Microstructural Studies of Nanocrystalline Nickel Oxide

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Abstract

Sol gel spin coating technique has been successfully engaged for the deposition of nanocrystalline nickel oxide (NiO) thin films. The films were annealed at 300-500°C for 1 hr in an air and changes in the structural and morphological properties were studied. The structural and morphological properties of nickel oxide films were studied by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively. XRD analysis shows that all the films are crystallized in the cubic phase and present a random orientation. Surface morphology of the nickel oxide film consists of nanocrystalline grains with uniform coverage of the substrate surface with randomly oriented morphology.

Keywords: Nickel oxide, Sol gel method, Structural properties, Morphological properties

1. Introduction

Metal oxides can adopt a large variety of structural geometries with an electronic structure that may exhibit metallic, semiconductor, or insulator characteristics, endowing them with diverse Chemical and physical properties. Therefore, metal oxides are the most important functional materials used for chemical and biological sensing and transduction. Moreover, their unique and tunable physical properties have made themselves excellent candidates for electronic and optoelectronic applications. Nanostructured metal oxides have been actively studied due to both scientific interests and potential applications [1, 2].

The nickel oxide thin films have been prepared using various techniques including thermal evaporation [3], spray pyrolysis [4], chemical vapor deposition [5], electrochemical deposition [6], sol–gel [7–8], sputtering [9–11], chemical solution deposition [12–16], etc. Among these, chemical solution deposition, also called as a chemical bath deposition, is an advantageous technique due to its low cost, low-temperature operating condition and freedom to deposit materials on a variety of substances. Verkey and Fort [14] deposited nickel oxide thin films using nickel sulfate and ammonia solution over the temperature range 330–350 K. Pramanik and Bhattacharya [12] prepared nickel oxide thin films from an aqueous solution composed of nickel sulfate, potassium persulfate, and ammonia at room temperature. Han et al. [15] studied growth mechanism of nickel oxide thin films following Pramanik's chemistry. Banerjee et al. [16] obtained hexagonal mesoporous nickel oxide using dodecyl sulfate as a surfactant and urea as a hydrolyzing agent.

In the present study, we report synthesis and characterization of nanocrystalline NiO thin films by simple and inexpensive sol-gel spin coating technique and effect of annealing on their structure and morphology properties.

2. Experimental Details

2.1 Synthesis of Nanocrystalline NiO thin films

Nanocrystalline NiO thin films have been synthesized by a sol-gel method using Nickel acetate $Ni(CH_3COO)_2.4H_2O$ as a source of Ni. In a typical experiment; 3.322 gm of nickel acetate was added to 40 ml of methanol and stirred vigorously at 60°C for 1 hr, leading to the formation of light green colored powder. The as prepared powder was sintered at various temperatures ranging from 300-500°C with a fixed annealing time of 1hr in an ambient air to obtain NiO films with different crystallite sizes. The nanocrystalline NiO powder was further dissolved in *m*-cresol and solution was continuously stirred for 11 hr at room temperature and filtered. The filtered solution was deposited on to a glass substrate by a single wafer spin processor (APEX Instruments, Kolkata, Model SCU 2007). After setting the substrate on the substrate holder of the spin coater, the coating solution (approximately 0.2 ml) was dropped and spin-casted at 3000 RPM for 40 s in an air and dried on a hot plate at 100°C for 10 min.

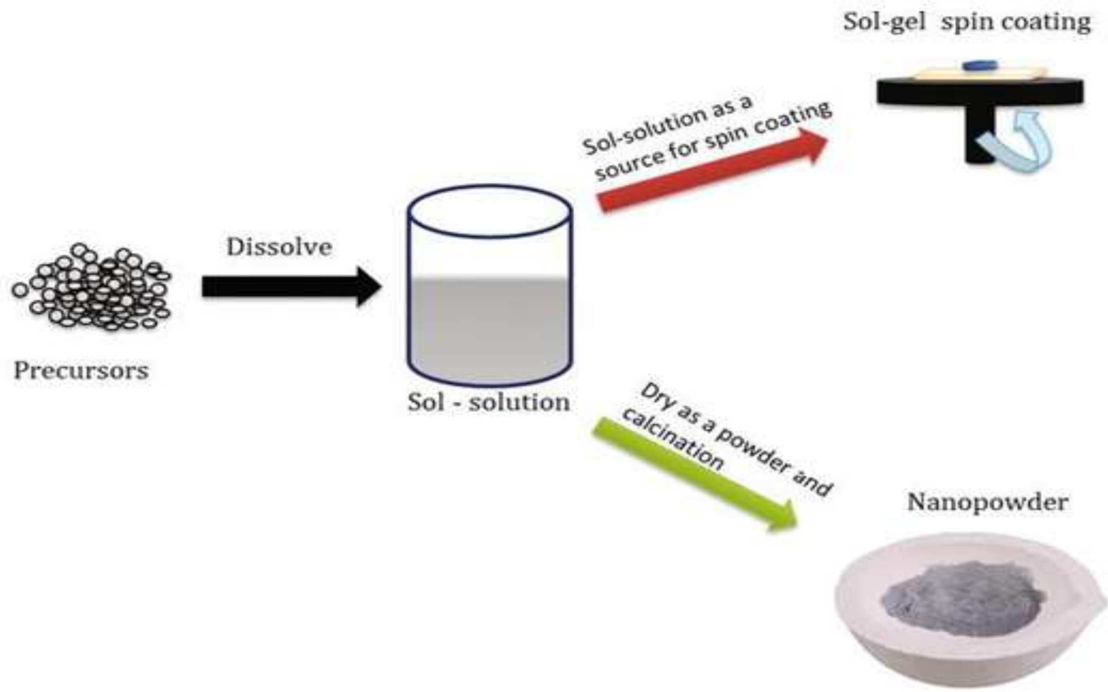

Fig.1. diagram for NiO films prepared from the sol-gel process using the spin-Coating method

2.2. NiO film formation mechanism

The mechanism of NiO film formation by the sol gel spin coating method can be enlightened as follows:

$$Ni(CH_3COO)_2.4H_2O + 2\ CH_3\text{-}OH \longrightarrow Ni(OH)_2 + 2CH_3COOCH_3 + 4H_2O$$

Since to improve crystallinity and remove hydroxide phase, films were annealed for 1 h pure NiO film is formed after air annealing by following mechanism:

$$Ni\ (OH)_2\downarrow + \text{Carbonaceous compounds} \xrightarrow[\text{Oxidation}]{\text{Air annealing}} NiO + H_2O \uparrow$$

2.3 Characterizations:

The structural properties of the films were investigated by means of X-ray diffraction (XRD) (Philips PW-3710, Holland) using Cu Kα radiation (λ=1.5406 Å). The surface morphology of the films was examined by scanning electron microscopy (SEM) (Model Japan), operated at 20 kV. The thickness of the film was measured by using weight difference method.

3. Results and Discussion

3.1 Structural analysis

Structural analysis of the NiO films annealed at 300-500 ^{o}C was carried out by using CuK_{α} radiation source of wavelength (λ = 1.54056A˚) and the diffraction patterns of films were recorded by varying diffraction angle (2θ) in the range 20– 80^{o}. Fig. 2 shows XRD pattern for the NiO films annealed at 300-500 ^{o}C .The observed'd' values are in good agreement with standard 'd' values and the diffraction peaks are indexed to the cubic phase of NiO with a=b=c= 4.1678 A˚ [Joint Committee on Powder Diffraction Standards (JCPDS) No. 73-1519]. It shows well-defined peaks having orientations in the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (222) planes. The absence of impurity peaks suggests the high purity of the nickel oxide. Compared with those of the largeness counterpart, the peaks are relatively broadened, which further indicates that the deposited material has a very small crystallite size [17]. The crystallite size (D) is calculated using equation as follows [18]:

$$D = 0.9\lambda/\beta \cos\theta \quad \text{----------} \quad (2)$$

where, β is the half width of diffraction peak measured in radians. The calculation of crystallite size from XRD is a quantitative approach which is widely accepted and used in scientific community [19–22]. The average crystallite size is increased with increasing annealing temperature revealing a fine nanocrystalline grain structure (Table 1).

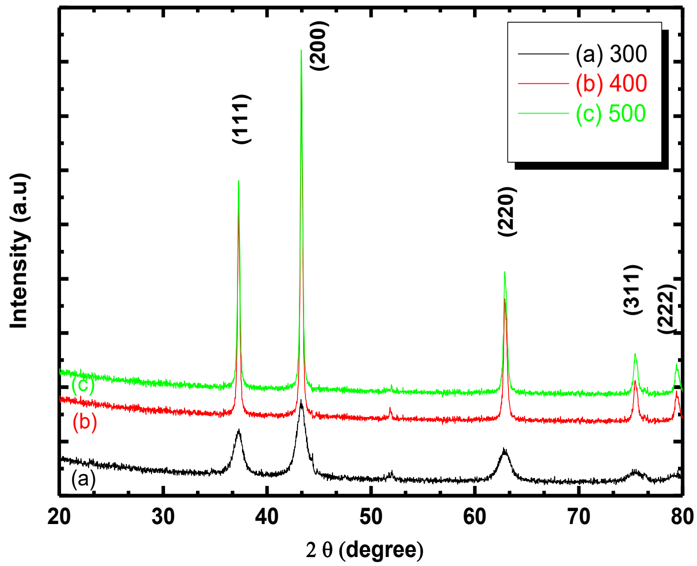

Fig. 2. X ray diffraction patterns of NiO film at different annealing temperatures

3.2. Surface morphological studies

The two-dimensional high magnification surface morphologies of NiO thin films annealed at 300-500 ^{o}C were carried out using SEM images are shown in Fig. 3(a -d). From the micrographs, it is seen that the film consists of nanocrystalline grains with uniform coverage of the substrate surface with randomly oriented morphology and the crystallite size is increased from 40–52 nm as annealing temperature increases from 300-500 ^{o}C. The crystallite size calculated from SEM analysis is quite in good agreement with that of crystallite size calculated from XRD analysis.

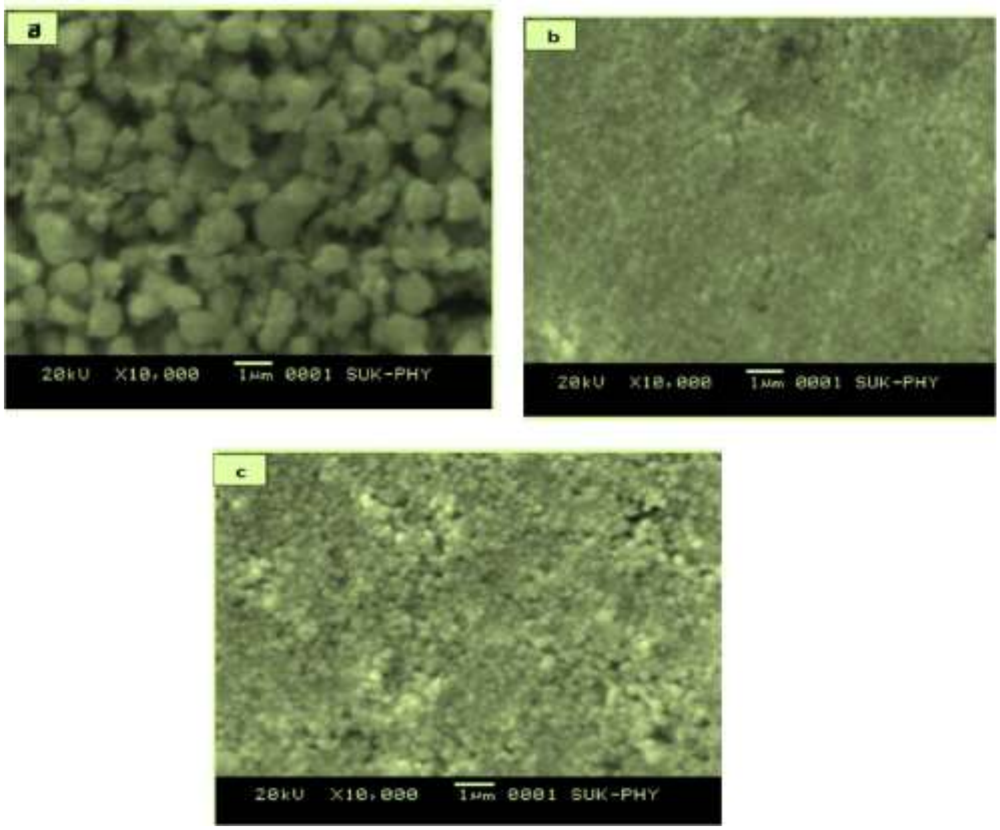

Fig. 3. SEM of NiO thin films anneled at a) 300°C b) 400°C c) 500°C

3.3 thickness measurement

Thickness was calculated by weight difference method using formula:

$$t = m / A \rho \text{ --------- } (1)$$

where t is film thickness of the film; m is actual mass deposited onto substrate; A is area of the film and is the density of nickel oxide (6.67 g/cc^2).

It was observed that increasing the annealing temperature resulted in a decrease in film thickness from 0.9061 µm (300°C annealing) to 0.4997µm (500°C annealing).

The NiO thin film thickness is presented in Table 1.

Table. 1 Effect of processing temperature on microstructural properties and thickness NiO thin film

Sr. No.	Annealing temperature °C	Crystallite size nm	Thickness µm
1	300	24.10	0.81
2	400	35.21	0. 68
3	500	41.57	0.59

4. Conclusions

Nickel oxide nanoparticles were derived by solvothermal technique. The NiO films were prepared for various temperatures between 300 to 500°C. The crystallographic investigations inferred that the nickel oxide have a nanocrystalline cubic structure. The microscopic studies revealed that a nanocrystalline morphology with an average particle size 24-42 nm.

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