Structural, Optical and photoluminescence Properties of Nanocrystalline NiO Thin Films

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Abstract

Thermal chemical spray pyrolysis technique has been successfully employed for deposition of nanocrystalline nickel oxide (NiO) thin films from hydrated nickel chloride salt solution on the glass substrate at temperature 450°C. The structural properties of nickel oxide films were studied by means of X-ray diffraction (XRD) and scanning Probe Microscope (SPM). XRD analysis shows that the film is polycrystalline nature with cubic structure along (111) orientation centered at $37.23°$. The crystallite size was evaluated to be 21.63 nm by using Scherrer's equation. The morphology and crystallite size was evaluated by using Atomic Force Microscope (AFM) images showed spherical shape particles on the surface are inhomogeneous and very smooth on the nanometer scale. The optical absorption spectra were taken to determine the band gap 3.8 eV, increase in band gap energy is revealed that nanostructure films. The photoluminescence spectrum of these samples were an excited at wavelength 250 nm and consist of the emissions band located at 240 nm, 370 nm, and 492 nm.

Keywords:

Nickel Oxide; Spray Pyrolysis; photoluminescence; Nanostructure.

1. Introduction

Nickel oxide (NiO) is a semitransparent p-type semiconducting material with band gap of about 3.8 eV [1]. It shows attractive material due to its excellent chemical stability, good dynamic range, durability, as well as optical, electrical and magnetic properties [2]. Other important application of nickel oxide in large scale optical switching glazing, anti-ferromagnetic material, electrochromic display devices, lithium ion batteries and functional layer material for gas chemical sensors [3]. Furthermore, (111) – oriented NiO films can be used as buffer layers that are deposited on oxide films with other orientations, such as c-axis –oriented perovskite-type ferromagnetic films and superconducting films. NiO thin films are grown using many different chemical and physical methods such as electrochemical deposition [4], thermal evaporation [5], Ion beam sputtering deposition [6], laser ablation [7], spray pyrolysis [8], and Sol-gel spin coating [9]. NiO exhibits fcc structure, it is a prototype p-type transparent conducting oxide due to vacancy at Ni^{+2} sites [10]. The color change from green to light black in NiO is due to the excess of oxygen in it produces Ni vacancies in NiO. For the charge neutrality of the Ni^{+2} converted to Ni^{+3}, which are responsible for color. It has also been found that NiO thin film is nearly transparent, wide band-gap semiconductor, and nonstoichiometry which shows p-type semiconductor conducting behavior. The present paper focuses on use of aqueous solution of nickel chloride to synthesis of nanocrystalline NiO thin films on glass substrates by spray pyrolysis technique, and their structural, optical and Photoluminescence properties studies.

2. Experimental Details

Nanocrystalline nickel oxide thin films were deposited using chemical spray pyrolysis technique. A 0.1 M precursor solution was prepared by dissolving Nickel chloride ($NiCL_2 .6H_2O$), 98% purity in 100 ml distilled water. The films were deposited onto the pre-heated glass substrates kept at (450°C). The glass substrates slides of ($1\times 25 \times 75$ mm^3 dimensions), were cleaned in acetone solutions in an ultrasonic bath for 20 minutes and rinsed in distilled water and dried in high air stream. This process is to ensure a clean surface, which is necessary for formation of nucleation center, required for film deposition. A spray time for 4 sec and an interval time for 25 sec to keep the substrate temperature constant, as the deposition temperature is an important parameter which influences the properties of the coated film [11]. The spray rate was kept constant at 6 ml/min. The overall reaction process can be expressed as heat decomposition of nickel chloride to clusters of nickel oxides in the presence of water and air oxygen. The deposited films may have disordered Ni(OH)$_2$ structure or nano-crystalline NiO structure according to the following reaction [12] :

$$NiCl_2 + 2H_2O \rightarrow 2HCl + Ni(OH)_2 \tag{1}$$

$$NiCl_2 + 2H_2O \rightarrow 2HCl + NiO + H_2O \tag{2}$$
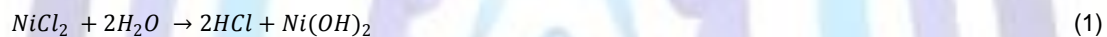
Optical interferometer method is used for measuring the thickness of the film by employing He –Ne laser (0.632 µm) wavelength with incident angle 45^0. The X-ray diffractometer (6000-Shimadzu) using CuKα radiation with a wavelength, λ=1.54060 Å was used for structural studies in the range of 2θ =$10 - 60^°$. The surface morphological of the films were studied by using scanning Probe Microscope (SPM , model AA3000 Angstrom Advanced .Inc). The optical absorbance of the films was measured using UV-visible spectrophotometer (SP-3000 Optima) in the wavelength range 200-1200 nm at room temperature. Photoluminescence of the NiO films was measured at an excitation wavelength of 250 nm by using Spectra Fluorometer (SFM- SL 174, Elico).

3. Result and Discussion

The nickel oxide thin films were analyzed by X-ray diffraction technique to study structural identification and changes in the crystalline. The XRD pattern of the NiO thin films (160 nm thick) were deposited on glass substrates heated to (450°C) is shown in figure 1. The film was identified to be polycrystalline nature with cubic structure along (111) orientation centered at $37.23^°$ according to the (JCPDS card no 36-1451) [13]. The existence of (111) planes oriented horizontally with respect to the substrate surface. The NiO (111) planes grown at a substrate temperature of 600 ℃ was almost similar to the bulk NiO. This means that compressive stress was applied to the perpendicular direction of the (111) planes of the films fabricated at a relatively low substrate temperature ($\leq 400℃$), and this stress was almost relieved under a higher substrate temperature [14]. The substrate temperature controls the mobility of the deposited atoms. As substrate temperature increases, the adsorbed atoms gain extrothermal energy and move to another preferred plane. Disappearance of (200) plane is due to increasing concentration of lattice imperfection coming from the internal microstrain within film [15]. It has been found that the development of preferred orientation in NiO film is primarily governed by surface energy. NiO film texture depends on both the oxygen content in the film and the deposition temperature. The crystal orientation of the film is controlled by nucleation and growth of the grains. The crystallographic orientations of NiO films are affected by the arrangement of O^{2-} under oxygen atmosphere and substrate temperature. The radius of O^{2-} (0.140 nm) is larger than that of Ni^{2+} (0.069 nm). In order to minimize the surface energy of the growing NiO film O^{2-} must be arranged in the most densely packed plane (111) under low ratio of oxygen at a high substrate temperature [3]. NiO films with (200) or (111) preferred orientations, are good candidates for the buffer layers of oriented oxide films, such as c-axis-oriented perovskite-type ferromagnetic films, and (111)-oriented spinel- type ferromagnetic films. This is because they are chemically stable, similar in symmetry to the oxygen ion lattice, and their lattice constants are between those of the NiO films and the oriented oxide films. Therefore, NiO film with a preferred crystallographic orientation is important when it is used as a buffer layer. The dependence of crystallinity on substrate temperature can be explained as follows. During the deposition process, atoms travel some distance before they impact on the sample surface to form the deposited film. At higher substrate temperatures, the extra thermal energy provided by the substrate to the atoms is used by the latter to reach equilibrium positions. Therefore, there is greater probability of

forming a more perfect crystalline structure at higher substrate temperatures [16].The grain size (D) of the crystallites was calculated for major reflex (111) using the Scherrer's formula [17].

$$D = \frac{K\,\lambda}{\beta\,cos\,\theta}$$

(3)

Where K= 0.94, $\lambda = 0.154\,nm$ is the wavelength of the X-Ray radiation used, θ is the Bragg diffraction angle of the XRD peak and β is the intrinsic full width at Half Maximum of the peak at an angle of 2θ. The grain size was found 21.63 nm, a small grain size implies a large surface to bulk ratio which may be important to enhance electrochromic performance [12].
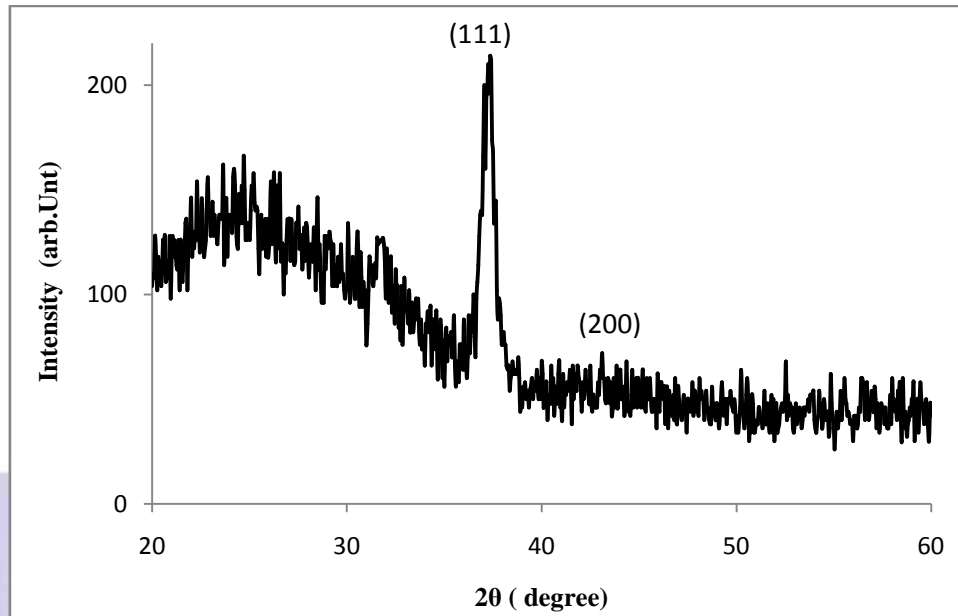
Fig 1: XRD patterns of NiO thin films (thickness=160 nm) deposited at temperature 450 °C on glass substrate.

Figure 2. Shows the morphological investigation of NiO film deposited on glass substrate at 450 ℃ by using atomic force microscope (AFM). Typical 2D and 3D AFM images showed spherical shape particles on the surface are inhomogeneous and very smooth on the nanometer scale. It is observed that the film consists of nanocrystalline grains with non uniform coverage of the substrate surface with randomly oriented morphology and average grain size is 75.60 nm. The increase of the crystallite size may be caused by columnar grain growth in the structure [15]. The root mean square (rms) roughness of the film surface is 0.212 nm indicating that the surface of spray deposited NiO thin film is very smooth. The grain size of the film can also be deduced from the AFM micrograph and distribution of grain size value is observed between a minimum of about 20 nm and a maximum of about 140 nm as illustrated in figure 3. The average grain size 75.60 nm is found to be larger than the grain size calculated from XRD data. This may be due to the aggregation of smaller grains which from bigger clusters on the surface of the films. On the background of a nanaocrystalline NiO structure the agglomeration of nanaoparticles tends to form circle shape closed clusters with the diameter of several tens of nanometers [18]. Small grains that are partially bonded into clusters. Straight grain boundaries separating individual grains are characteristic for phases crystallizing in face-centered cubic structure of NiO.
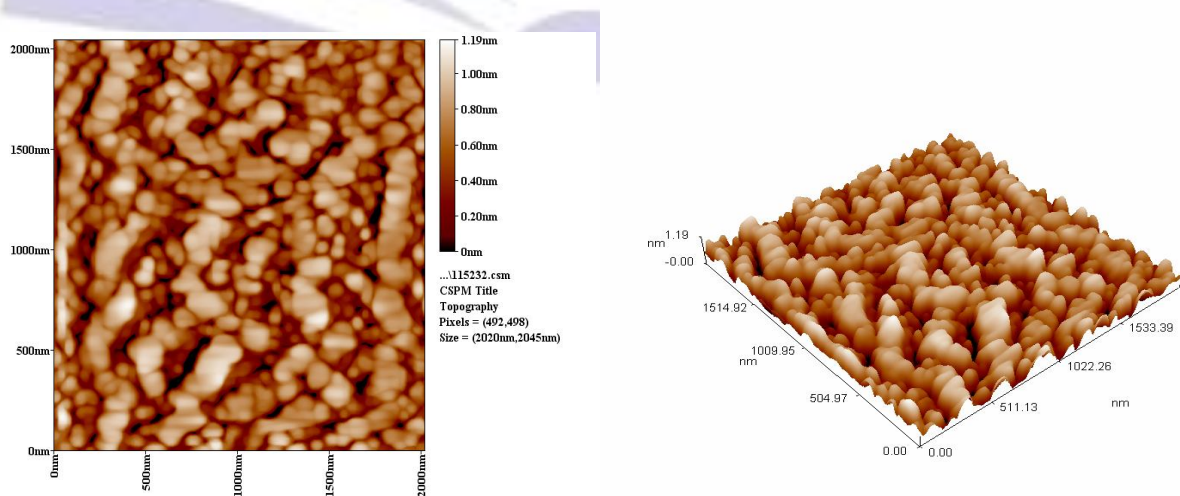
Fig 2: AFM surface morphology of NiO film (scan area 2 x 2 μm^2) deposited on glass substrate at 450℃ .

Figure 4. Shows the optical transmission spectra of nickel oxide films deposited at 450 ℃ on the glass substrate at wavelength range of 250 to 1000 nm. It is clear that film demonstrate more than 83% transmittance at the visible range. Below 400 nm there is a sharp fall in the T% of the films, which is due to the strong absorbance of the film in this region. The lower transmittance is associated with an excess of oxygen in the lattice which creates Ni^{3+} ions and appears the color centers. A large transmittance values at elevated substrate temperature due to improving crystalline microstructure of the film and leads to less defect scattering Ni^{3+} [2].
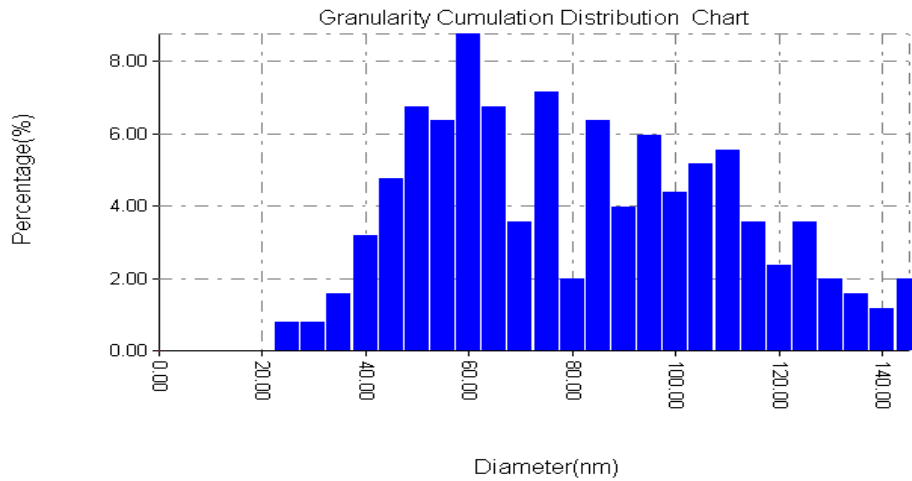
**Fig 3: Granularity distribution of nanostructure NiO thin films deposited at 450 ℃ .**

Nickel oxide is a high band gap semiconductor with the absorption edge in the UV region and no absorption in the visible region. The presence of Ni^{3+} ions in the oxide lattice shows charge transfer transition, with the consequent absorption in the visible region [8]. The optical energy bandgap E_g of the films were derived assuming a direct transition between the edges of the valence and the conduction band, using the tauc's relationship as follows [19].

$$\alpha = A \left(h\nu - E_g \right)^n \tag{4}$$

Where α is the absorption coefficient, A is a constant, hν the photon energy E_g the band gap, $n = 1/2$ for the direct transitions. Figure .5 shows plot of $(\alpha h\nu)^2$ versus photon energy (hν) for NiO film. An extrapolation of the linear part of the above plot $(\alpha h\nu)^2 = 0$ gives the energy gap value of the film, which was found to be about (3.8 eV), and is attributed to charge transfer transition between the valence bands of O (p) states to conduction bands of Ni (d) states, which is in good agreement with Anandan and Rajendran [20]. The large value of band gap of the NiO film is due to quantum size effect [15]. Quantum size effect is expected to influence the energy band diagram of NiO. The energy band gap E_g for spherical particle of radius R is given by [20].

$$E_g = E_{g1} + \frac{h^2 \pi^2}{8 \mu R^2} \tag{5}$$

Where E_{g1} is bulk energy band gap, μ is the reduce mass of the carrier (electron or hole). The degree of confinement increases with decrease in the particle size and cause increase in the energy band gap value.
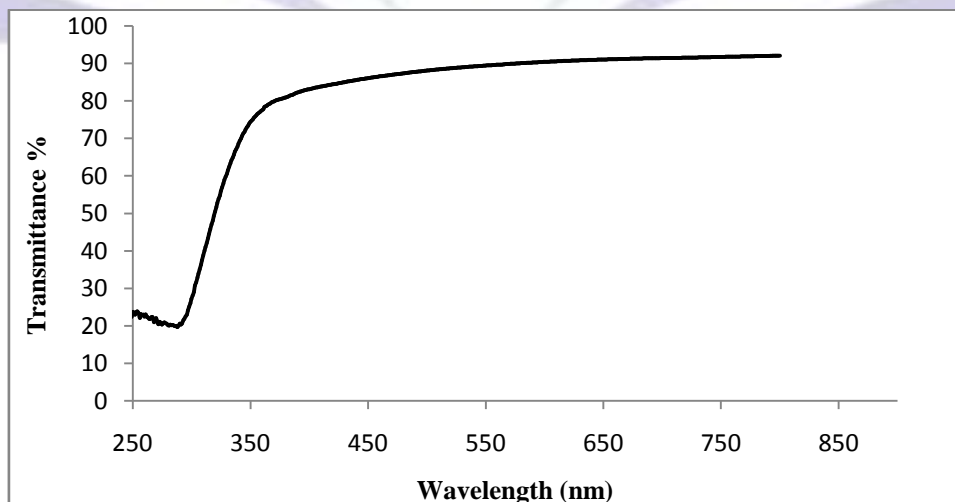
Fig 4: Optical transmittance versus wavelength of NiO thin film deposited at 450 ℃ .
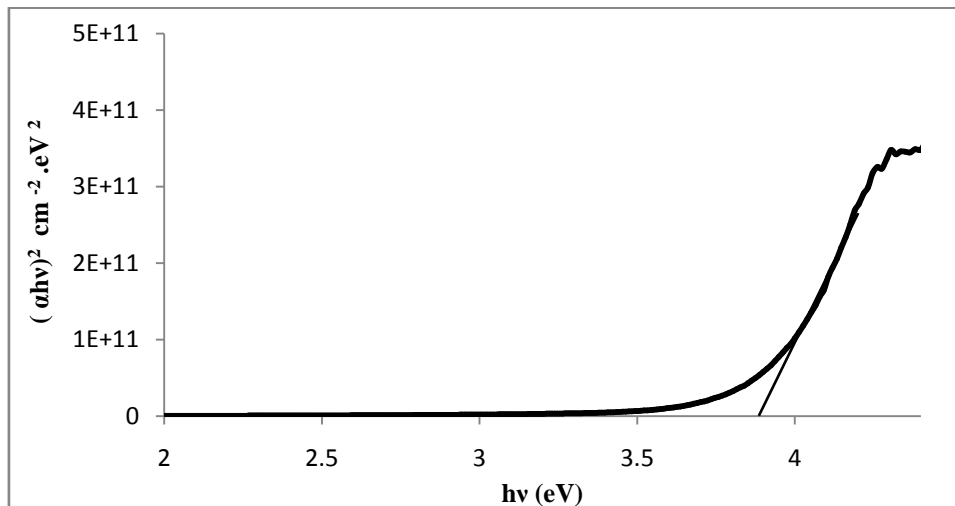
Fig 5: Plot of $(\alpha h\nu)^2$ versus hv for as deposited NiO thin film at 450℃.

The analytical dispersion equation for thin films on glass substrate was used to determine the wavelength dependent refractive index [21].

$$n^2(\lambda) = N^2 \left[a + \frac{b}{\lambda^2} + \frac{c}{\lambda^4} \right] \qquad (6)$$

Where a, b and c are constant to be determined from the refractive indices calculated from the transmittance spectra for first, second ,and third order minima, respectively. The refractive index (n) was calculated by using the following relationship [11].

$$n = \left(\frac{1+R}{1-R} \right) + \sqrt{ \left(\frac{4R}{1-R} - k^2 \right) } \qquad (7)$$

figure 6. shows the variation of refractive index with wavelength for a range 300 nm to 1000 nm. The refractive index of the film remains almost equal through the visible region with value of 1.7, which is slightly lesser value from (Sriram & Thayumanavan) [22]. The strong dependence of the refractive index values on the reflectance values as above equation, where the refractive index increases rapidly at low energies and then reach to peak value at the energies which is corresponding to energy gap of the film. Then refractive index decreases at photon energy which is larger than the energy band gap because of the increasing the direct electronic transition at that energies. From the calculate absorption (α) values the extinction coefficient of the films were calculated by using the following formula [22].

$$k = \frac{\alpha \lambda}{4\pi} \qquad (8)$$

The variation of extinction coefficient as a function of wavelength is shown in figure 7. It is clear that extinction coefficient decreases rapidly with increasing wavelength from 300 nm to 400 nm and after that the value of (k) remains constant. The rise and fall in the extinction coefficient is directly related to the absorption of light. The lower value of (k) in the visible wavelength implies that these films absorb light very easily. In the case of polycrystalline films extra absorption of light occurs at the grain boundaries [23]. This leads non –zero value of extinction coefficient for photo energies smaller than the fundamental absorption edge.
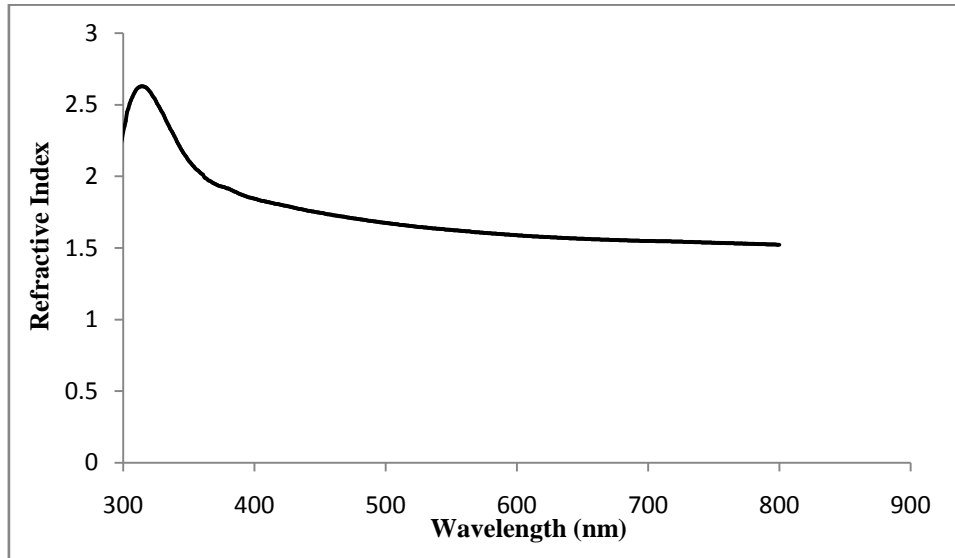
**Fig 6: Refractive index (n) versus wavelength of the NiO thin films.**
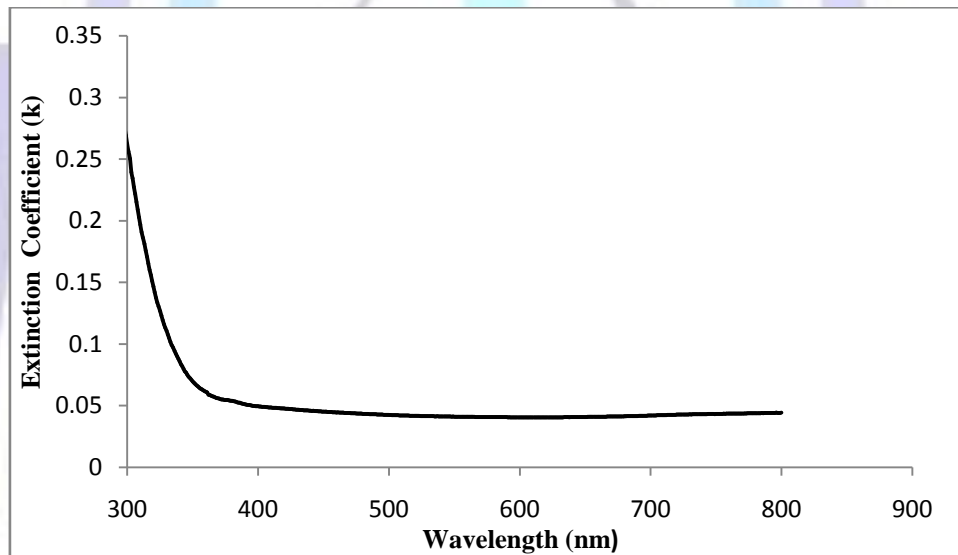
Fig 7: Extinction coefficient (k) versus wavelength of NiO thin films.

Photoluminescence is very sensitive to the quality of crystal structure and to the presence of defects. The band to band excitation of NiO promotes electrons from valence band to the conduction band, leaving holes in the valence band. The holes migrate from the valence band to deep levels and recombination occurs between electrons from either the conduction band or shallow donor levels and trapped holes on deep levels [24]. In NiO the existence of several transitions at energies below band gap, the photoluminescence was attributed to transitions involving $3d^8$ electrons of the Ni^{3+} ions. For the clusters of NiO, the photoluminescence spectra are broad and lightly dependent with its maximum on the excitation wavelength [25]. PL emission spectrum was done for as prepared NiO thin films electrochromic films (transparent bleach state) deposited on glass substrate is shown in figure 8. UV excitation wavelength ($\lambda_{ext} = 250\, nm$) was used to excite the electrons from the material valence band. A widening for the PL broad peak with maximum intensity at about $= 370\, nm$, this strong peak is clearly related to the electronics transition of the Ni^{2+}. The band gap for layer is estimated to have value of 3.35 eV is calculated by using the following equation [26].

$$E_g = \frac{1240}{\lambda(nm)}$$
(9)

 Adler and Feinleib [20] reported a series of absorption peaks below 4 eV as purely intraionic $3d^8$-$3d^8$ transition of Ni^{2+}. Other peak is also observed at wavelength of about 492 nm (2.52 eV). It may correspond to inter band transitions surface energy states due to defects such as oxygen vacancies, Ni interstitial or other impurities in addition to incomplete bonding. The blue emission (2.52 eV) can be ascribe to the direct recombination of conduction electron in the Ni_{3d} band and a hole in the O_{2p} valance band . This emission have originated from the transition due to the oxygen antisite vacancy defect O_{Ni} [27]. The third peak emission is appear at 240 nm (5.2 eV) p-d charge transfer transition in NiO center is related with the

transfer of O 2p electron to the partially filled $3d_{eg}$ subshell with formation on the Ni-site of the configuration of nominal Ni^+ ion isoelectronic. These mechanism are related to p (π) - d and d (e_g) – d (e_g) charge transfer transition [28].
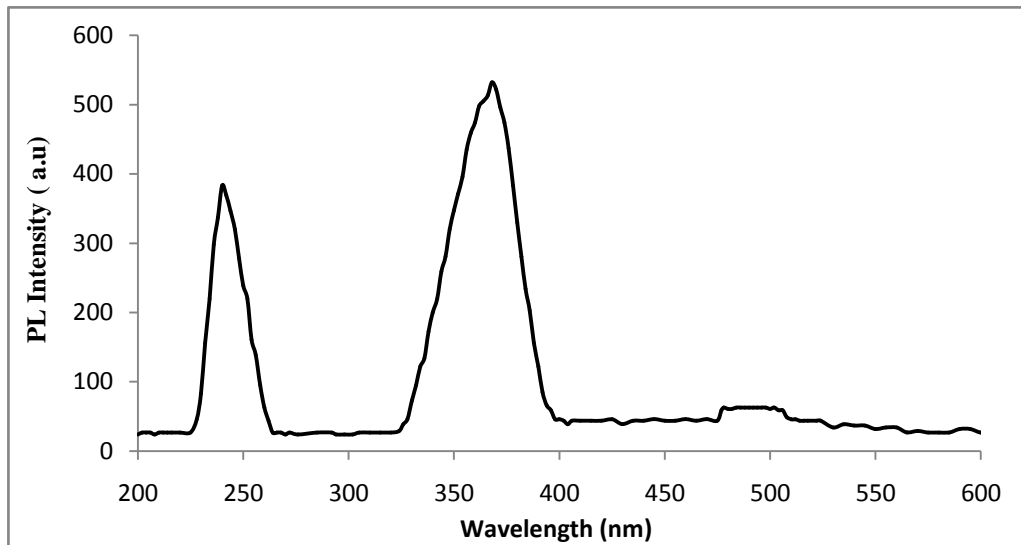
Fig 8: Photoluminescence Spectrum of the NiO thin films on glass substrate.

4. Conclusion

Nickel oxide thin films have been prepared onto glass substrate kept at 450℃ by employing an inexpensive simplified spray technique. XRD studies shows that the film is polycrystalline in nature with cubic structure having preferential orientation along the (111) plane. AFM images showed nano sized grains (75.60 nm) with very smooth surface of the film. Optical absorption studies showed that film has transmittance more than 83% at wavelength range of 250 to 1000 nm. The band gap values obtained from the absorption spectra was found to be 3·8 eV. The PL spectra consist of three emissions band located at $370\ nm$, this strong peak is clearly related to the electronics transition of the Ni^{2+}. The second peak is observed at wavelength of about 492 nm, it may correspond to inter band transitions surface energy states due to defects such as oxygen vacancies, Ni interstitial. The third peak emission is appear at 240 nm (5.2 eV) p-d charge transfer transition in NiO center

Acknowledgment

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