EFFECT OF PRECURSOR CONCENTRATION ON NICKEL OXIDE THIN FILMS BY NEBULIZED SPRAY PYROLYSIS TECHNIQUE

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Abstract:

The interest in Nickel oxide has been growing fast because of its applications in Science and Technologies. Nickel oxide is a p-type transparent semiconductor material with cation deficit and wide band gap of 3.6eV – 4.0eV. This material exhibits most prominent cubic and techniquestructure. It has an excellent chemical stability which is favourable to optical, electrical and magnetic properties. In the present work, Undoped Nickel oxide thin films were deposited on preheated substrates using a simple, low cost Nebulized Spray Pyrolysistechnique at different range of precursor molarities. Effects of precursor concentration on structural and optical properties were investigated. The X-ray diffraction indicated that intensity was increased with increase in molarity concentration and had a most prominent cubic structure. From the optical studies it is confirmed that the film thickness increased with increase in molarity and the transmittance decreased and the band gap energy for NiO thin films varied with increased molarities.

Keywords: thin films, diffraction pattern, crystallite size, thickness, bandgap.

Introduction:

Transparent conducting oxide thin films have been widely used in optoelectronic industry due to their unique combination of optical transparency and electrical conductivity. Among this Nickel oxide thin film is an attractive material due to its excellent chemical stability as well as electrical, optical and magnetic properties. NiO is a p-type semiconducting material with a wide band gap 3.6-4.0 eV and has cubic rock salt crystal structure. The interest in NiO thin films is growing fast because of their importance in many applications in Science and Technology [1]. It is a NaCl type antiferromagnetic oxide semiconductor. Its offers promising candidature for many applications such as solar cells, gas sensing, optoelectronic devices and electrochromic applications etc. Nickel oxide thin films have prepared by various techniques such as Sputtering, Electrodeposition, Sol-gel, Electron beam evaporation, atomic layer epitaxy and Spray pyrolysis. Among this, Nebulized Spray Pyrolysis has been employed more frequently because of its low cost, simple, large area of high homogeneity and easy control of structure of the deposited thin films. In the present work, NiO thin films have been prepared by Nebulized spray technique and the effect of molarities on the structural and optical properties of NiO thin films have been studied.

Experimental technique:

Nickel Oxide thin films have been grown on glass substrates which were chemically and ultrasonically cleaned before coating. The glass substrates were kept at a temperature of about 450^{0}C. Nickel Chloride hexahydrate was chosen as the precursor for the preparation of NiO thin films. It was dissolved in distilled water. The Nickel Chloride concentration in the solvent was varied from 0.05 to 0.1M [2]. This solution was then sprayed in fine droplets using compressed air as carrier gas. The pyrolytic decomposition for NiO thin film formation for a Chloride precursor is given as

$$NiCl_2.6H_2O \rightarrow NiO + 2HCl + 5H_2O\uparrow$$

Uniform NiO thin film with good adherence is formed when aqueous nickel chloride is sprayed on preheated glass substrates. Formation of fine droplets occurs because of pyrolytic decomposition when droplets make contact with the hot surface.

Tab. 1: Optimum Deposition parameters used for the preparation of NiO thin films

Source solution	$NiCl_2.6H_2O$
Molarity	0.05M, 0.075M, 0.1M
Total volume of spray solution	10ml
Substrate temperature	450^{o}C
Nozzle to substrate distance	7cm
Carrier gas pressure	1 bar
Solution flow ratae	10ml

The spray coated NiO thin films were subjected to X-ray diffraction, UV-Visible and Photoluminescence spectral analysis.

Results and Discussion:

X-ray Diffraction Analysis:

The structure of the NiO thin films was analyzed by X-ray diffraction. The XRD pattern of NiO thin films deposited at the substrate temperature of 450^{0}C for various molarities shown in the fig.1. Three Bragg peaks indicate the formation of polycrystalline nature having a cubic structure and preferentially oriented along (111), (200), (220) and (311) planes [3]. The (200) plane for 0.075M is the predominant peak. Also the crystalinitynature of the films was found to increase with the increased molarities of the solution. The intensity of the diffraction peaks were increased with the increase of concentrations and the observed peaks were in good agreement with the JCPDS values card no: 04-0835 [4]. Lower intensity peak of planes (220) increases gradually as precursor solution increased from 0.05M to 0.1M. The crystallite size of the dominant peaks for the planes (200), (111) and (220) using DebyesScherrer formula was found to be 8.7, 24.9, 42.8 and 15.8nm respectively.

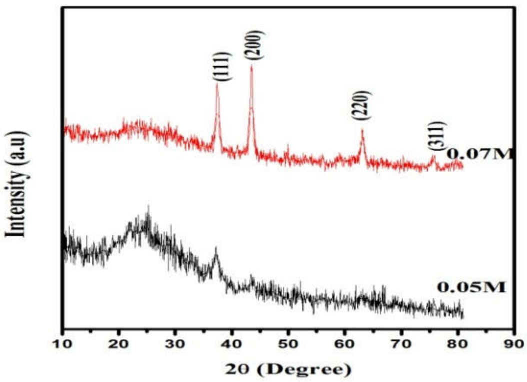
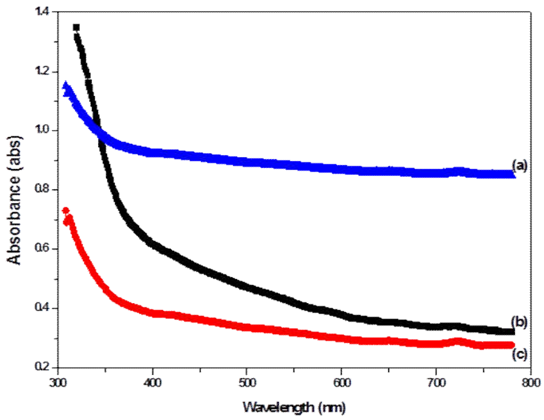


Fig. 1 X-ray diffraction patterns of NiO thin films

Optical properties:

UV-Visible Spectroscopy:

A strong increase in absorption in the UV region is observed at wavelengths smaller than 360nm while a broad absorption appears in the visible and near infra-red regions. The strong absorption in the UV region is due to bandgapabsorption in NiO[5]. This increase of energy is due to the interaction of the material electrons with the photons which have enough energy for the occurrence of electron transitions. It is observed that the absorbance increases as the concentrations of the solution increases [6].The optical transmittance is recorded in the wavelength range of 300-800nm. The fig 3. showed that the transmittance of the film found to be about 60%. . Films that were prepared from higher solution concentrations showed a relatively lower transmittance [4, 7]. This is attributed to the increase in the film thickness, with the increase in absorption. For the concentration of 0.1M showed less sharp absorption edge which indicate the deposition of bigger clusters. The obtained transmittance may be attributed to imperfection and non-stoichiometry of the NiO films due to the increase of concentration of the solutions. The energy band gap is the important physical parameter that determines mainly the electrical and optical characteristics of the material. It is the separation between the lower of conduction band the top of the valence band where the energy states are not allowed. The band gap energy of the material was found to be 3.4, 3.3 and 3.2 eV for the concentrations 0.05, 0.075 and 0.1M respectively shown in fig.4. The value of optical band gap shifted towards the lower energy and the slope of the plot decreases as the molarity increases.



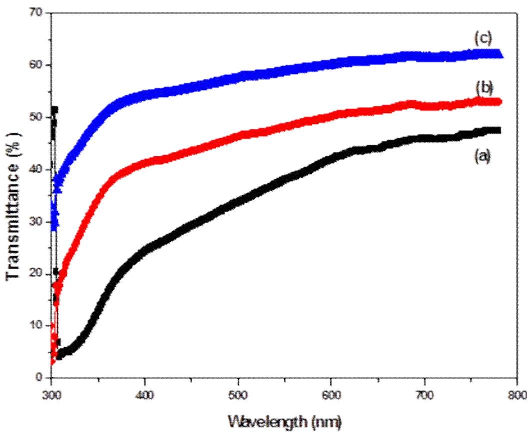


Fig 2→ Absorbance spectra of NiO thin films *Fig 3→ Transmittance spectra of NiO thin films*

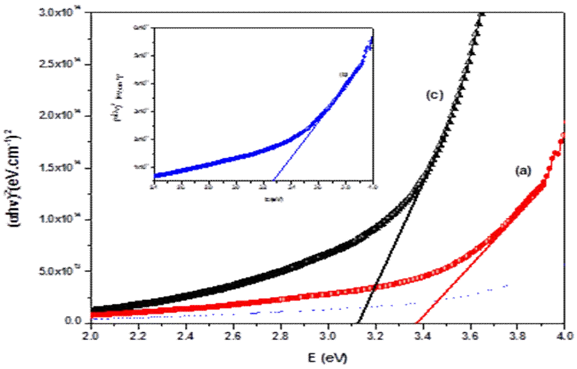


Fig 4→Bandgap energy of NiO thin films

Photoluminescence Studies:

The fig 5 showed the typical emission spectra of NiO thin films prepared by Nebulized Spray Technique. The excitation spectra of NiO films showed a strong band below 300nm. The PL emission spectrum was found to exhibit two emission peaks centered at 370 and 490nm respectively. The origin of the strong peak at 375nm was attributed to the electronic transitions of Ni^{2+} and O^{2-} ions. The shoulder emission peaks at 490 and 520nm may be attributed to the oxygen related defects[8].

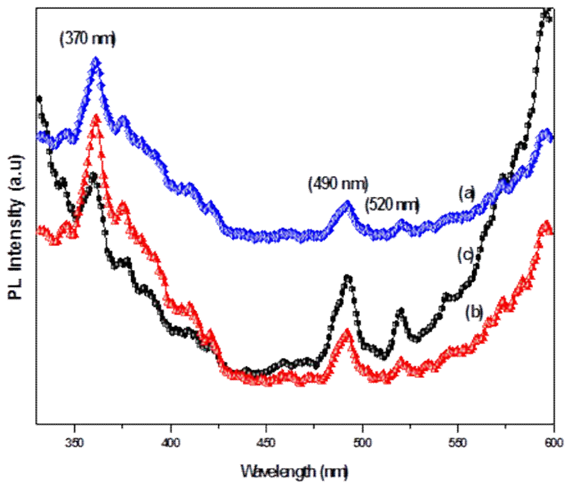


Fig 5→ PL Emission spectra of NiO thin films

Conclusion:

Thin films containing NiO nanoparticles were synthesized successfully on glass substrates by a low cost, simple Nebulized Spray Pyrolysis method. Through this technique good quality film was prepared by keeping the substrate temperature at 450^{0}C. The effect of varying the precursor concentration of NiO films on structural and optical properties was studied with a view to optimize the material for solar cell device applications. The results as discussed showed that varying the concentrations has effect on the structural and optical properties of the NiO thin films. The thickness of the film increases as the concentration of the solution increases.The films were polycrystalline in nature with preferred orientations at (111), (200) planes. Improvement on crystallinity, higher peak intensity and diffraction were recorded for 0.075M concentration. By increasing the molar concentration above this limit leads to bulk crystal nature and increased thickness which in turn decreases the optical transmittance and the band gap of the material. Therefore NiO thin films for the concentration 0.075M might be suitable to expose solar cell applications.

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