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STRUCTURAL AND OPTICAL PROPERTIES OF NANOCRYSTALLINE NICKEL OXIDE THIN FILM BY SPRAY PYROLYSIS TECHNIQUE

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Abstract— **It is necessary to study the optical properties of thin films to fabricate optoelectronic and interference devices. One of the methods in thin film preparation is the spray pyrolysis technique, which involves many technical aspects for the preparation of uniform coating. In the present study, Nickel Oxide (NiO) thin film is prepared by spray pyrolysis technique. NiO thin film was deposited using 0.5M aqueous solution of nickel chloride onto ultrasonically cleaned glass substrate at Tsub = 350ºC. The film is more homogeneous and there is no pinhole. The structural and optical properties of the sample were examined by X-Ray Diffraction (XRD), UV-Visible and Photoluminescence (PL) spectral analysis. XRD study revealed that the film exhibited (1 1 1) orientation with cubic structure. The thickness of NiO film was 0.16 µm and the calculated grain size was 51 nm. UV – Visible spectral study of the film exhibit high optical transmittance in the visible region and the film possess direct band gap value of 3.5 eV. The reflectance and refractive index are also calculated from the optical measurements. The room temperature excitation PL spectrum of NiO thin film shows a strong dominant peak at 362 nm. These results suggest that this NiO thin film can be used as an anti-reflection coating in solar cells.**

Keywords – Nickel Oxide Thin Film, Spray pyrolysis technique, XRD, UV – Visible and PL.

I. INTRODUCTION

Solar cells have in last decades established their importance as an eco-friendly, sustainable energy source. Although encouraging progress has been made in recent years, thin film based solar cells have attracted great research interest.

Transition metal oxides like, SnO_2, ZnO, CdO, NiO *etc* has a wide band gap of around 3 to 4 eV. Among these thin films, nickel oxide (NiO) is an attractive material because of its chemical stability as well as structural, optical, electrical and magnetic properties. Nickel oxide thin film is a *p*-type semiconducting material with wide band gap of 3.6 - 4 eV, and has cubic rock salt like crystal structure [1, 2]. Nickel oxides have been used in different applications like positive electrode in batteries [3], fuel cell [4], solar thermal absorber [5], gas sensors [6], photodetectors [7] and electrochromic devices [8,9]. Nickel oxide (NiO) is a selective AR coating material due to its suitable optical properties. The optical constants of NiO thin films provide us with information concerning with microscopic characteristics of the material.

Out of number of techniques such as chemical vapor deposition [10], pulsed laser deposition [11], sputtering [12], chemical bath deposition [12,13] and sol-gel technique [14], the spray pyrolyis is one through which the films of very thin layers of uniform thickness [15] can be coated on large area.

In the present work, the NiO thin film was prepared by a spray pyrolysis method which was annealed at 500ºC. The structural and optical properties of the prepared NiO thin film was characterized by X-Ray diffraction (XRD), UV-Visible and Photoluminescence (PL) spectral studies.

II. EXPERIMENTAL DETAILS

Nickel Oxide thin films are deposited from 0.5M aqueous solution of nickel chloride ($NiCl_2.6H_2O$) by a spray pyrolysis technique onto chemically and ultrasonically well cleaned glass substrate. Substrate cleaning has an important role in the film deposition. The glass slides were boiled in chromic acid for 1 hour, washed with detergent, rinsed in acetone and dried in open air. This process of cleaning is to ensure a clean surface, which is necessary for the formation of nucleation centers, required for film deposition. During the film deposition, the substrate temperature (T_{Sub}) was maintained at 350ºC and the other coating conditions such as spray rate 1ml/min, substrate to nozzle distance 18 cm, spraying time 1 min and the carrier gas (filtered compressed air) at a pressure of 1 bar were maintained. The film was allowed to cool slowly to room temperature and finally it was annealed at 500°C for 1 hour in a muffle furnace.

The spray coated NiO films were subjected to X-Ray Diffraction (XRD), UV-Visible and Photoluminescence (PL) spectral analysis. The structural properties of the NiO films were examined using X'PERT PRO X-ray diffractometer which was operated at 40 KV and 30 mA. The Optical properties of the films were examined by SCHIMADZU 1800 UV – Visible spectrophotometer in the range of 200 to 1100 nm wavelength. The room temperature photoluminescence (PL) spectrum of the prepared film was recoded using a Varian Cary Eclipse Fluorescence Spectrophotometer. The optical reflectance of the prepared film was recorded over the wavelength range from 200 to 1000 nm using, Semiconsoft Mprobe Visible Spectroscopic Reflectometer. A laboratory developed computer program was used to calculate the thickness, reflectance, refractive index and dielectric constant of the prepared film.

III. RESULT AND DISCUSSION

A. *Structural Analysis*

The XRD pattern of the prepared NiO film annealed at 500°C was shown in Figure 1. It shows two dominant peaks at 2θ = 31.74° 37.27° which are assigned to (3 1 1) and (1 1 1) crystal planes and less intense peaks at and 43.32°, 62.93° and 79.45° which are assigned to (2 0 0), (2 2 0) and (2 2 2) crystal planes respectively. All these diffraction peaks can be perfectly indexed to cubic crystalline structure. The obtained XRD pattern is in excellent agreement with standard JCPDS (File No 78-0643). The strong peak intensity indicates the high degree of crystalinity of the phase

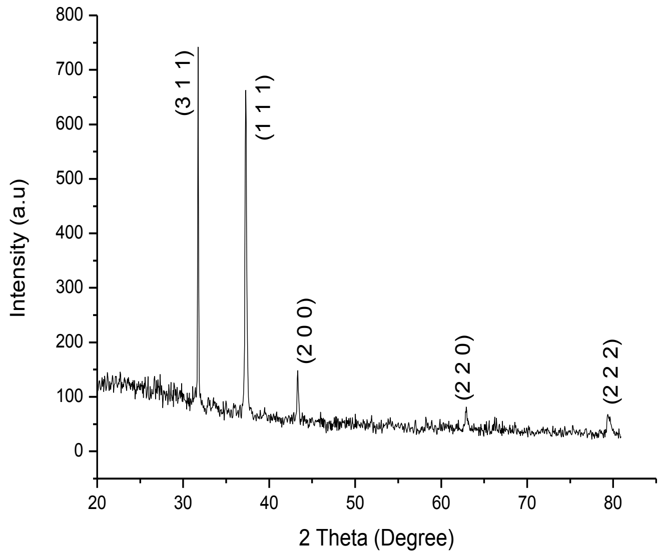

Fig. 1. XRD pattern of NiO thin film annealed at 500° C

The crystallite size was calculated using Debye – Scherrer formula and the values are shown in Table 1.

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (1)$$

where D - crystallite size, k - 0.94, λ – wavelength of X-ray, θ -Angle of diffraction and β - Full Width at Half Maximum. The calculated average crystallite size was 51nm.

The dislocation density (δ) of the NiO films was estimated using (2) as 0.038 x 10^{16} lines/m^2, where D is the crystallite size.

$$\delta = \frac{1}{D^2} \quad (2)$$

The strain in the films is related to lattice misfit, which depends on the deposition conditions. The micro strain (μ) produced in the spray coated NiO thin film was calculated using (3), [16]

$$\mu = \frac{\beta \cos\theta}{4} \quad (3)$$

The calculated micro strain of the prepared NiO thin film was 0.0405.

The estimated crystallite size, dislocation density, micro strain and lattice constant of the NiO thin film annealed at 500° C are given in Table 1.

TABLE 1: STRUCTURAL & OPTICAL PARAMETERS OF NiO THIN FILMS

Crystallite Size (*D*)	51 nm
Dislocation Density (δ)	0.038 x10^{16} lines/m^2
Strain (μ)	0.0405
Thickness	161 nm
Refractive index (n) at 550nm	1.871
Dielectric Constant (ε) at 550nm	3.49
Transmittance (T) at 550nm	83%
Reflectance (R) at 550nm	7%
Direct Band Gap (E_g)	3.25 eV

B. Optical Analysis

Figure 2 shows the UV –Visible transmittance spectra of the prepared NiO thin film annealed at 500°C.

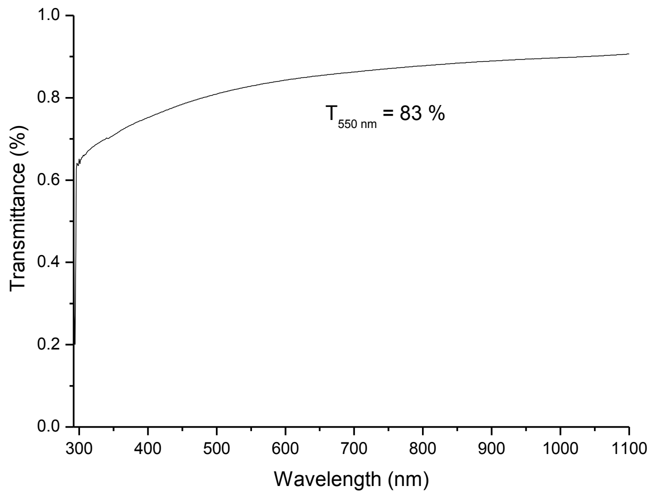

Fig. 2. Transmittance spectra of NiO thin film annealed at 500^0 C

The transmittance of the film was found to be 83% at 550 nm. The obtained high transmittance may be attributed to perfection and the stoichiometry of better optical quality NiO film.

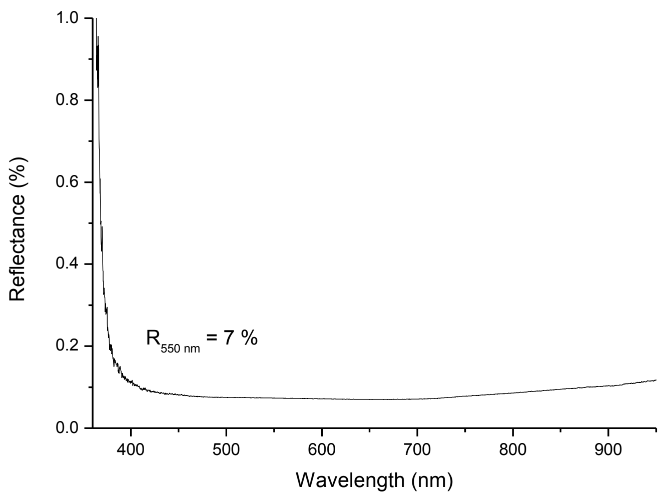

Fig. 3. Reflectance spectra of NiO thin film annealed at 500^0 C

The reflectance of the film was measured to be 7% at 550 nm. The obtained low reflectance of the film prepared suggests that could be used as an anti-reflection coating material in solar cells.

The refractive index of the prepared NiO film was measured as 1.871, which is one of the fundamental properties for an optical material as it is closely related to the electronic polarization of ions and the local field inside the material.

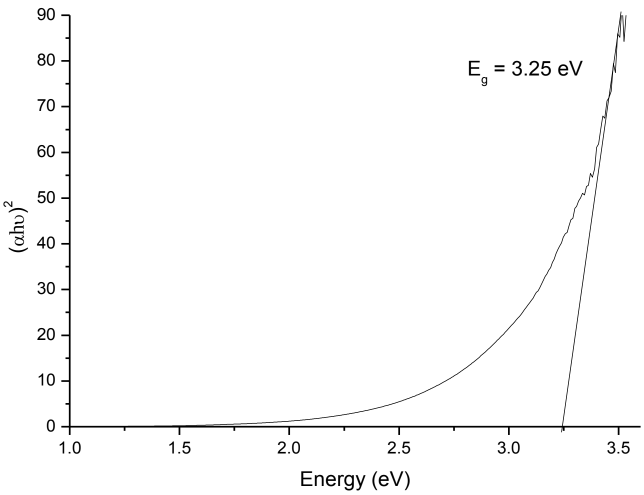

Fig. 4. Direct energy gap (E_g) of NiO thin film annealed at 500°C

The direct band gap (E_g) can be calculated from the plot made between $(\alpha h\nu)^2$ and photon energy ($h\nu$) which is shown as Figure 4. The relation between absorption coefficient and photon energy is given by the relation,

$$\alpha h\nu = A(h\nu - E_g)^n \quad (5)$$

where h is the Planck constant, ν is the frequency of radiation, E_g is the energy gap and n is a constant which represents the nature of transition. The value of n is ½ and 2 respectively, for allowed direct and indirect transitions. The calculated optical direct band gap energy of the prepared NiO thin film was found to be 3.25 eV.which is in good agreement with the reported band gap values of 3.15-3.80 eV for NiO films [17].

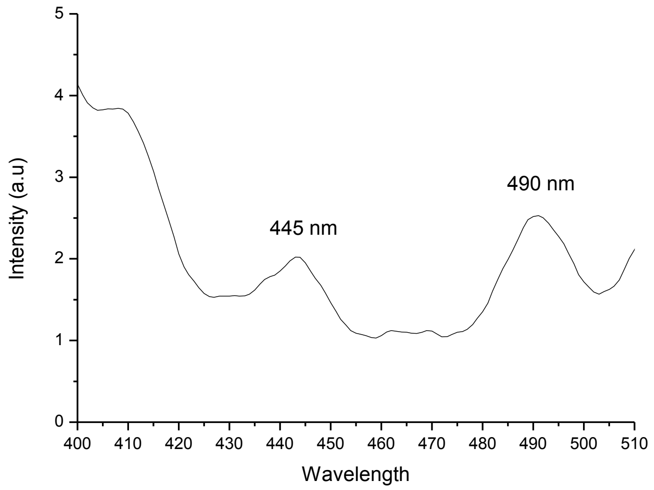

Fig. 5. PL emission spectra of NiO thin film annealed at 500ºC

PL spectrum was recorded at room temperature with an excitation wavelength of 325 nm. Figure 5 shows the photoluminescence (PL) emission spectra of the NiO thin film. The role of surface and native defects has been invoked to explain the observed PL behavior. The PL emission spectrum is found to exhibit two emission peaks centered at 445 nm and 490 nm with the energy band gap of 2.78 eV and 2.53 eV respectively. The origin of the strong peak at 490 nm was attributed to the electronic transitions of Ni^{2+} and O^{2-} ions. The shoulder emission peak at 445 nm might be attributed to oxygen related defects. Similar results have been reported by Wang et al., [18].

IV. CONCLUSION

NiO thin film was successfully coated on the glass substrate by using advanced spray coating technique. The structural and optical properties of the prepared film were analyzed. The XRD analysis revealed that the film exhibited cubic structure. The transmittance and reflectance of the NiO films was 83% and 7% at 550 nm wavelength respectively. The direct band gap derived from Tauc's plot was 3.2 eV. The room temperature PL spectrum of the NiO thin film was observed in the visible region and it originates from electronic transition of Ni^{2+} and O^{2-}ions. These structural and optical study results suggest that the *p*-type NiO thin film coated by advanced spray pyrolysis technique is more suitable for anti-reflection coating in solar cell.

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