



# INVESTIGATION ON PURE AND CESIUM (Cs) DOPED NICKEL OXIDE (NiO) THIN FILMS FOR HETEROJUNCTION DIODE APPLICATION

Elakkiya R

M.Sc., M.Phil., Assistant Professor

Nadar Saraswathi College of Arts & Science, Theni-625531

Mother Teresa Women's University-Kodaikanal

**ABSTRACT** - Pure and different concentrations of Cs doped NiO thin films were deposited by Sol-gel spin coating method. X-ray diffraction, Atomic Force Microscopy, Field Emission Scanning Electron Microscopy, UV-Visible-NIR spectrophotometer and I-V characteristics studies were carried out for structural, morphological, optical and electrical properties of coated samples. Thickness of the films was found 354 nm. XRD analysis reveals that the films have a face centered cubic structure of NiO nanostructure (JCPDS Card No: 78-0643) with 2 2 0 plane and crystallite size was found to be in the range between 20-25 nm. AFM images shows that the spherical in shape and addition to that size of the grains of the samples were increase with raise in Cs dopant concentration and found to be in the range from 30 to 45 nm. FE-SEM images shows that the Cs content strongly influences the growth of the grain and density of the NiO thin films. The optical band gap of the pure and doped films decrease in the range from 3.74 to 3.65 eV. The ideality factor of the device ( $n$ ) value is found to be in the range of 2.2 for the pristine device, which further increases from 2.2 to 4 with different Cs:NiO/n-Si of fabricated devices. Therefore, Cs doped NiO is one of the suitable candidates for fabrication of heterojunction diode.

**Keywords:** XRD, Sol-gel, FE-SEM, AFM, Heterojunction diode

## I. INTRODUCTION

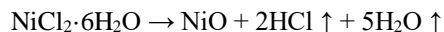
Cesium (Cs) doped NiO thin films were deposited by Sol-gel spin coating method. The prepared thin films were characterized by X-ray Diffraction, UV-Visible-NIR spectrophotometer, Atomic Force Microscopy and its heterojunction

diode p-Cs-NiO/n-Si(100) characteristics were studied. Thickness of the films was found 354 nm. The influence of Cs on the structural, morphological, optical and electrical properties of NiO thin films coated on glass substrates by sol-gel spin-coating technique for diode application has been studied (7,8). Obtained results were analysed for charge transport of the fabricated diode. The interface of the metal-semiconductor structure plays significant role in electronic devices and has application in semiconductor technology. Generally, a metal oxide is placed on the semiconductor surface, which improves the charge transport properties. Despite its advantages in conventional p-n junction diodes, which is suffers from high series resistance, high-density interfacial defects, which could be effectively controlled by the NiO thin films in diode. It is assumed that the efficiency of heterojunction diode depends on the quality of the improved properties of NiO thin films. Hence, pure and different w% of Cs (1, 3 & 5 w%)-doped NiO thin films were deposited and analyzed for investigation of heterojunction diode. The important diode parameters such as ideality factor ( $n$ ), barrier height ( $\phi_B$ ), leakage current ( $I_0$ ), and series resistance ( $R_s$ ) were measured by the I-V characterization method as a function of annealing temperature. The effect of Cs dopant on NiO thin film was studied and electrical transport behaviour of heterojunction diode has been interpreted in detail.

## II. EXPERIMENTAL DETAILS

Nickel oxide thin films were synthesized with deposition time of 30 sec on glass substrates using spin coating technique. The fabricated samples were kept inside the thermal treatment at annealing temperature in the range 350 °C. precursor solution was prepared from a mixture of 0.1 M nickel chloride ( $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ ) and de-ionized water. For uniform

deposition of thin films the prepared solution was sprayed through a linearly moving glass nozzle onto the preheated glass substrates, solute precipitation and pyrolytic decomposition, thereby resulting in the formation of nickel oxide thin films according to the following reaction equation.



Some of the factors are decided the quality of the thin films, such as the substrate temperature, spin rate, annealing temp and spinning time. The glass substrates were ultrasonically cleaned before depositing process. At first step, the substrates were washed with detergent solution 'Labolene' and then washed with water. Next step is substrates were kept in nitric acid for 15 min. These substrates were further dipped in 4 M NaOH solutions for 15 min to remove the acidic contamination. Finally these substrates were washed with distilled water and then treated with ultrasonic waves for 15 min, prior to the deposition. Several initial trials were made to optimize the deposition conditions before real sample preparation. Thickness of prepared film was determined by weight difference method using a sensitive microbalance as:  $d = (m)/(m \cdot l \cdot L)$ . where  $m$  is the difference between the mass after and before the coated operation,  $l$  the length,  $L$  the width and  $m$  is the density

### Structural Properties

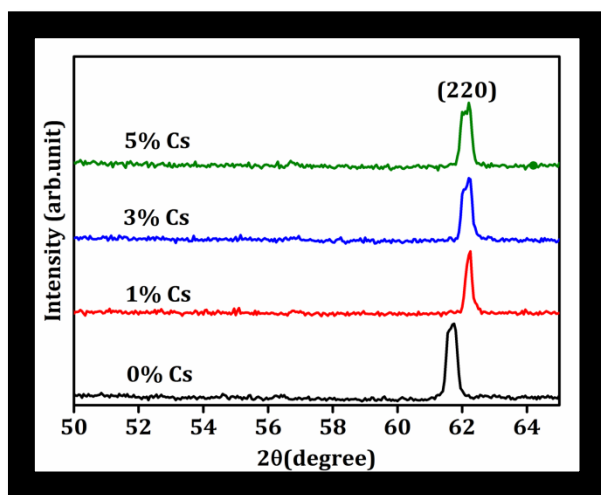


Figure 1 represents the XRD pattern of NiO thin films with various concentrations of Cs dopant (a) Pure, (b) Cs (1 wt.):NiO (c) Cs (3 wt.):NiO and (d) Cs(5 wt.):NiO

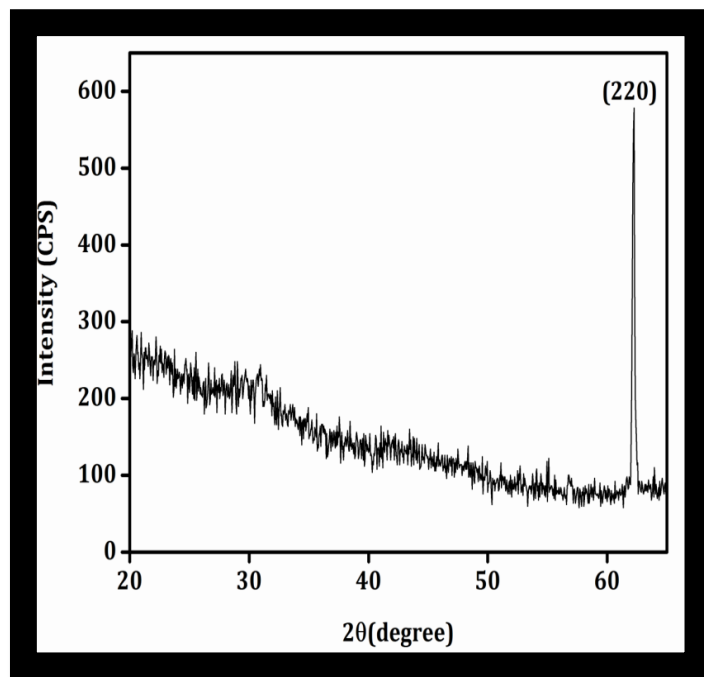


Figure 2 represents the Full Scan-XRD spectra of NiO Thin Films

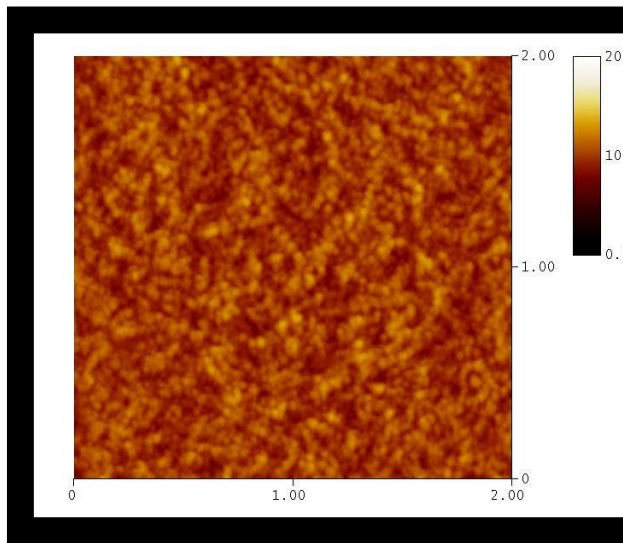
Structural properties of Pure and Cs doped NiO thin films were investigated by X-Ray Diffraction. The XRD pattern of pure and Cs doped NiO thin films was shown in Figure 4.1. XRD result revealed that only single peak at  $2\theta=62^\circ$  correspond to (220) plane of face centered cubic of NiO nanostructure. Figure 4.2 shows that the XRD pattern of NiO thin films noted in the  $2\theta$  range from  $20^\circ$  to  $70^\circ$ . XRD pattern expose that the single crystalline structure of the deposited thin films aligned along with (220) plane. XRD peak shifts towards the higher angle owing to huge difference between the ionic radius of Cs and Ni, which leads to lattice distortion. The large Full width Half Maximum (FWHM) and corresponding low intensity of the diffraction peak is due to the nanocrystalline nature and the size of the nanocrystallite was determined by Debye-Scherrer's equation,

$$D = \frac{0.94\lambda}{\beta_{hkl} \cos \theta}$$

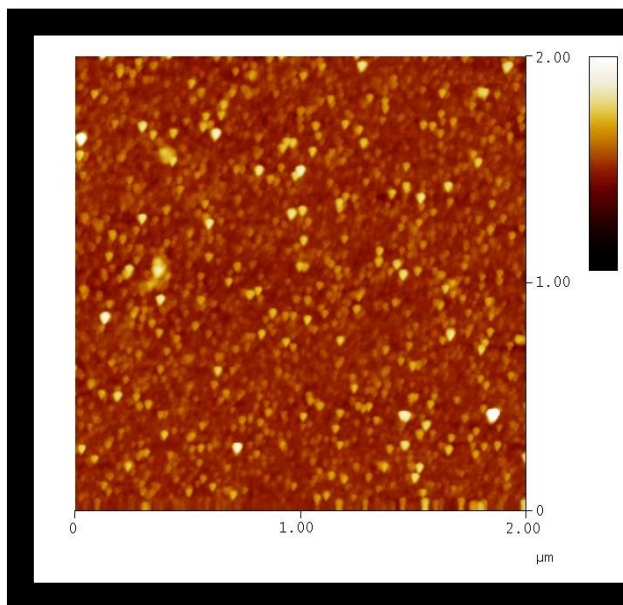
Crystallite size was found to be in the range of 20-25 nm. Crystallite size of 0%Cs NiO thin film was 20 nm. When 1% Cs is doped, crystallite size increased to 25 nm and further increasing the doping concentration to 3% and 5% crystallite size was found to be 22 and 22.5 nm. Considerable change is

observed in peak intensity and crystallite size upto 3% Cs concentration above the XRD pattern show no change in the crystal structure. Single crystalline growth towards (220) plane can be attribute to the texture of the n-Si (100) and less surface energy of the corresponding plane.

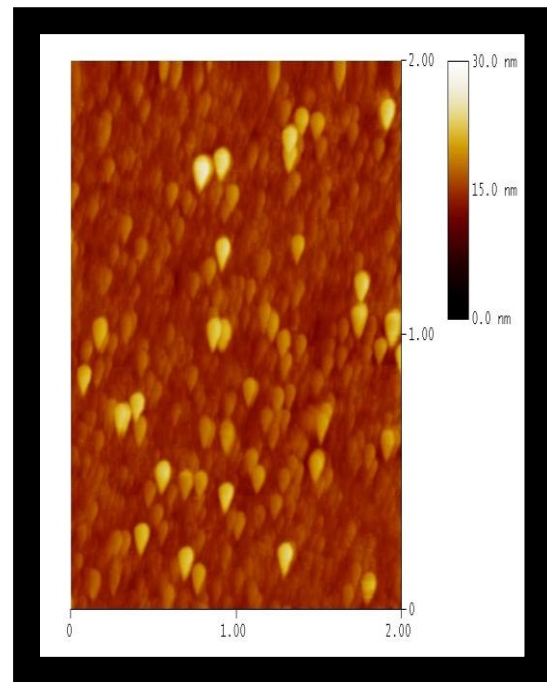
### III. SURFACE TOPOGRAPHY



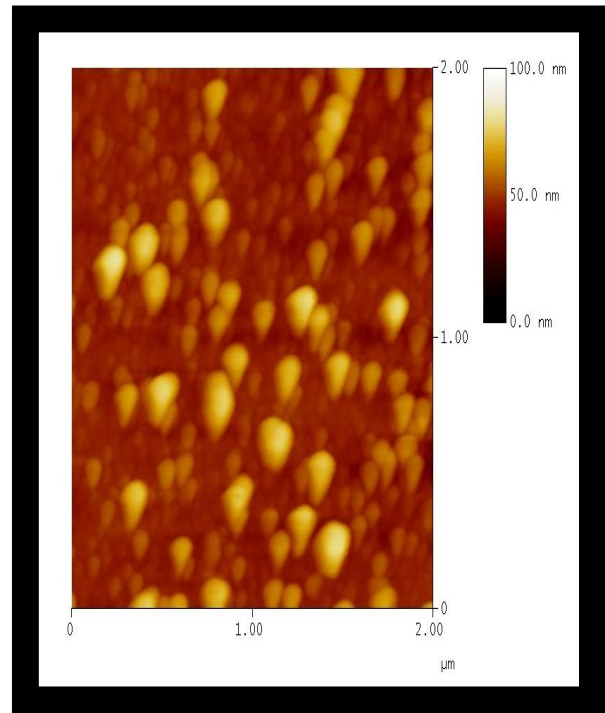
*Figure 3 (a)* represents the AFM image of the pure NiO thin film



*Figure 3 (b)* represents the AFM image of the 1 wt. % Cs doped NiO thin film



*Figure 3 (c)* represents the AFM image of the 3 wt. % Cs doped NiO thin film



*Figure 3 (d)* represents the AFM image of the 5 wt. % Cs doped NiO thin film



Figure 3(a-d) shows that the AFM image of pure and various dopant ratio of (0%- 5%) Cs doped NiO thin films.

From these images, the variation in surface roughness of the samples due to varies concentration of the dopant. The roughness  $R_a$  and the root-mean-square (RMS) surface roughness  $R_q$  quantify that the impact of Cs dopant concentration on the topography. The determined  $R_q$  and  $R_a$  values for  $2 \mu\text{m} \times 2 \mu\text{m}$  film area scan are shown in below table.

Table 1 Value of  $R_q$  and  $R_a$

Concentration of the Dopant (wt%)	Root-mean-square (RMS) surface roughness ( $R_q$ ) nm	Average roughness ( $R_a$ ) nm
0	1.013	0.816
1	1.041	0.834
3	1.731	1.169
5	7.372	5.562

From the above table it is ensure that the both  $R_q$  and  $R_a$  values are increase with raise in concentration of Cs dopant. Which are shows that Cs dopant has major impact on the surface texture of the fabricated thin films. Increase in roughness of the samples is due to high compressive stress that formed while raise in dopant concentration. This can be attributed to the more angle of shift in XRD peak. An AFM image shows that the very small tiny grains on the surface uniformly spread over the samples without any tiny pin holes. The grains are found to be spherical in shape and also size of the grains of the samples were increase with raise in Cs dopant concentration and found to be in the range from 30 to 45 nm.

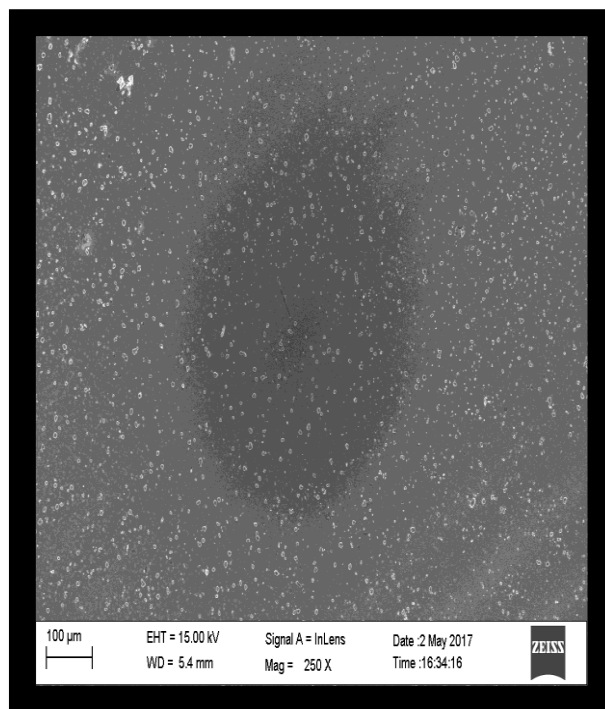


Figure 4 (a) represents the FE-SEM image of the pure NiO thin film

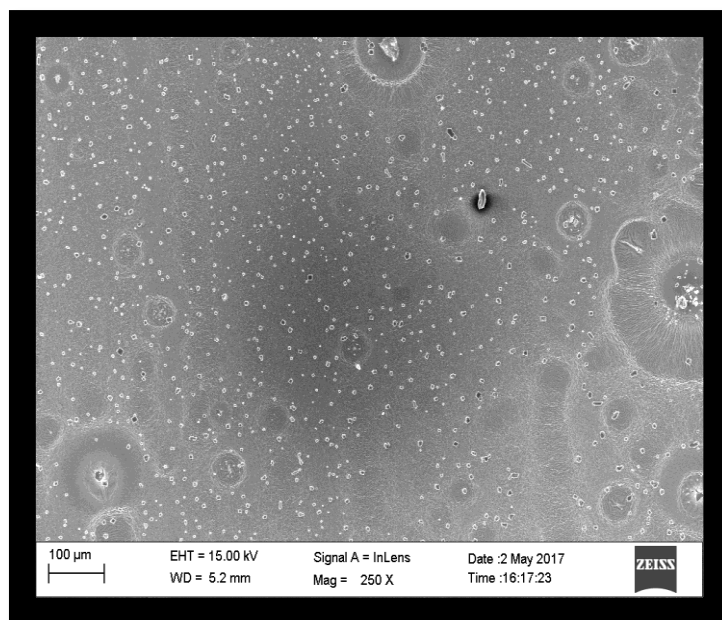


Figure 4 (b) represents the FE-SEM image of the 1 wt. % Cs doped NiO thin film

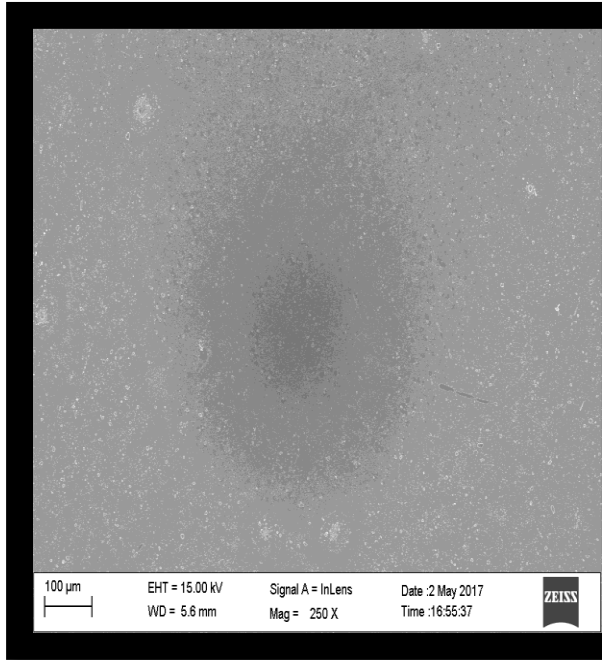


Figure 4 (c) represents the FE-SEM image of the 3 wt. % Cs doped NiO thin film

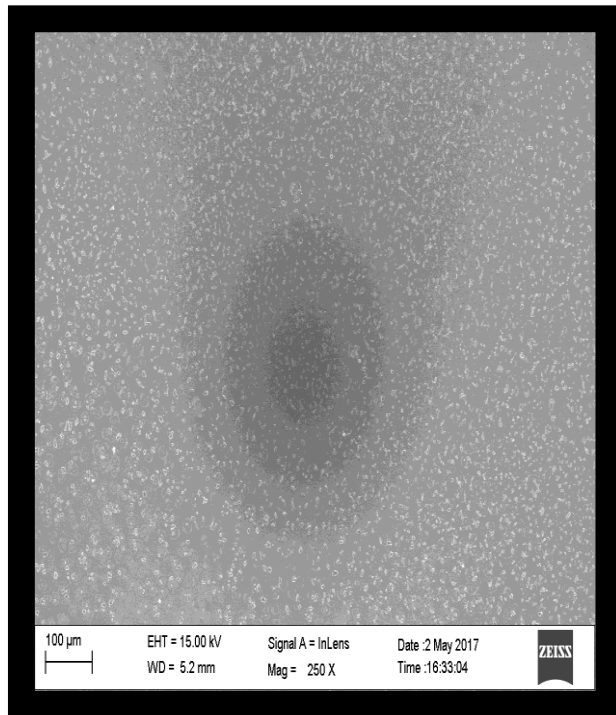


Figure 4 (d) represents the FE-SEM image of the 5 wt. % Cs doped NiO thin film

Figure 4 shows the FE-SEM images of various concentrations of Cs-doped NiO thin films. The grain size was slightly modified in the case of 1 wt. % of Cs:NiO surfaces of thin film (Figure 4(a)). Figure 4(b) shows that the grain size of 3 wt. % of Cs:NiO thin film was further reduced. In higher doping concentrations of 3 and 5 wt. % of Cs:NiO, nano-sized grains were noticed as shown in Figure 4(c)-(d). These images expose that the Cs content strongly influence the growth of the grain and density

of the NiO thin films. Increasing concentration of dopant can increase stress in the NiO grains, which will create the process of grain growth and decrease the nucleation agent in the system.

#### IV. OPTICAL PROPERTIES

The UV visible diffuse reflectance spectrum of pure and Cs doped NiO thin films are shown in Figure 5 (a-d).

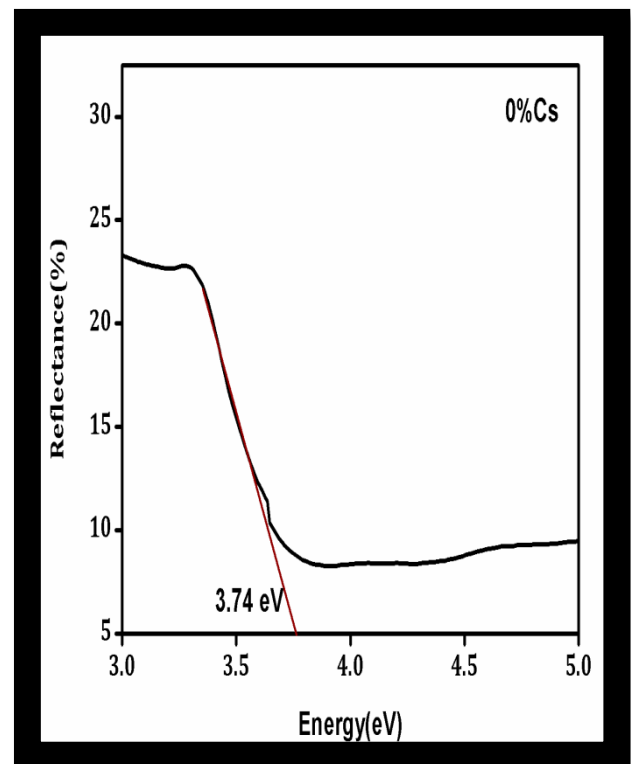
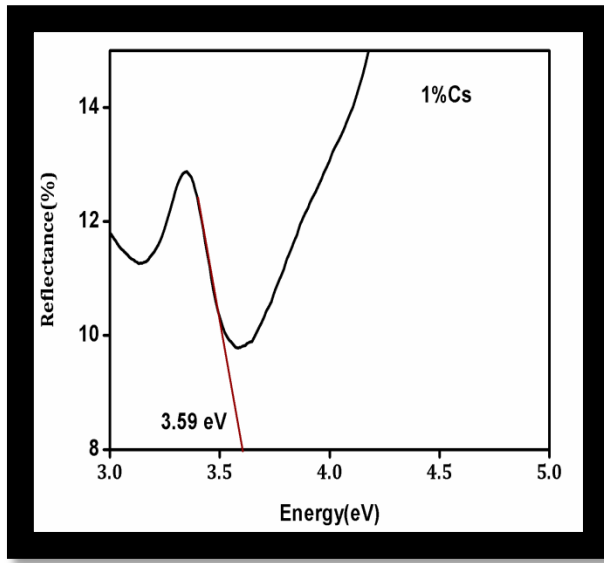
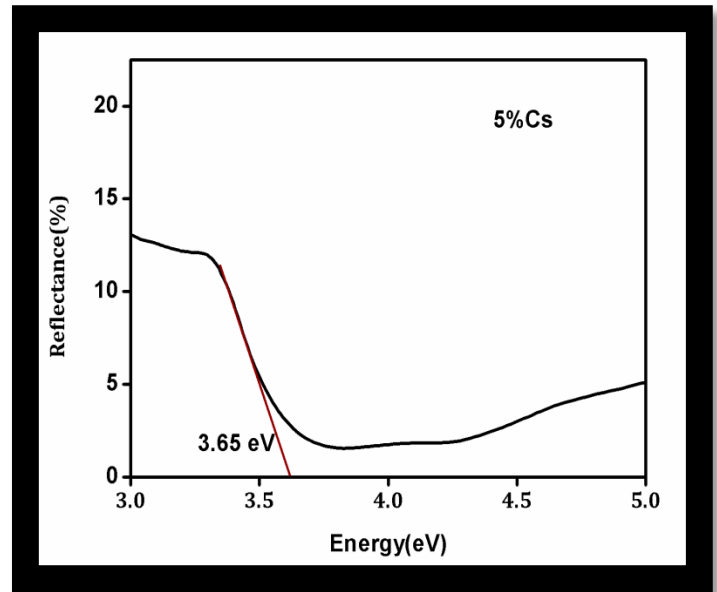


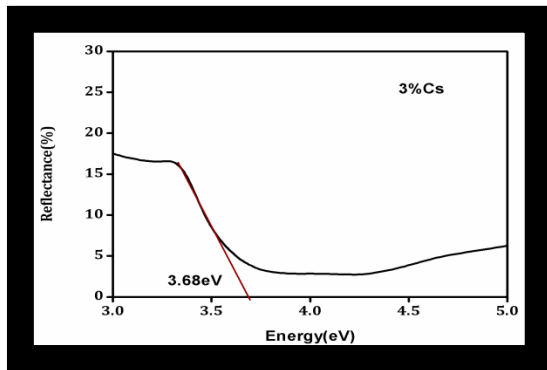
Figure 5(a) represents the UV visible diffuse reflectance spectra of pure NiO thin film



**Figure 5(b)** represents the UV visible diffuse reflectance spectra of pure 1wt. % Cs doped NiO thin film



**Figure 5(d)** represents the UV visible diffuse reflectance spectra of pure 5 wt. % Cs doped NiO thin film



**Figure 5(c)** represents the UV visible diffuse reflectance spectra of pure 3 wt. % Cs doped NiO thin film

NiO is positive type semiconductor material; consequently the optical behaviour of the NiO thin films is significant for fabrication of electronic devices. Optical properties of the deposited NiO thin films were characterized by using Diffused Reflectance Mode (DRS). The UV visible diffuse reflectance spectrum of pure and Cs doped NiO thin films are shown in Figure 4.5 (a-d). The band energy were observed to be 3.74 eV, 3.59 eV, 3.68 eV, 3.65 eV for 0 wt. % Cs, 1 wt. % Cs, 3 wt. % Cs, and 5 wt. % Cs respectively. The optical band gap energy of the fabricated thin films was consistent with previous articles [1]. The decrease in the optical band gap energy for 1 wt. % of Cs doped thin film can be ascribed to the raise in the crystallite size. The optical band gap energy is inversely proportional to the crystallite size of the thin films. The band gap energy of the thin films was established to be in the UV region; therefore samples should shows higher transference in electromagnetic spectrum visible region. In this type of thin films can be utilized in the uv filter a transparent in microelectronic devise applications.

V. DEVICE FABRICATION

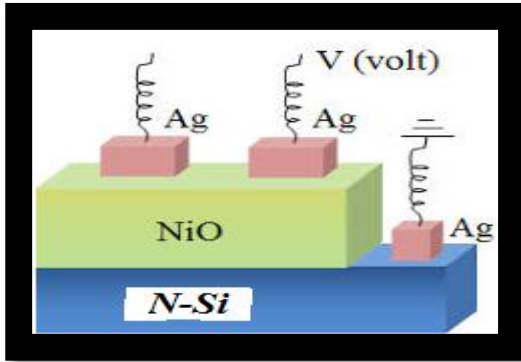


Figure 6 represents the Schematic representation of N-Si/Cs:NiO/Al Hetrojunction diode

The NiO is coated on a N-Si wafer (100) by the sol-gel spin-coating method. Before device fabrication, N-type silicon wafers were chemically cleaned using piranha solution (i.e., H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> (1:2)). HF:H<sub>2</sub>O (1:10) was used to remove the native oxide on the surface of Si substrates and finally the wafers were rinsed using deionized water for 30 s. Nicole chloride pentahydrate was dissolved in 10 ml of ethanol, and the solution was stirred at 333 K for 24 h at ambient condition. The silicon substrate is fixed onto the sample holder of the spin coater. A drop of prepared solution was kept on the glass substrate using a fine nozzle and the substrate was allowed to rotate at a spin rate of 2500 rpm for 30 s. The coated wafers were annealed in a vacuum oven for 1 h. After the annealing process, a high-purity aluminum metal contact with a thickness of 200 nm thermally evaporated from the tungsten filament onto the metal side and silicon wafer and NiO at a pressure of  $1 \times 10^{-6}$  mbar.

Heterojunction Diode Characteristics

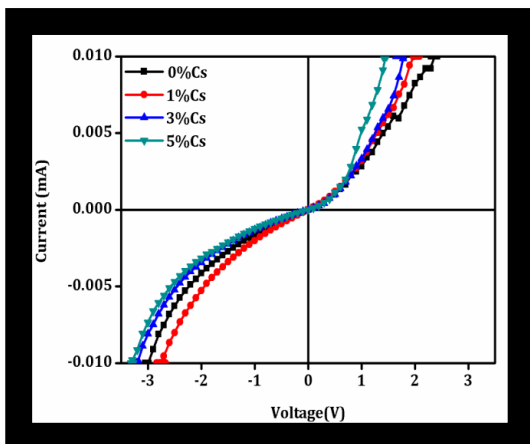


Figure 7 represents the Heterojunction diode characteristics of p-Cs doped NiO/n-Si(100)

Figure 7 shows that the heterojunction diode characteristics of p-Cs doped NiO/n-Si(100) thin films. Both undoped and doped NiO thin films show good rectifying behaviour was noticed. Increase in concentration of dopant, which leads to exponential raise in the forward bias. Threshold energy for the all the fabricated thin films is less than 0.5 V and the flow of current attain saturation for 0.010 mA. The device ideality factor was calculated from the slope of the forward bias  $\ln I$  vs.  $V$  curve by below given equation. [2]

$$n = \frac{q}{kT} \frac{dV}{d \ln I}$$

where,  $k$  is the Boltzmann constant and  $dV/d \ln I$  is the inverse slope of  $\ln I$  vs.  $V$  curve.

The value of the ideality factor of the p-Cs doped NiO/n-Si(100) heterojunction is determined from the slope of the straight line region of the forward bias  $\ln I$ - $V$  characteristics of the samples. The calculated ideality factor was increase with raise in concentration of the dopant and found to be in the range from 2.2 to 4 for the prepared samples. The higher value of ideality factor was observed for the fabricated heterojunction diode is attributed to the interface states and series shunt resistance effects [3]. And addition to that the valance state of dopant in the concentration of Cs and positive charge carrier concentration in p-NiO and also the conductivity of the samples was increases. raise in electrical conductivity of p-NiO is owing to increase in the Ni dopant vacancies, finally which breaks the junction. Due to interface defects like SiO<sub>2</sub> elements, hence increase in reverse and forward bias of the heterojunction diodes. [4]

The barrier heights ( $\Phi_B$ ) of the fabricated heterojunction diode have been modified from 0.77 to 0.96 eV. Better devious quality was attained at a higher wt% of Cs(5 wt.%):NiO/p-Si heterojunction diode. Leakage current  $I_0$  decreases with raise in Cs dopant content in the NiO samples, which shows that the electron trapping at the grain boundaries is segregated by dopant ions. Minimize in barrier height ( $\Phi_B$ ) with the incorporation of dopant content is ascribed to an raise in charge carrier concentration, which increases the Fermi level and lowers the barrier height. The leakage current was determined in the range from 1.293 to 0.55 nA owing to the Cs dopant. [5]





## VI. SUMMARY AND CONCLUSION

The important conclusions drawn from the present work are summarized here.

Different concentrations of Cs (1, 3 & 5 wt. %) doped NiO thin films were prepared and characterized for Cs:NiO/n-Si heterojunction diode. XRD analysis reveals that the films have a face centered cubic structure of NiO nanostructure with 2 2 0 plane. AFM images carried out topographic information of the grains range from 30 to 45 nm and  $Rq$  and  $Ra$  values are increase with raise in concentration of Cs dopant concentration on the topography. UV-Vis analysis showed the band gap to decrease from 3.74 to 3.65 eV with increase in Cs concentration. FE-SEM images shows that the Cs content strongly influences the growth of the grain and density of the NiO thin films. The optical band gap energy is inversely proportional to the crystallite size of the thin films. Device ideality factor ( $n$ ) is increased from 2.2 to 4. The barrier heights ( $\Phi_B$ ) of the fabricated heterojunction diode increased from 0.77 to 0.96 eV. The leakage current ( $I_0$ ) is decreased from 1.293 to 0.55 nA in Cs dopant. From the above results of diode parameters, it is seen that Cs (5 wt. %):NiO thin films offer better performance for Cs:NiO/n-Si heterojunction diode.

## VII. REFERENCES

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