions in the solution leading to the formation of aggregated particles and larger size of ZnO crystalline than those in other solvents [31].

3.2. Crystallographic orientations

The XRD intensity ratios provide information about the degree of relatively preferred orientations and crystal structure of

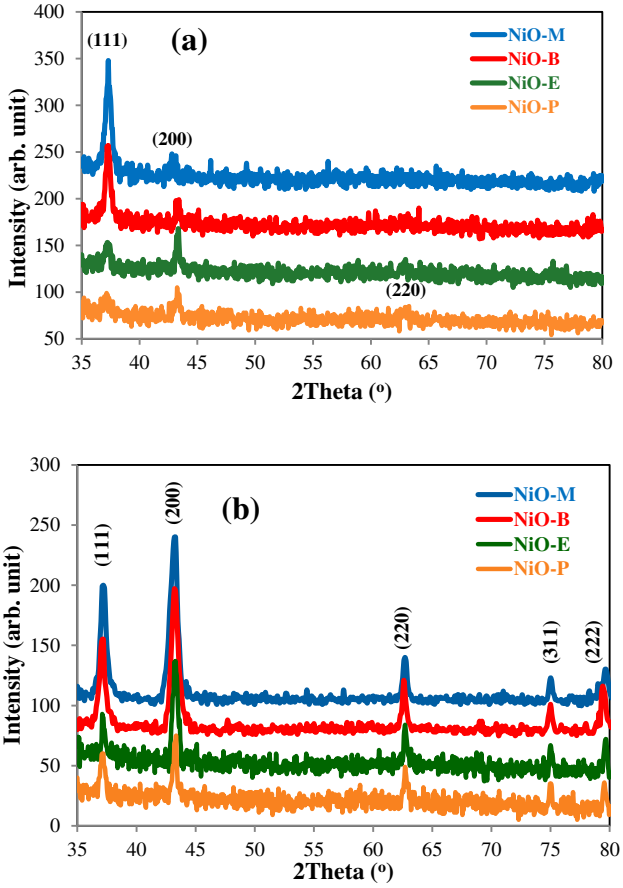

Fig. 1. X-ray diffraction patterns of synthesized NiO (a) films and (b) powders using different solvents.