Preparation and Optoelectrical Properties of Spray Pyrolyzed NiO Thin Films

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Abstract : A simple and inexpensive spray pyrolysis (SP) technique was employed to deposit nickel oxide (NiO) thin films. NiO thin film was deposited using 0.1 M to 0.3 M aqueous solution of nickel chloride ($NiCl_2 \cdot 6H_2O$) onto ultrasonically cleaned glass substrate at 450 °C. The effect of solution concentration on the structural, optical, photoluminescence and electrical properties of the NiO films were studied by X-ray diffraction (XRD), UV-vis-NIR spectrophotometer, Photoluminescence (PL) spectrophotometer, Hot probe and Hall effect measurement system. The XRD study reveals that the NiO films were polycrystalline in nature with cubic structure. Also, the crystallite size increases with the increase in solution concentration. The UV study shows that the transmittance and consequently the band gap energy decreases with the increase in solution concentration. The PL spectrum of the NiO thin film originates from electronic transition of Ni^{2+} and O^{2-} ions. The electrical study shows that all the NiO films were p-type.

IndexTerms - **Nickel oxide, Thin films, Spray pyrolysis, Cubic structure, Photoluminescence.**

I. INTRODUCTION

Nickel oxide may exist in various forms like NiO, NiO_2, NiO_4 and Ni_2O_3. Among them NiO is an anti-ferromagnetic material with a density of 6.67 g/cm^3 and having a cubic structure. NiO is a semiconductor compound, having an energy gap of 3.6-4.0 eV [1]. NiO thin films are interesting for a variety of applications, such as antiferromagnetic material, gas sensors, electrochromic devices, solar cells etc.

NiO thin films have been fabricated by various physical and chemical deposition techniques, such as pulsed laser deposition, electrodeposition, chemical vapor deposition, chemical bath deposition, vacuum deposition, RF magnetron sputtering, DC magnetron sputtering, ion beam sputtering, thermal evaporation, e-beam evaporation, molecular beam epitaxy, co-precipitation, sol-gel, spray pyrolysis etc.

Owing into simplicity and inexpensiveness, the spray pyrolysis technique [2,3] is a better chemical method at a lower cost for the preparation of thin films with a larger area. This method is convenient for preparing pinhole free, homogenous, smoother thin films with the required thickness. In the SP technique, various parameters like air pressure, deposition rate, substrate temperature, solution concentration, distance between nozzles to substrate, cooling rate after deposition also affect the properties of the thin films. The film properties are sensitive not only to their structure but also to many other parameters including thickness, surface states, morphology, optical, electrical etc. The SP technique has been found to be useful for the preparation of metallic oxides, semiconducting oxides, binary and ternary chalcogenides and superconducting thin films of various materials.

Using the SP technique, the NiO films have been prepared and the results obtained have been reported. The present work is to study the structural, optical, photoluminescence and electrical properties of crystalline NiO thin films using spray pyrolysis.

II. EXPERIMENTAL

2.1 Film Preparation

Nickel oxide (NiO) thin films have been prepared on glass substrates by spray pyrolysis technique using a solution of Nickel (II) chloride hexahydrate ($NiCl_2.6H_2O$) and distilled water. During the film deposition the glass substrate temperature was kept constant at 450ºC. The effect of solution concentration on the NiO films were studied for 0.1 M to 0.3 M.

2.2 Film Characterization

The thickness of the films were measured using the surftest SJ–301 stylus type surface roughness and thickness measuring instrument. A Rigaku X-ray diffractometer (XRD) with a CuKα radiation (λ=1.5418Å) was used for structural studies in the range of 2θ = 10–90°. The optical transmittance spectra of the films were taken from a Perkin Elmer Lambda UV-vis-NIR spectrophotometer in the spectral range of 200–2400 nm. The band gap of the films was calculated using the optical method. The photoluminescence (PL) spectra of the NiO films were recorded using a Varian Cary Eclipse Fluorescence Spectrophotometer. The majority carrier type of the as-deposited films were carried out by the Hot probe technique and Hall effect measurement system. The electrical resistivity of the films were measured by the Ecopia HMS 5000 Hall effect system.

III. RESULTS AND DISCUSSION

3.1 Structural Properties

In our study, NiO particles were prepared by spray pyrolysis technique using $NiCl_2.6H_2O$ and distilled water. Fig. 1 shows the XRD results obtained for NiO films prepared at a temperature 450°C and different solution concentrations (0.1 M to 0.3 M) in the range of 2θ from 10-90°. The XRD analysis is within the acceptable range of the experimental errors.
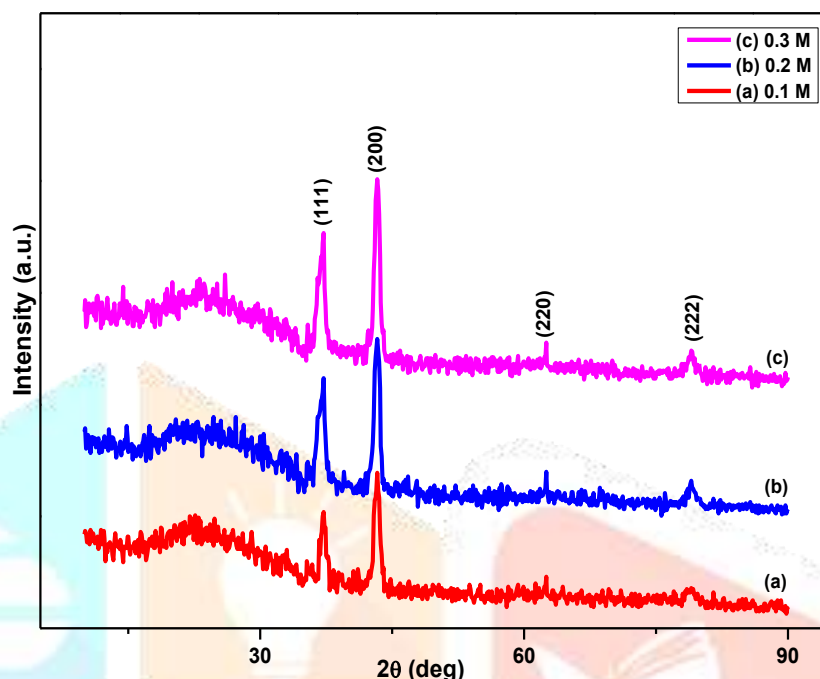

FIG.1 X-RAY DIFFRACTION OF NIO FILMS

It is found that all samples are polycrystalline in nature with cubic structure, have a strong reflection along (200) plane compared to (111) plane. Other planes such as (220) and (222) are also present, but their intensities are very small. It is well known that the (111) plane is polar and unstable. In contrast, (200) plane of ionic rock salt material is considered as a non-polar cleavage plane and is thermodynamically stable. No peaks, any else phase of NiO or impurity peaks are observed, which indicates the high purity of the obtained NiO particles. In the cubic NiO, the lattice parameter (a) can be evaluated from the relation [4]:

$$a = d_{hkl} \sqrt{h^2 + k^2 + l^2} \qquad (1)$$

where a is the lattice parameter, d_{hkl} is the inter-plane spacing, and h, k & l are the indices of the planes.

The lattice parameter for (200) plane varies from 0.4186 nm to 0.4184 nm for the different solution concentrations (0.1 M to 0.3 M). The average lattice parameter for (200) plane was found to be 0.4185 nm which is very close to the standard value for bulk NiO taken from JCPDS file no. 04-0835. The crystallite size (D) is calculated for major reflex (200) using the Scherrer's formula [5]:

$$D = \frac{k\lambda}{\beta \cos \theta} \qquad (2)$$

where λ is the X-ray wavelength, k is the dimensionless number equal to 0.9, θ is the Bragg diffraction angle and β is the full width at half maximum (FWHM) respectively. The crystallite size of the NiO films for (200) plane increases from 17.86 nm to 22.47 nm as the solution concentration increases from 0.1 M to 0.3 M.

3.2 Optical Properties

The optical transmittance curves as a function of wavelength at different solution concentrations were plotted in Fig. 2. The optical transmittance spectra of the NiO films were recorded in the wavelength range of 200-2400 nm. The optical transmittance decreases when the solution concentration increases from 0.1 M to 0.3 M. The optical band gap is calculated by using the following equation [6]:

$$\alpha h v = A(hv - E_g)^n \qquad (3)$$

where α is the absorption coefficient, A is an energy-independent constant, E_g is the band gap energy, h is Planck's constant, ν is the frequency of the incident photon and n is a number equal to 1/2 for direct band gap and 2 for indirect band gap compound.

Fig. 3 indicates the direct band gap transition in the films from the plot of $(\alpha h v)^2$ versus (hv) for the NiO films. On extrapolating the linear plot of the $(\alpha h v)^2$ versus photon energy (hv) on the x-axis at $(\alpha h v)^2 = 0$, the value of band gap is obtained. The direct band gap energy for the NiO film decreases from 3.94 eV to 3.71 eV as the solution concentration varies from 0.1 M to 0.3 M. The values are in agreement with theoretical values.
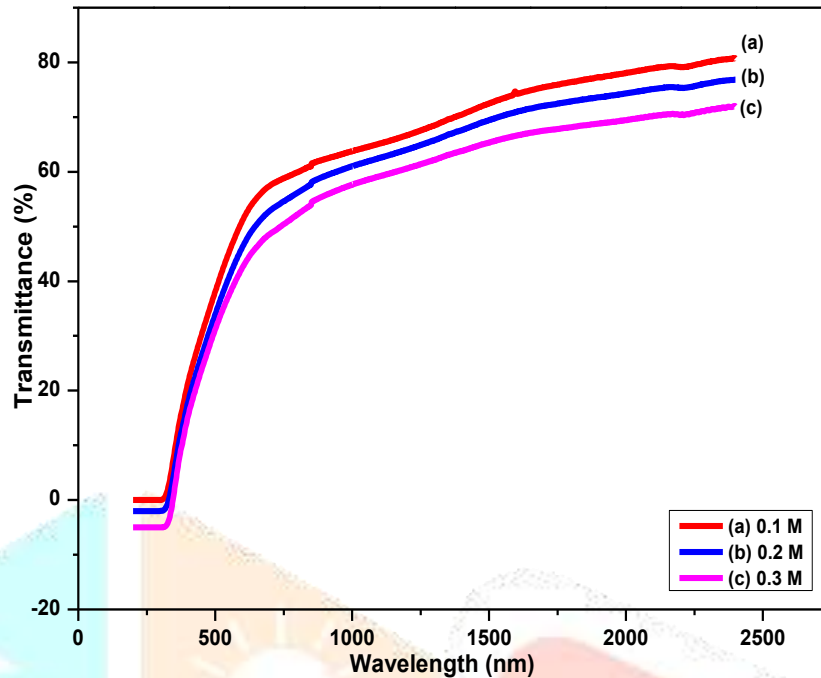
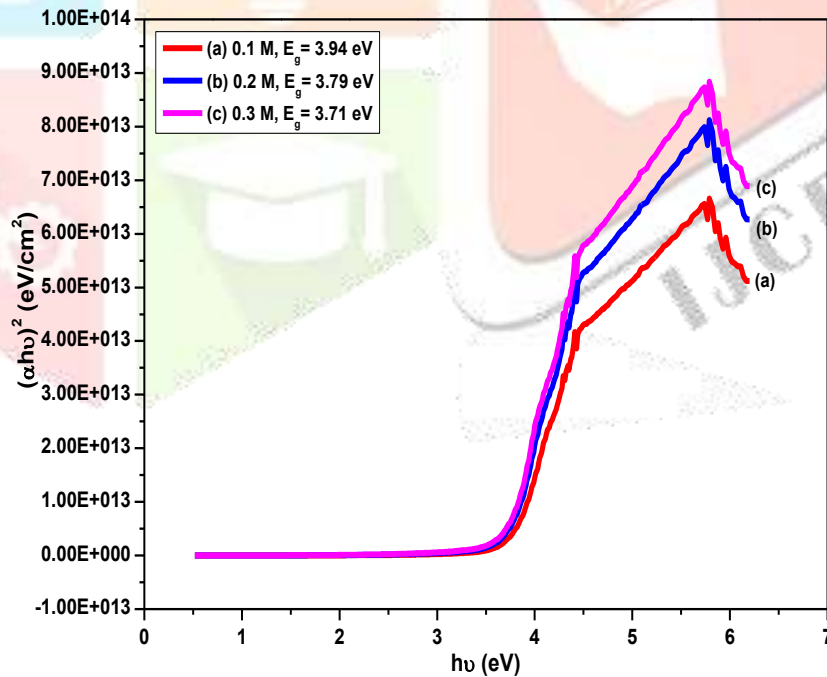FIG.2 TRANSMITTANCE SPECTRA OF NIO FILMS

FIG.3 OPTICAL BAND GAP OF NIO FILMS

3.3 Photoluminescence Properties

The photoluminescence (PL) emission spectra at room temperature of NiO thin films deposited at different solution concentrations were shown in Fig.4. The energy band gap from photoluminescence spectra of the NiO film is calculated by using the following equation [7]:

$$E_g = \frac{1240}{\lambda \, (nm)} \tag{4}$$

The role of surface and native defects has been invoked to explain the observed PL behavior. The PL emission spectrum consist of two emission peaks. For the emission peaks 365 nm and 467 nm the energy band gaps are found to be 3.40 eV and 2.66 eV respectively. A strong PL emission peak found at 365 nm is attributed to the electronic transitions of Ni^{2+} and O^{2-} ions. The second emission peak at 467 nm might be attributed to oxygen related defects.
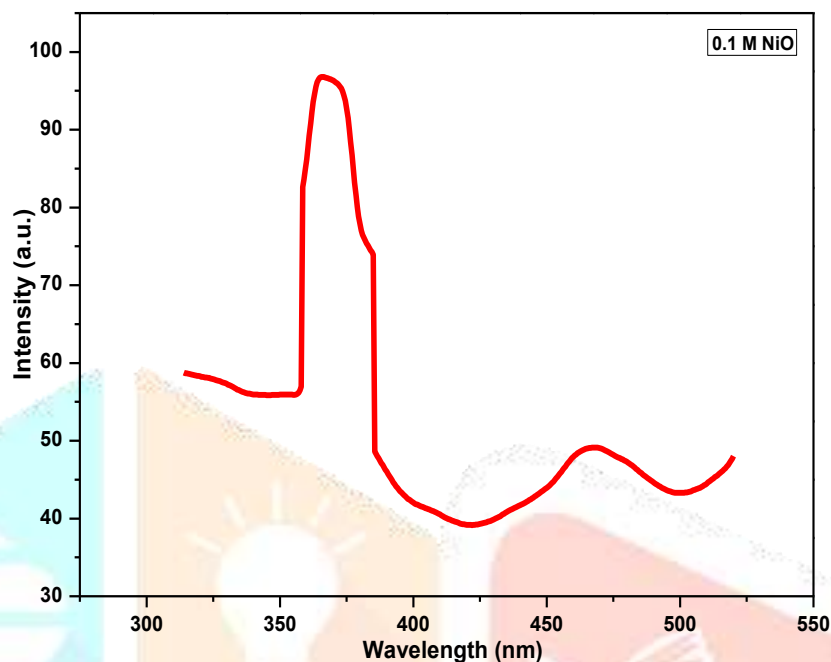

FIG.4 PHOTOLUMINESCENCE SPECTRA OF NIO FILM

3.4 Electrical Properties

The charge carrier p-type and the resistivity of the NiO films were measured with the help of Hall effect measurement system. Hot probe technique confirmed that all the films were p-type. Fig. 5 shows the resistivity and conductivity of NiO films for different solution concentrations. The resistivity of the NiO film increases from 3.20×10^2 Ω cm to 7.84×10^2 Ω cm as the solution concentration increases from 0.1 M to 0.3 M. As the electrical conductivity is inverse of resistivity, the electrical conductivity decreases with solution concentration. Low electrical resistivity in our nickel oxide thin film may be due to formation of non-stoichiometric film with excess oxygen or less oxygen.
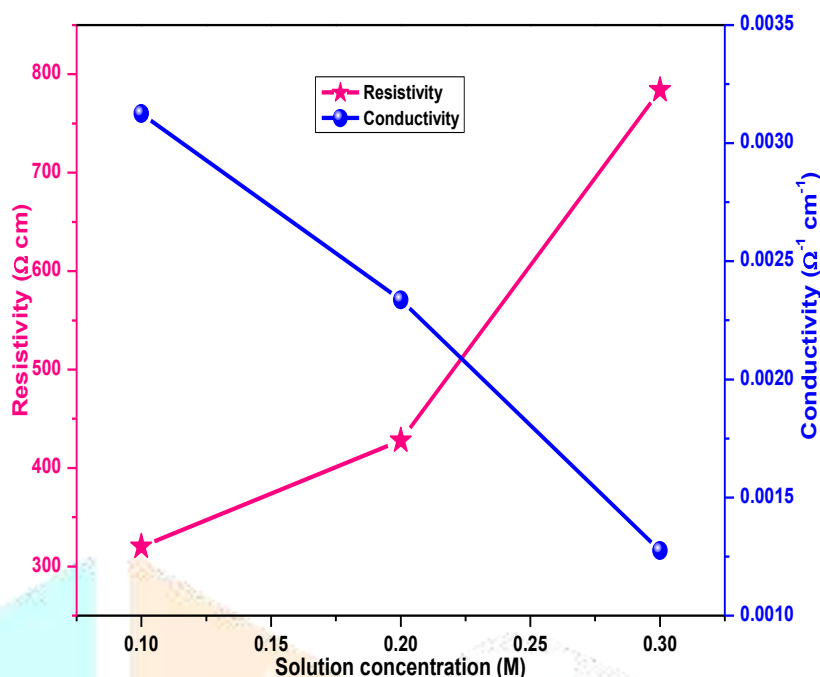
FIG.5 RESISTIVITY AND CONDUCTIVITY OF NIO FILMS

IV. CONCLUSION

NiO films have been deposited on glass substrates by spray pyrolysis technique using $NiCl_2.6H_2O$ and distilled water. The properties of the NiO films depend strongly on the solution concentration. The XRD study shows that the NiO films were polycrystalline with cubic structure and a preferred orientation along (200) plane. The crystallite size of the NiO films lies between 17.86 nm to 22.47 nm with the increase in solution concentration from 0.1 M to 0.3 M. The optical study shows that the transmittance decreases and the band gap varies from 3.94 eV to 3.71 eV as the solution concentration increases. Photoluminescence investigation reveals that the NiO show strong emission peak at 365 nm. The electrical study shows that all the NiO films were p-type and the conductivity of the NiO films depend on the solution concentration. The p-type conduction of NiO films are the main properties for its application as TCO in optoelectronic devices as well as in solar cells.

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