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# Band Gap Engineering in Spray Pyrolysis Grown Nanocrystalline NiO Thin Films by Fe Doping

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Thin films of Fe doped nickel oxide (NiO:Fe) with different Fe doping concentration (from 0 % to 10 %) were grown on glass substrate by employing simple spray pyrolysis technique. The effect of different doping concentration of Fe on the structural, morphological, optical and electrical properties has been studied. XRD diffraction patterns show that at low Fe concentration only NiO lattice is present in the deposited thin film with cubic crystal structure, whereas $NiFe_2O_4$ compound with cubic crystal structure is deposited at higher Fe concentration. The crystallite size of the films is found to decrease from 15.16 nm to 7.41 nm with an increase in Fe concentration. Morphology of the prepared NiO:Fe thin films was characterized by field emission scanning electron microscopy (FESEM) attached with energy dispersive spectrometer (EDS). FESEM images show that Fe doping did not have any significant effect on the morphology of NiO:Fe thin films. EDS spectra confirm the formation of Fe doped NiO over the substrate surface. The optical investigation revealed that the absorbance in the visible region is found to be increased with an increase in Fe concentration. The optical band gap decreases with an increase in Fe concentration. All the films have electrical resistivity of the order of $10^4$ Ω.cm and are found to be increased with Fe concentration.

**Keywords:** NiO, Fe doped, Spray pyrolysis, XRD diffraction, Optoelectronic properties.

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## 1. INTRODUCTION

Among the metal oxides, the importance of nickel oxide (NiO) thin films is increasing day by day for many applications, due to its unique and technologically important properties such as excellent chemical stability, excellent durability [1], low material cost [2], cubic rock salt like crystal structure, wide band gap, transparency and *p*-type semiconducting ability [3] and possibility of manufacturing it by variety of techniques [4], etc. Also NiO thin films have been employed in multiple applications such as gas sensor, solar cell application, antiferromagnetic material, as an electrochromic material and UV photodetector [1], photocatalyst [5] and energy efficient smart windows [6] etc. due to their unique physicochemical properties. NiO thin films of great technological importance have been prepared using various methods such as chemical deposition method, successive ionic layer adsorption and reaction (SILAR), sol-gel spin-coating method, RF sputtering, reactive gas deposition, pulsed laser deposition, e-beam evaporation, spray pyrolysis technique, one-step electrostatic spray deposition [1, 7]. Although numerous techniques were employed for the preparation of NiO thin films, chemical deposition methods were preferred because they are low cost processes and comparably good quality thin films were prepared to those obtained by more sophisticated and expensive physical deposition process. Among these methods, spray pyrolysis is simple and inexpensive. In addition, it enables large area coating and also involves the preparation of uniform and transparent thin films with good adherence and reproducibility [8].

Doping is one of the simplest ways of alteration of electrical conductivity and the energy band gap of NiO thin films. Xie et al. [9] studied the enhanced photovoltaic performance of inverted planer perovskite solar cells by using cobalt doped NiO hole transport layer. Diha et al. [10] also studied the preparation of highly transparent Co doped NiO thin films having good crystallinity and optoelectronic properties. Doping of different elements, such as Cu [11], Zn [12], In [13], Li [14], La [15], etc. helps to engineer the optical and electrical properties. Keeping this in mind, in the present study, we report the synthesis of pure and Fe doped NiO thin films by the simple spray pyrolysis technique. The influence of Fe concentration on the structural, morphological and optoelectronic properties of NiO thin films has been investigated.

## 2. EXPERIMENTAL

### 2.1 Deposition of NiO:Fe Thin Films

Simple spray pyrolysis technique was employed for the deposition of Fe doped nickel oxide (NiO:Fe) thin films on commercially available microscopic glass substrates (25 mm × 75 mm × 1.35 mm), ultrasonically cleaned with acetone for 20 min followed by rinsing with distilled water.

An appropriate quantity of nickel chloride hexahydrate ($NiCl_2.6H_2O$) (Loba chemie, ~ 99 % purity) as a precursor of Ni, ferric chloride hexahydrate ($FeCl_3.6H_2O$) (Loba chemie, ~ 97 % purity) as a dopant and deionized

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water as a solvent were used as a source materials for preparation of NiO:Fe thin films using spray pyrolysis technique. Both $NiCl_2.6H_2O$ and $FeCl_3.6H_2O$ were dissolved separately in deionized water at concentration of 0.1 M. For the deposition of NiO:Fe thin films, the final solutions were prepared by mixing the solutions of 0.1 M $NiCl_2.6H_2O$ and 0.1 M $FeCl_3.6H_2O$ in appropriate volumetric proportions to get various concentrations (0 %, 2 %, 4 %, 6 %, 8 % and 10 %) of Fe. Homogeneous mixture of aqueous solution, which was sprayed on the pre-cleaned glass substrates, was achieved by constant stirring using magnetic stirrer. During the thin film deposition the glass substrate temperature was kept constant at $350 \pm 5$ °C to form NiO:Fe thin films and the distance between the nozzle and the substrate was 28 cm.

To investigate the effect of Fe doping on the properties of the NiO thin films, XRD, FESEM, optical absorption measurements and the two-point-probe methods were used. The structural and phase properties of the thin films were characterized by X-ray diffraction (XRD) method in the $2\theta$ ranging between 20° to 80° using Bruker AXS, Germany (D8 Advanced) X-ray diffractometer. The film morphology was analyzed by field emission scanning electron microscope (FESEM, S-4800 Type-II, Hitachi High Technology Corporation Tokyo, Japan). To study the optical characteristics of the film, absorbance spectra were recorded in the range 300-800 nm by means of JASCO UV-VIS spectrophotometer (V-630). The resistivity of the prepared NiO:Fe thin films was determined by two-probe method.

## 2.2 Results and Discussion

Fig. 1a-d shows the XRD patterns of the NiO:Fe thin films with 0 %, 4 %, 6 % and 10 % Fe doping concentrations, respectively. In the XRD patterns of pure NiO, NiO:Fe (4 %) and NiO:Fe (6 %) thin films, a well-defined peak is observed at $2\theta \approx 37.33°$, which corresponds to (1 1 1) reflection of NiO cubic phase matches with JCPDS card no. 73-1519. This suggests that the films grow according to a preferred orientation of the cubic phase. However, other low intensity diffraction peaks are visible in the XRD patterns of the NiO:Fe (6 %) thin films shown in Fig. 1c. In particular, the peak at $2\theta \approx 43.20°$ assigned to the (2 0 0) plane of NiO cubic phase and the peak at $2\theta \approx 31.72°$ refers to the (6 2 0) orientation of the cubic phase of the $NiFe_2O_4$ (JCPDS card no.03-0875). Therefore, the XRD spectra indicate that at high Fe concentration (above 6 %) the crystallographic structure of NiO:Fe thin films changes. Hence we deduce that the spray pyrolysis technique is only suitable for growing NiO:Fe thin films when the Fe concentration is lower than a few percent. Besides, the increase in the Fe content causes the decrease in the peak

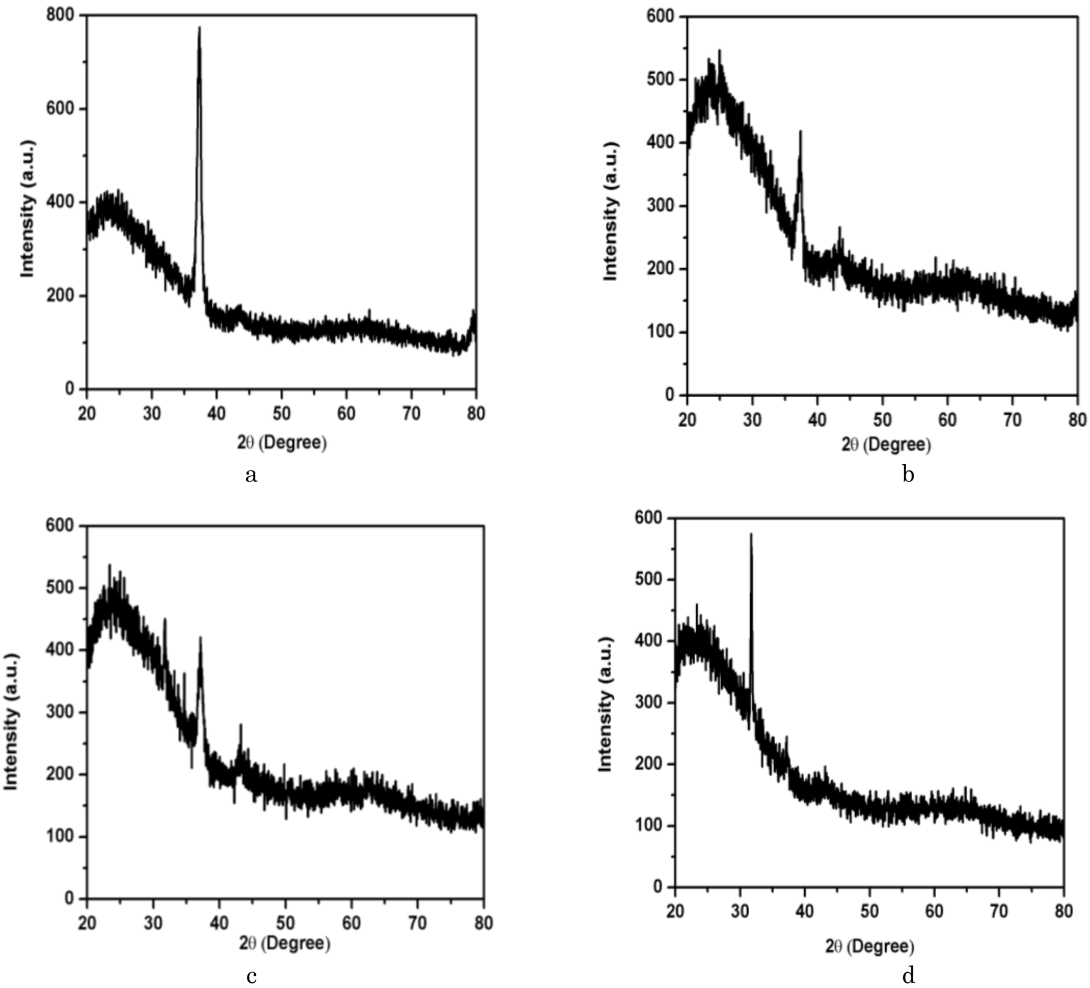



**Fig. 1** – X-ray diffraction patterns for spray deposited Fe-doped NiO thin films

intensity corresponding to $2\theta \approx 37.33^o$, which results in increase in FWHM corresponding to a decrease of the average crystallite size of the films. In fact, the values of the crystallite size ($D$) estimated by using Debye-Scherrer formula [16] of NiO:Fe thin films prepared using simple spray pyrolysis technique are given in Table 1.

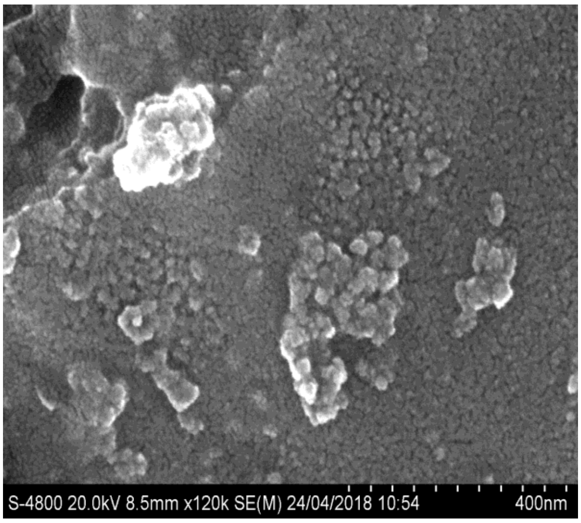
The crystallinity of the NiO:Fe thin films might deteriorate with increasing Fe concentration indicating that the large amount of Fe doping may create lattice distortion [12].

**Table 1** – Structural information of NiO:Fe thin films prepared using simple spray pyrolysis technique

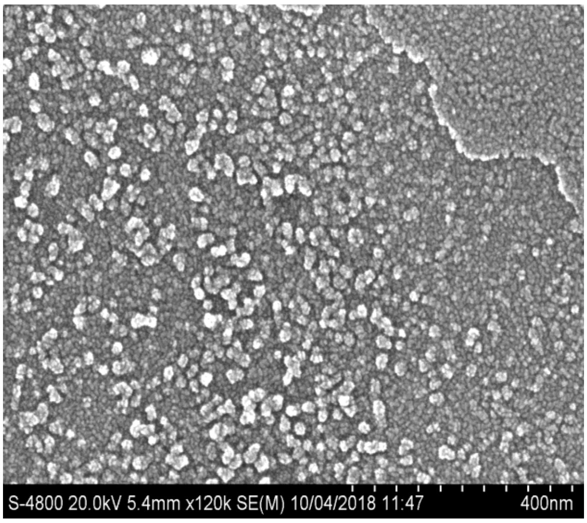
| Sample | 2θ (deg.) | FWHM (rad.) | D (nm) | (hkl) |
|---|---|---|---|---|
| Undoped NiO | 37.33 | 0.0028 | 15.2 | (1 1 1) |
| NiO:Fe (2 %) | 37.33 | 0.0126 | 11.6 | (1 1 1) |
| NiO:Fe (4 %) | 37.33 | 0.0134 | 10.9 | (1 1 1) |
| NiO:Fe (6 %) | 37.33 | 0.0177 | 8.2 | (1 1 1) |
| NiO:Fe (8 %) | 37.33 | 0.0144 | 7.4 | (1 1 1) |

The surface morphology study of NiO:Fe thin films at different doping concentrations was done by FESEM analysis and is shown in Fig. 2a-f. It can been seen that all the films are homogeneous and crack free with porous surface morphology. FESEM images show that Fe doping did not have any significant effect on the morphology of NiO thin films, however in case of NiO:Fe (10 %) thin films agglomeration of spherical particles was evident from the FESEM image shown in Fig. 2f. At the same time, surface of the films becomes dense when NiO was doped with Fe. This is due to the enhanced grain growth within NiO, which was caused by the Fe doping [17]. The porous morphology evident from FESEM images and a small crystallite size evident from XRD study of NiO:Fe thin films may provide a large specific surface area, which will adsorb more gases to enhance the gas sensing properties of the sensor [18].

The EDS spectra of NiO:Fe (10 %) thin films are shown in Fig. 3. The analysis confirms the presence of Ni, O and Fe elements. It is very important to note that no additional peaks attributed to impurities are observed in EDS spectra of Fe doped NiO thin films, which confirms the purity of the prepared thin films.



a



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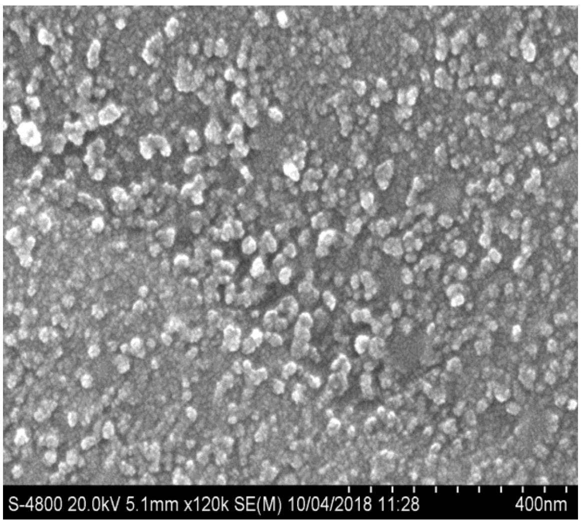
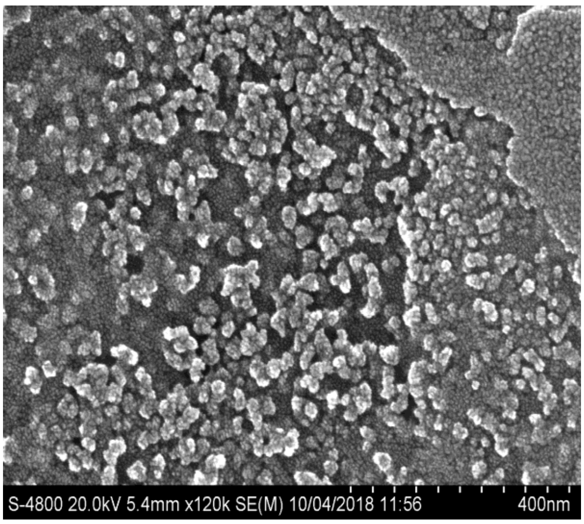


c



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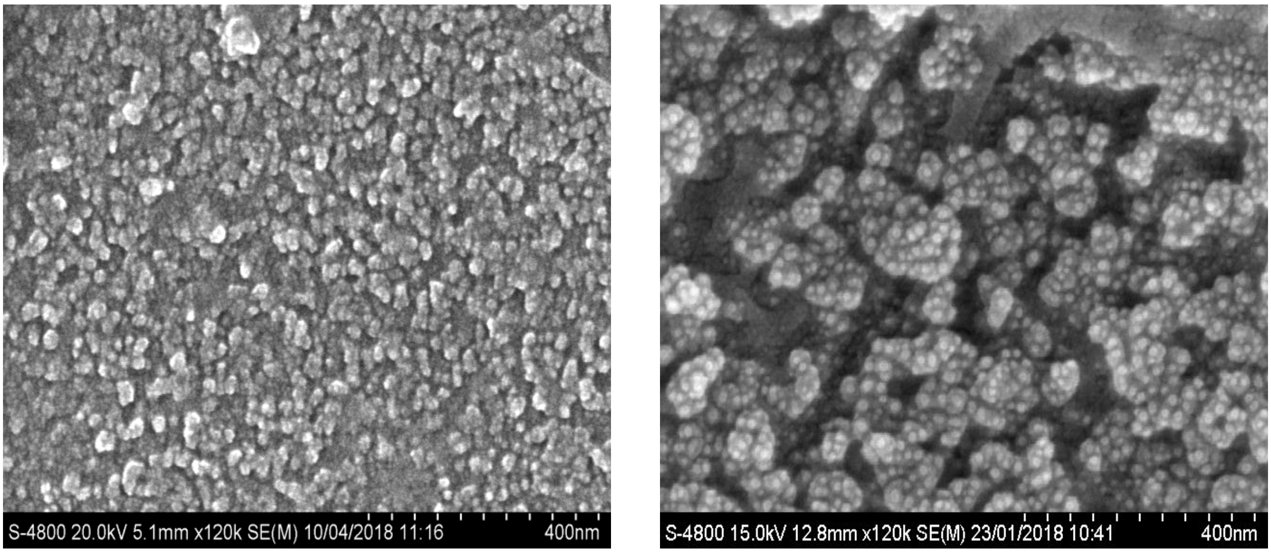


e f

**Fig. 2** – FESEM images of spray deposited NiO thin films doped with 0 wt. % (a), 2 wt. % (b), 4 wt. % (c), 6 wt. % (d), 8 wt. % (e) and 10 wt. % (f) Fe concentration

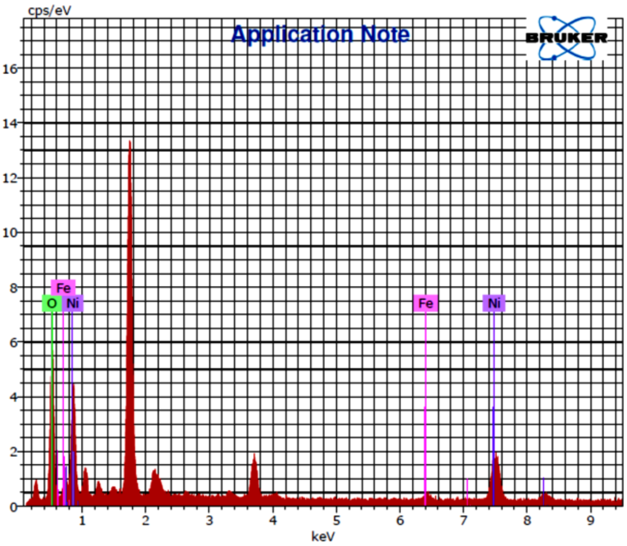


**Fig. 3** – Typical EDS spectra of spray deposited NiO thin films doped with 10 wt. % Fe concentration

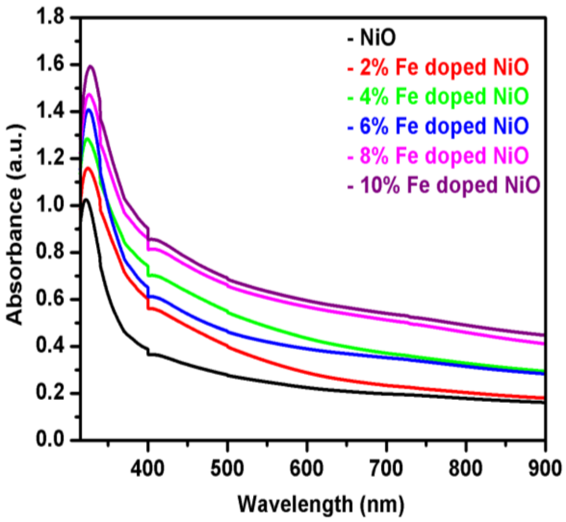


**Fig. 4** – Plot of absorbance with respect to wavelength for spray deposited Fe-doped NiO thin films

The optical absorption spectra of the NiO:Fe samples were determined by UV-Vis spectrophotometer. The optical absorption curves as a function of wavelength for different Fe concentration are plotted in Fig. 4. The absorbance has been found to be increased with the increase in Fe concentration and it is maximum for 10 % of Fe doping. This shows that Fe doped NiO thin films possess relatively large absorbance compared to that of pure NiO films. This is in good agreement with the XRD results, where we have observed the decrease in crystallite size at the higher Fe concentration. The absorption spectra were used to determine the band gap values of the NiO:Fe thin films using the well-known Tauc relationship. The band gap has been calculated by extrapolating the linear region of the plot of $(\alpha h\upsilon)^2$ versus hv on the energy axis. Fig. 5 shows typical plot of $(\alpha h\upsilon)^2$ versus hv for NiO:Fe (10 %) thin films deposited using simple spray pyrolysis technique. The linear fit of the plot indicates the existence of the allowed direct band-gap transition. The band gap value of the NiO:Fe (10 %) thin film is found to be equal to 2.8 eV. The reported value of the band gap is in good agreement with the value reported previously, where solution based chemical bath deposition technique was used for the preparation of NiO thin films [19]. The variation of band gap of NiO:Fe thin films versus Fe concentration is shown in the inset of Fig. 5. It can be noted that as Fe concentration in the film increases from 0 to 10 %, the optical band gap value of NiO:Fe thin films decreases from 3.48 eV to 2.86 eV. The decrease in the optical band gap observed with increased Fe doping could be related to structural deformation in the NiO thin films caused due to replacement of nickel ions in the NiO films by Fe ions or may be related to the Burstein-Moss effect [20].

Standard two point probe method was employed for the study of variation of *DC* electrical resistivity with temperature of spray deposited NiO:Fe films. The variation of $\log \rho$ versus the inverse of absolute temperature ($1000/T$) for the undoped NiO films is shown in Fig. 6.

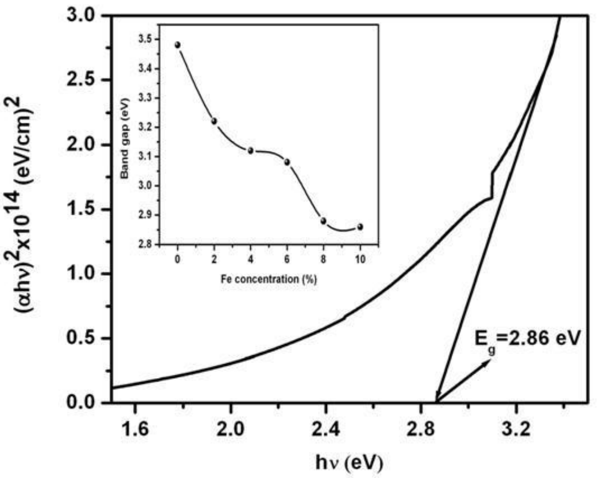


**Fig. 5** – Typical plot of $(\alpha h\nu)^2$ versus hv for spray deposited NiO thin films doped with 10 wt. % Fe concentrations. Inset shows the variation in the band gap versus Fe concentration of NiO:Fe thin films

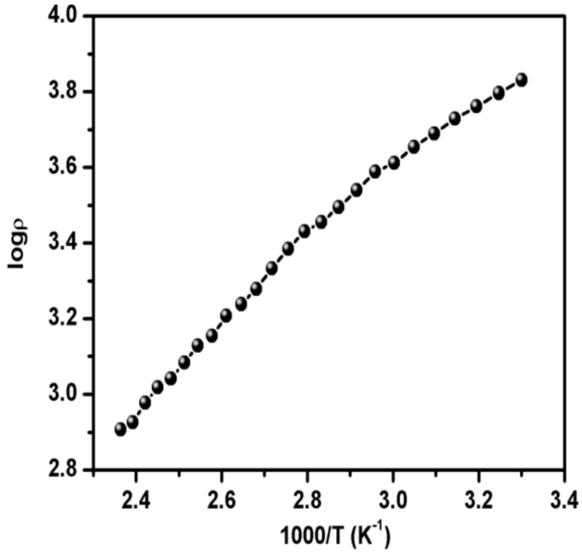


**Fig. 6** – Temperature-dependent resistivity plot for spray deposited pure NiO thin films

It is observed that the resistivity decreases with increase of temperature, which confirms the semiconducting behavior of the NiO films. The dependence of electrical resistivity of NiO films with Fe concentrations is shown in Fig. 7. The room temperature electrical resistivity was found to vary from $0.68 \times 10^4$ Ω.cm for un doped NiO to $11.94 \times 10^4$ Ω.cm for NiO:Fe (10 %) films which is comparable to the value of resistivity reported earlier [2].

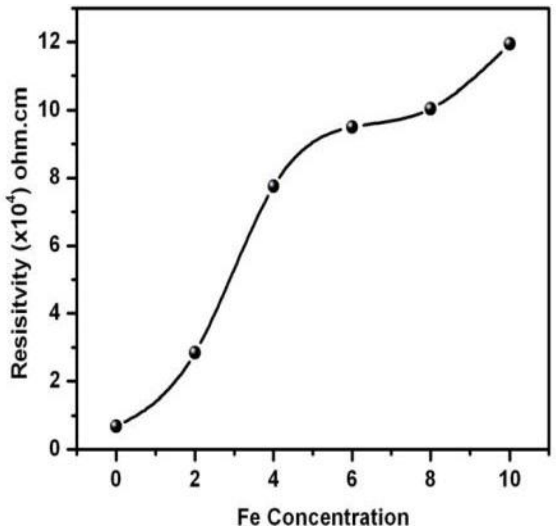


**Fig. 7** – Electrical resistivity variation versus Fe concentration of NiO:Fe thin films

## 3. CONCLUSIONS

NiO:Fe thin films were prepared using spray pyrolysis technique on glass substrate at 350 °C. The effect of Fe doping concentration on the physical properties of NiO thin films was investigated. XRD studies revealed that all the films represented cubic structure of NiO with preferred orientation along the (1 1 1) plane for low Fe concentration. While crystallite size decreases with Fe concentration, no significant change in surface morphology was observed with the introduction of Fe atoms. Optical absorbance of NiO:Fe thin films increases with the Fe concentration. The band gap energy decreased from 3.48 eV to 2.86 eV with Fe doping. The resistivity of the films increases with increase in Fe concentration.


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## Інженерія забороненої зони в нанокристалічних тонких плівках NiO, отриманих методом спрей-піролізу з розпиленням Fe


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Тонкі плівки оксиду нікелю, легованого Fe (NiO:Fe), з різною концентрацією Fe (від 0 % до 10 %) вирощували на скляній підкладці методом спрей-піролізного розпилення. Досліджено вплив різних концентрацій Fe на структурні, морфологічні, оптичні та електричні властивості. Рентгенограми показують, що при низькій концентрації Fe в осадженій тонкій плівці з кубічною кристалічною структурою присутня тільки NiO, тоді як $NiFe_2O_4$ з'єднання з кубічною кристалічною структурою осідає при більш високій концентрації Fe. Встановлено, що розмір кристалітів плівок зменшується з 15.16 нм до 7.41 нм із збільшенням концентрації Fe. Морфологія виготовлених тонких плівок NiO:Fe вивчалася скануючою електронно-емісійною мікроскопією (FESEM) з енергодисперсійним спектрометром (EDS). Зображення FESEM показують, що легування Fe не впливало на морфологію тонких плівок NiO:Fe. Спектри EDS підтверджують утворення NiO, легованого Fe, на поверхні підкладки. Оптичні дослідження показали, що поглинання у видимій області збільшується зі збільшенням концентрації Fe. Оптична ширина забороненої зони зменшується зі збільшенням концентрації Fe. Всі плівки мають електричний опір порядка $10^4$ Ом·см, який збільшується з концентрацією Fe.


**Ключові слова:** NiO, Легований Fe, Спрей-піроліз, XRD-дифракція, Оптоелектронні властивості.