Growth and Characterization of Amorphous Nickel Oxide thin films by SILAR Method

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Abstract

This work presents a chemical route for the preparation of NiO thin films on glass substrates. A simple and inexpensive Successive Ionic Layer Adsorption and Reaction (SILAR) technique was employed to deposit NiO thin films using $NiCl_2.6H_2O$ as the precursor and Sodium Hydroxide (NaOH), Distilled Water as solvents. Three different samples 0.1M, 0.15M and 0.2M were synthesized. The samples were annealed and the change in the properties of annealed with respect to un-annealed samples were studied. Structural characterization by XRD reveals the films to be amorphous in nature. Surface morphology of the films has been studied by Atomic Force Microscopy (AFM) and the samples show clear presence of coalesced grains. Heat treatment makes the sample surface smoother and this is seen in the surface roughness values. Further, the samples were subjected to UV-Visible spectroscopy and various optical properties viz., Transmittance and Band Gap of the film samples were estimated. We find that the value of the optical transmittance gradually reduces as the molarity of the samples increases. Conversely, the direct band gap has been found to vary proportionally with molarity.

Keywords: SILAR, Nickel Oxide, Thin films, Characterization

1. Introduction

The optical properties of thin films are very important for many applications, including interference devices, such as anti-reflection coatings, laser mirrors, monochromatic filters as well as optoelectronics, integrated optics, solar power engineering, micro-electronics and optical sensor technology depending on the absorption and transmittance properties of the films during their preparation [1]. Nickel Oxide (NiO) is the most exhaustively investigated transition metal oxide [2]. It is a NaCl-type antiferromagnetic oxide semiconductor [2]. Nickel Oxide (NiO) is a promising p-type semiconducting oxide material [4]. Due to its enormous potential applications such as chemical sensors, electro chromic devices, catalysts, dye sensitized solar cells (DSSCs), it has attracted various researchers around the world [4].

The attractive features of NiO include (1) excellent durability and electro-chemical stability, (2) low material cost, (3) promising ion storage material in terms of cyclic stability, (4) large span optical density, (5) possibility of synthesising the material by a variety of techniques, (6) electro-catalysis, (7) positive electrode in batteries, (8) fuel cells, (9) electro-chromic devices, (10) solar thermal absorber, and (11) catalyst for oxygen evolution and photo electrolysis[1, 2]. Nickel Oxide thin films have been fabricated using many growth methods such as Electron Beam Evaporation, Reactive Sputtering, Plasma Enhanced Chemical Vapour Deposition, Successive Ionic Layer Adsorption and Reaction, Pulsed Laser Deposition, Spray Pyrolysis, Chemical Bath Deposition etc. In this work, we have made use of Successive Ionic layer Adsorption and Reaction (SILAR) growth technique to deposit the films on cleaned glass substrates. We have chosen this method because it is simple, versatile and inexpensive. The influence of the concentration of the precursor solution on the optical and structural properties of the NiO films are studied and discussed.

2. Experimental Procedure

NiO films were grown using SILAR process as shown in Fig 1. The precursor solution was made by dissolving Nickel chloride hexahydrate [$NiCl_2.6H_2O$] and distilled water. NaOH solution was added drop wise till the pH of the solution reached 12. Three sets of precursor solutions (0.1M, 0.15M, and 0.2M) were prepared. All the precursor solutions were prepared fresh for film growth. The substrates were cleaned in distilled water and again cleaned in chromic acid over-night. The substrates were maintained in a neutral pH scale by using necessary reagents. Later they were cleaned again with acetone in order to remove any stains on it and then they were heat treated at a temperature of 300^0C for 1 hour. During the film deposition the distilled water was maintained at a temperature of 80^0C and the final bath was kept at room temperature. Adsorption, reaction and rinsing times were set constant for these films. One SILAR cycle contained two steps: (a) The substrate was first immersed into boiling distilled water and (b) immersed in final precursor solution. The immersion of the substrate for 1 cycle in each solution was for 30 seconds and the total number of cycles was 60. After 60 continuous cycles a thin film was formed on the glass substrate. As-deposited films were annealed at a temperature of 400^0C for about 2 hours. The annealed films were uniform and homogenous. The deposition is practically completed in about 2 hours. Thicker films can be prepared by re-immersing the initially deposited thin films into a fresh bath. Optical investigation of the films were carried out using UV-Visible spectrophotometer (Shimadzu, model UV-1700).

Fig 1: Synthesis process of NiO films by SILAR Method.

3. Results and Discussion

3.1 Structural Characterization

Fig 2 Depicts the XRD pattern of the as-grown films. It is evident from the XRD pattern that the films are amorphous in nature. Heat treatment of up to 400^0C has not induced any crystallinity in the samples. Hence, the various lattice parameters have not been estimated.

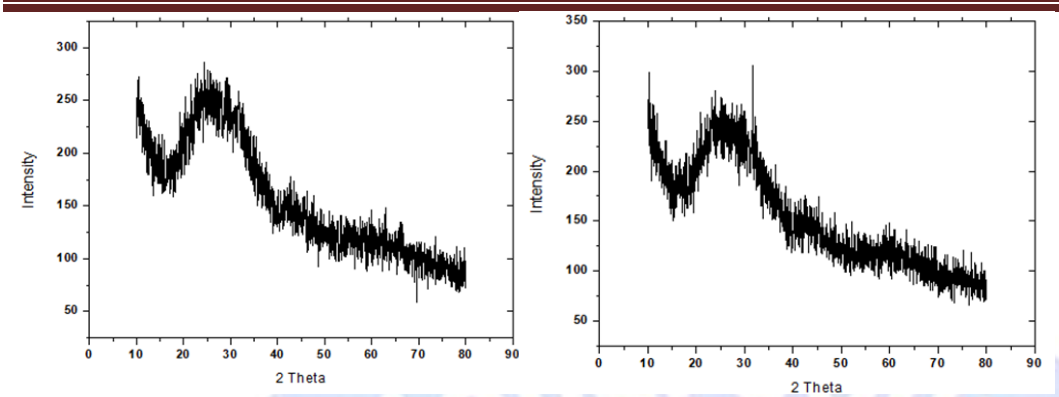


Fig 2. XRD pattern of un-annealed and annealed samples.

3.2 Surface Morphology

Fig 3.2a and 3.2b Depicts the 2-Dimensional and 3-Dimensional Atomic Force Microscope (AFM) morpho-graphs of the annealed and un-annealed samples. We find that surface to be smoother in the case of annealed samples. The surface roughness has been estimated to be 1.11µm for un-annealed sample and about 320nm for annealed films.

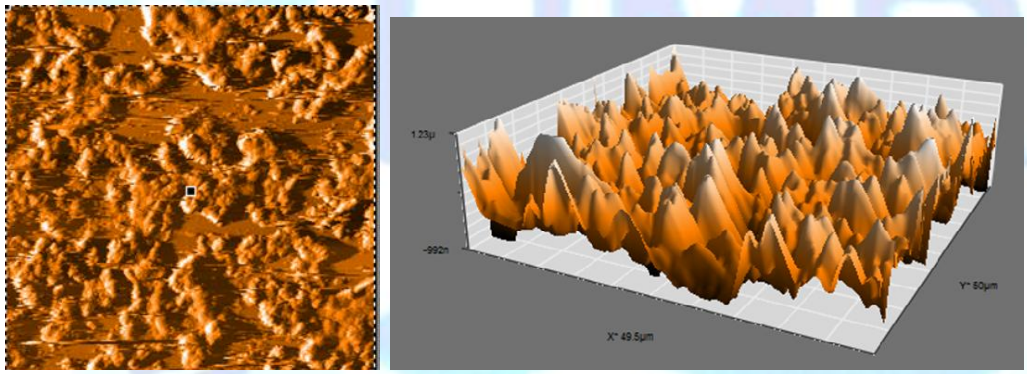


Fig 3.2a AFM 2-D and 3-D images of un-annealed samples

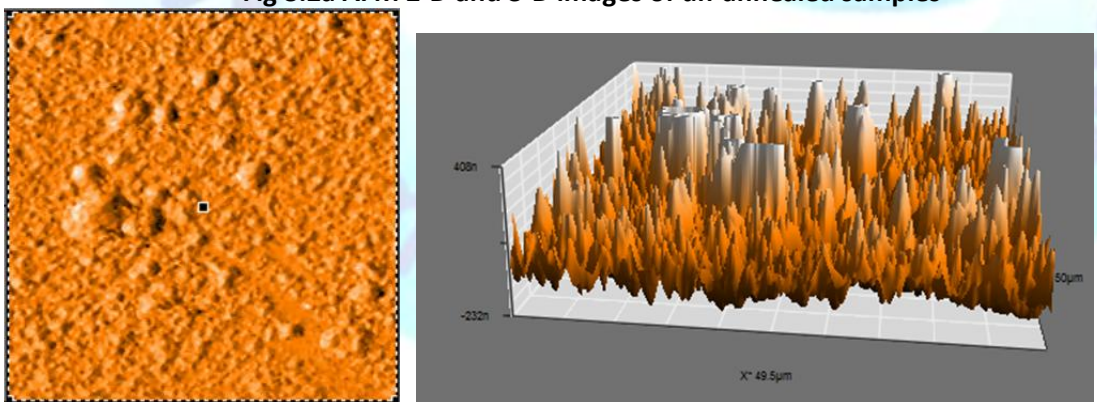


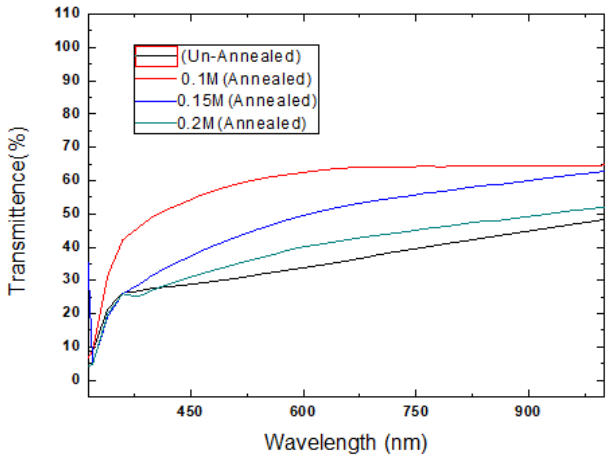
Fig 3.2b AFM 2-D and 3-D images of annealed samples

3.3 Optical Characterization

Fig 3.3b presents the combined Transmittance for all the samples. We find optical transmittance to be higher in all the un-annealed films as compared to the annealed samples. However this value reduces with increase in molarity.

Table 3.3a Effects of Molarity variation for Transmittance, Direct Band-Gap,

SAMPLE	TRANSMITTENCE @ 550nm	DIRECT BAND GAP VALUE (eV)	INDIRECT BAND GAP VALUE (eV)
Un-Annealed	31.75%	3.53	3.08
0.1M (Annealed)	60.81%	3.44	3.44
0.15M (Annealed)	46.03%	3.67	3.18
0.2M (Annealed)	37.05%	3.6	3.13



Indirect Band-Gap values

Fig 3.3b Combined %Transmittance Graphs.

Fig 3.3c and 3.3d depicts the direct and indrect band-gap of all the samples combined. The optical direct band gap is found to vary between the un-annealed and annealed samples. No direct variation of band-gap is exhibited in all of the film samples. The optical indirect band gap is found to decrease with increase in molarity.

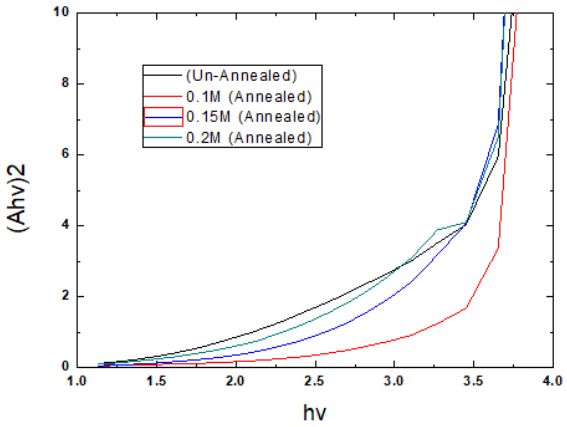


Fig 3.3c Direct Band-Gap Graph

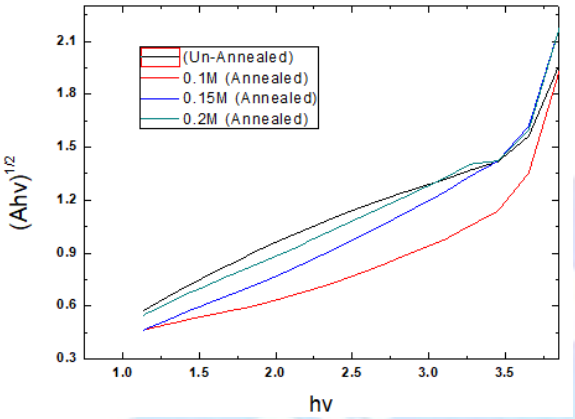


Fig 3.3d Indirect Band-Gap Graph

4. Conclusion:

Chemically synthesized NiO thin films grown by SILAR Method have been found to be amorphous in nature. The amorphous nature does not get altered after heat treatment up to a temperature of 500^0C. Surface Morphology studies using AFM indicate that the surface of the films get smoother due to heat treatment as shown in the 2-D images of AFM.The surface roughness has been estimated to be 1.11µm for un-annealed sample and about 320nm for annealed films. In comparison to the un-annealed sample, the optical transmittance in the visible region of the electromagnetic spectrum for the annealed films is found to increase. However this value varies inversely with the molar concentration. The optical direct band gap is found to vary between the un-annealed and annealed samples. No direct variation of band-gap is exhibited in all of the film samples.

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