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Saju Joseph
Research & Development Centre, Bharathiar University, Coimbatore 641046, Tamilnadu, India, sajuismyname@gmail.com

O. N. Balasundaram
Department of Physics, PSG College of Arts and Science, Coimbatore – 641014, Tamilnadu, India, sajuismyname@gmail.com

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Effect of W Doping on NiO Thin Films and its Optical, Morphological and Diode Characteristics

Saju Joseph [1,*] *and O. N. Balasundaram* [2]

[1] Research & Development Centre, Bharathiar University, Coimbatore 641046, Tamilnadu, India

[2] Department of Physics, PSG College of Arts and Science, Coimbatore – 641014, Tamilnadu, India

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Abstract: In this work, we demonstrate the preparation of simple and inexpensive spray route for the preparation of pure and W doped NiO thin films on the quartz glass plates. The microstructure and morphological properties were investigated using an X-ray diffraction and Scanning electron microscopic (SEM) studies. SEM images notify the presence of hollow sphere and the energy dispersive spectrum confirms the existence of both Ni and W in the prepared films. Electrical properties were investigated by two probe conductivity studies. In addition to these studies (n-Si/NiO/Au and n-Si/W:NiO/Au) diodes were fabricated and their chattels were deliberated.

Keywords: W-NiO thin films, spray pyrolysis, electrical conductivity, diode.

1 Introduction

In this current era Transparent conducting oxides (TCO's) are considered as a potential candidate for optoelectronic, field effect transistor, resistive switching, electrochromic device, super capacitor, photocatalysts and medical diagnosis applications [1-4]. Among TCO's NaCl type FCC structured antiferromagnetic NiO is one of the attractive materials with the band gap of 3.6 eV to 4 eV. Due to their high thermal stability, low cost, less toxicity, redox activity and controllable nanostructure [5-8]. Already it is known that NiO thin films can be prepared by various techniques, including sol-gel, chemical vapor deposition, thermal evaporation, molecular beam evaporation, RF sputtering, chemical bath deposition technique, dip technique, spray pyrolysis and electrochromic deposition [9-15].

Among these, spray route provides economical and experimentally favorable condition for the film preparation. Because it allows us to control the deposition temperature, molarity concentration and film thickness, etc. which are the significant parameters in the determination of the quality of the film for various applications. In order to increase the transparency and conductivity previously NiO was mixed with different metals (Cu, Co, Li, Fe, Al and Mg) and their properties were premeditated [16].

The present paper mainly focused on the preparation of pure and W doped NiO thin films by spray deposition method. The structural, morphological, optical and electrical and diode properties were taken for the both pure and W doped NiO and the effect of W doping were deliberated in detail.

2 Experimental Details

2.1 The Fabrication of W-NiO Thin Films and p-WNiO/n-Si Diodes

The pure and W-NiO thin films were prepared with different doping concentrations of (0, 3, 5 and 7 wt %) W by using NSP pyrolysis technique. The precursor materials of nickel acetate and tungsten hexachloride were purchased from Sigma Aldrich, ~99.9 % purity. The precursor materials of (0.20 M) nickel acetate and tungsten hexachloride were dissolved in triple distilled water and

*Corresponding author: sajuismyname@gmail.com

stirred at room temperature. The prepared 5 ml of spray solution was deposited on well cleaned glass substrate at substrate temperature 450 °C. For the p-WNiO diode preparation, the silicon wafer cleaning process an important because of the dust, grease, metallic impurities and organic residues on the surface. The silicon wafer cleaning steps details reported by Mohanraj etc., al [17]. The prepared spray solution 1.5 ml was taken and sprayed on n-Si wafer (1 X 1 cm) at 450 °C. After the W-NiO film formation on n-type Si wafer, thermally evaporated Au (100 nm thickness and 200 μm diameter) was used to make the metal contact at both sides and dried 5h for each side. This Au contact plays the main role in prepared diodes such as good adhesion, high conductivity and low sheet resistance. The developed p-WNiO/n-Si
diode schematic diagram shown in Fig 1.

3 Results

3.1 Structural Analysis

and recorded W-NiO thin films X-ray diffraction patterns depicted in Fig 2. From the XRD pattern, well defined XRD peaks are observed for the NiO thin films at 37.32° and 43.29° correspond to (222) and (400) planes. This result indicates the prepared films are single phase polycrystalline nature with cubic structure and all diffraction peaks well matched with JCPDS card no: 89-5881. Fig 2 clearly illustrates the diffraction peaks are shifted from 37.32 to 37.69 due to increase of W doping level such as 0, 3, 5 and 7 wt%. The crystallite size of pure and W-NiO thin films are calculated using Scherrer formula (1) [18-20],

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

where k is shape factor (0.94), λ is the incident wavelength of the X-ray (λ = 1.542Å) (CuKα), β is the full width at half maximum (FWHM), and θ is the diffraction angle. The calculated average crystallite size of pure and W-NiO thin films are around 24 nm.

$$\alpha h\vartheta = A(h\vartheta - E_g)^{1/2} \quad (3)$$

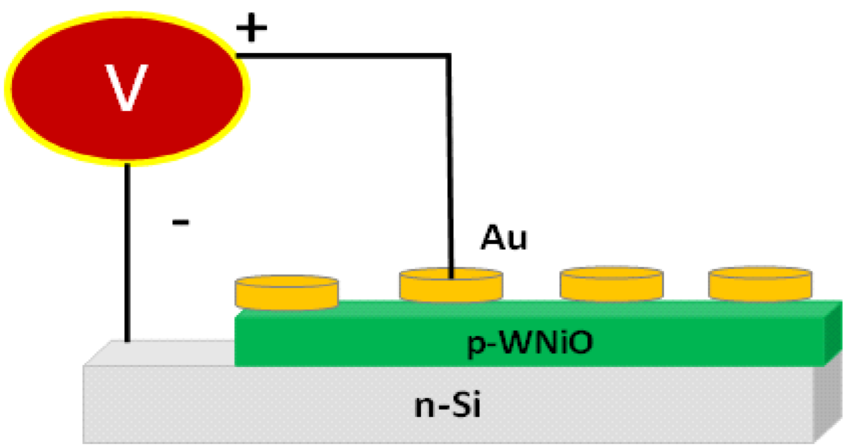

Fig. 1: Schematic diagram of p-WNiO/n-Si diode.

3.2 Optical Properties

Pure and W-NiO thin films optical property was investigated by using UV-Visible spectrometer. The obtained spectra transparency has been slightly varied with W doping. The absorption coefficient (α) is calculated by following equation (2) [21].

$$\alpha = \frac{\ln(1/T)}{t} \quad (2)$$

Where T-transmittance and t-thin film thickness. The pure and W-NiO thin films optical band gap can be determined from following equation (3),
The prepared W-NiO thin films has polycrystalline nature

Fig 3 depicts the αhυ versus hυ plot, which is indicates the band gap value Eg obtained from the intercept of the linear portion of the graph. This graph provides band gap values are 3.59, 3.41, 3.10 and 3.0 eV correspond to doping levels 0, 3, 5 and 7 wt% of W.

3.3 Morphological Studies

The morphology of pure and W doped NiO thin films were studied by scanning electron microscopy (SEM). Fig 4 (a-d) illustrated the obtained SEM images of pure and different wt% (0, 3, 5 and 7 wt%) of W doped NiO thin films.

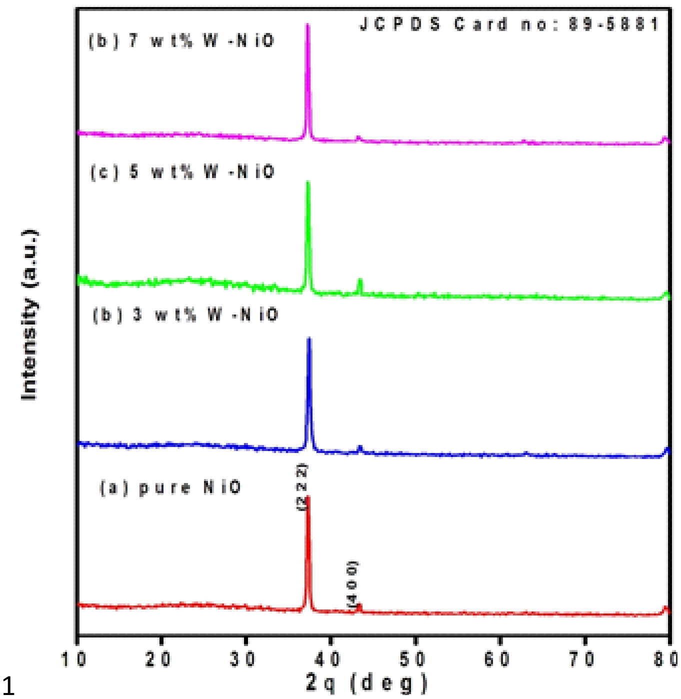

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Fig. 2: XRD patterns of W-NiO thin films.

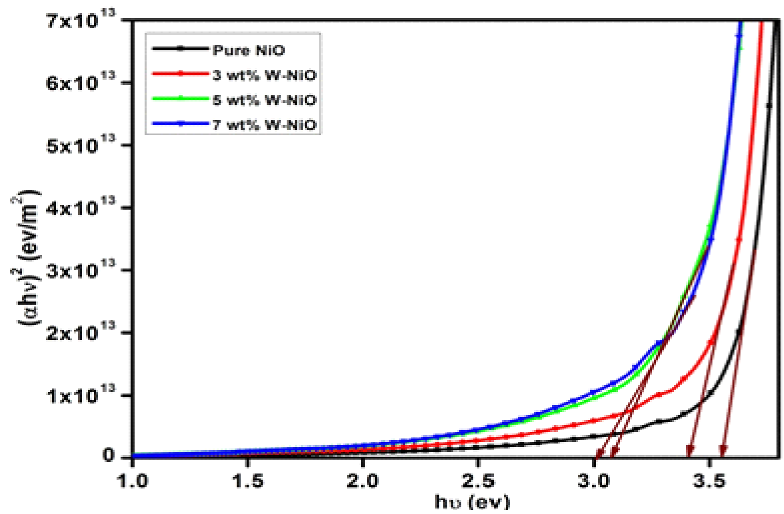


Fig. 3: The band gap energy of pure and W-NiO thin films.

3.3 Morphological Studies

The morphology of pure and W doped NiO thin films were studied by scanning electron microscopy (SEM). Fig 4 (a-d) illustrated the obtained SEM images of pure and different wt% (0, 3, 5 and 7 wt%) of W doped NiO thin films.

Fig 4 (a) depict the pure NiO SEM image, it is clearly displayed the non-uniformed hollows sphere with holes shape. Fig 4 (b-d) shows the W doped NiO films, which is revealed the agglomerated small hollows spheres with holes from 3 to 7 wt% with particle size decreased and increased the agglomeration as confirmed by XRD results.

3.4 Elemental Composition

Energy dispersive X-ray spectroscopy (EDX) analysis represented the elemental compositions of pure and W doped NiO. Fig 5 (a and b) shows the EDX spectra of pure and 7 wt% w doped NiO thin films. The observed atomic percentage of pure and 7 wt% W doped NiO is illustrated in Fig 5 (a-b) inset tables. These results are good evidence of the presence of W, Ni, and O elements. From the EDX spectrum (Fig 5b) clearly depicts that the new peak of W appeared in 7 wt% W doped NiO, which is owing to the W ion incorporation into the NiO lattice site.

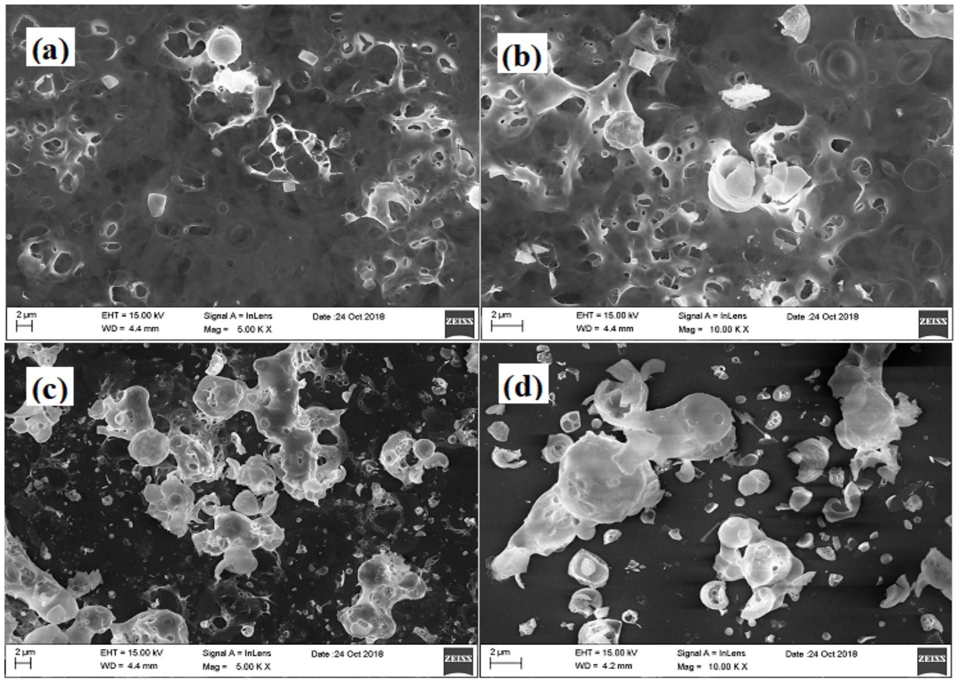


Fig. 4 (a-d): SEM images of (a) pure and (b) 3 wt% W-NiO, (c) 5 wt% W-NiO, and (d) 7 wt% W-NiO thin films.

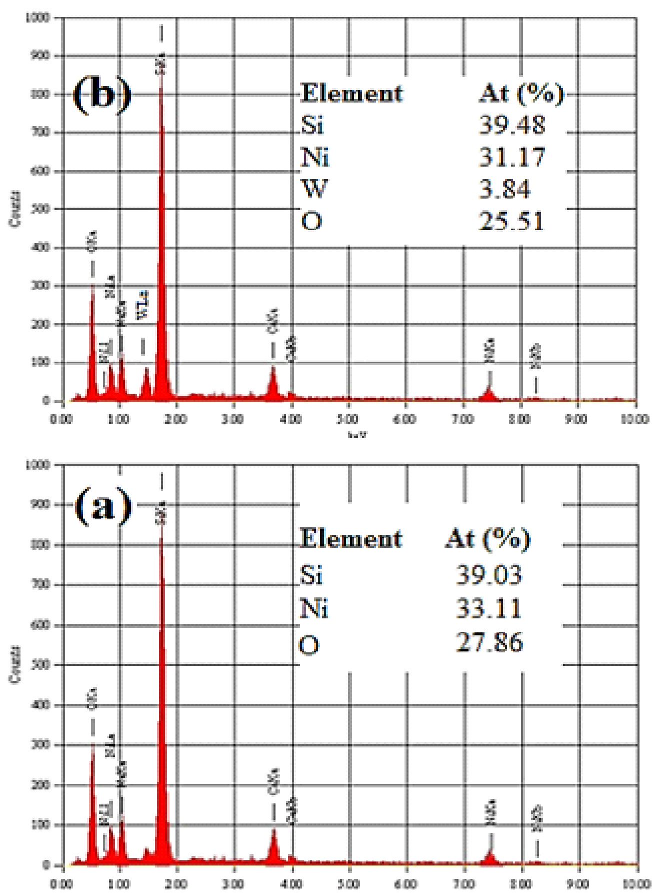


Fig.5 (a and b): EDX spectra of pure and 7 wt% W doped NiO thin films.

3.5 DC Conductivity

I-V characteristics of pure and W doped NiO thin films were measured by Keithley electrometer 6517B with two probe setups at applied voltage range 10 to 100 V. The measured I-V characteristics curve depicted in Fig 6. The curve indicates the increased voltage with linearly increasing the current value. This behavior represents the semiconducting nature of the deposited thin film. The pure and W doped NiO thin films conductivity was calculated by following equation (1) [22].

$$\sigma = \left(\frac{I}{V}\right) \times \left(\frac{d}{A}\right) \qquad (4)$$

where I is current, V is applied voltage, d is inter-probe distance and A is cross-sectional area of the thin film.
Fig. 7 reveals that the conductivity of the film increased with increasing W doping concentrations such as 0, 3, 5, and 7 wt%. The obtained average conductivity values are 9.30×10^{-9}, 2.32×10^{-8}, 3.52×10^{-8}, and 3.91×10^{-8} for corresponding W doping levels for example 0, 3, 5, and 7 wt%. The conductivity results represent that the extrinsic doping has good electrical conductivity compared to the pure NiO.

3.6 J-V Characteristics of p-NiO/n-Si and p-WNiO/n-Si Diode

The J-V characteristics of prepared p-NiO/n-Si and p-WNiO/n-Si diode were studied under halogen lamp by using Keithley electrometer 6517B. The measured I-V curve displayed in Fig 8 (a-b) and corresponding applied voltage from +6 to -6 V. Fig 9 (a-b). Shown the semi-logarithmic plot of current density (ln J) versus voltage (V). From the figure 8, the forward bias current increases as the applied voltage increases. These results suggest that the p-NiO/n-Si and p-WNiO/n-Si diode exhibits the good rectification behaviour and it's almost good result for an ideal diode. According to the thermionic emission theory (TE), the current density of p-NiO/n-Si and p-WNiO/n-Si diode calculated as follows [23, 24],

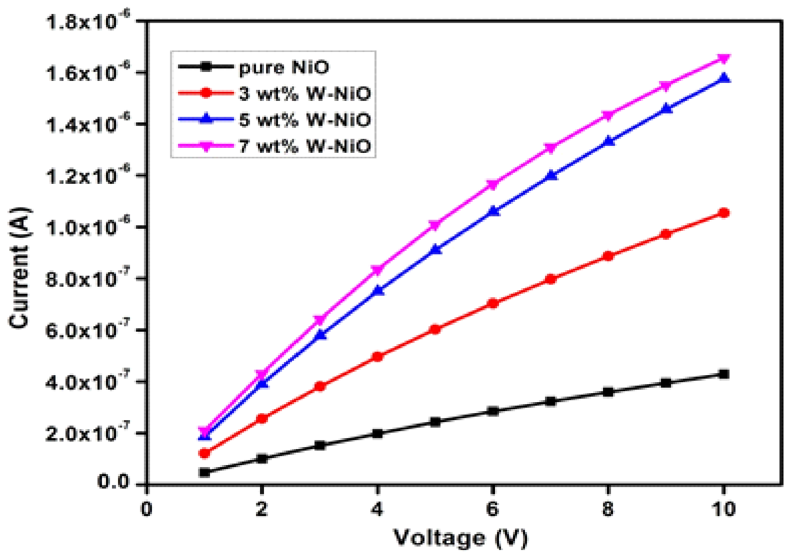


Fig. 6: I-V characteristics curve of pure and W doped NiO thin films.

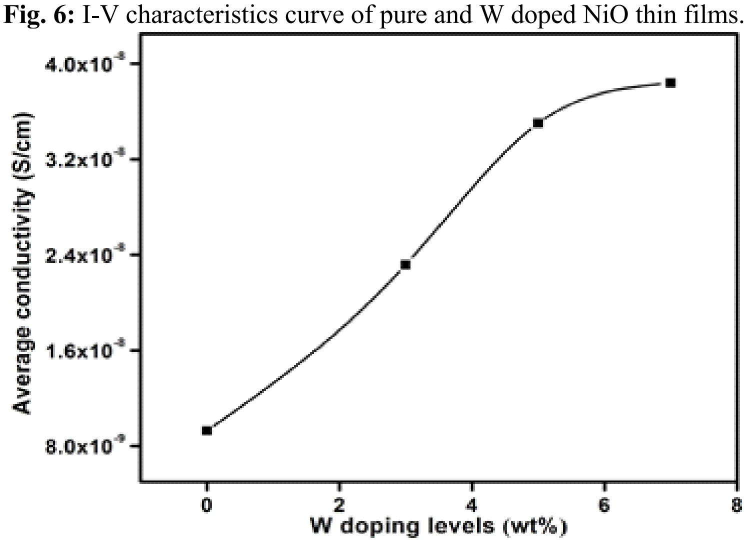


Fig. 7: Average conductivity of pure and W doped NiO thin films.

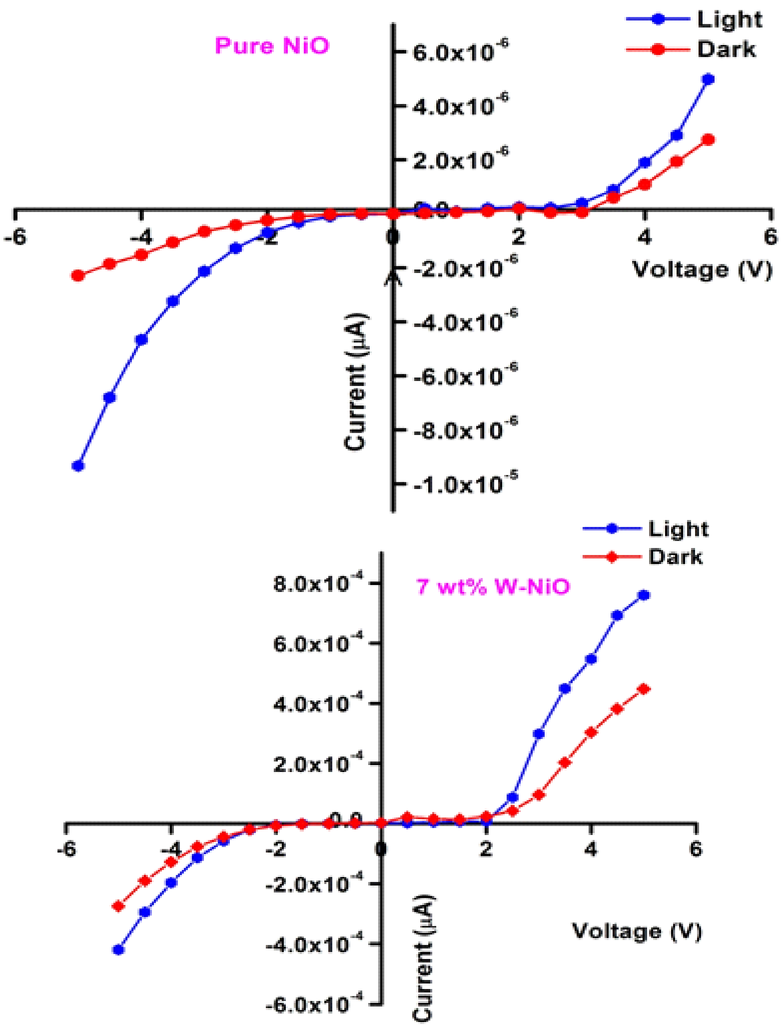
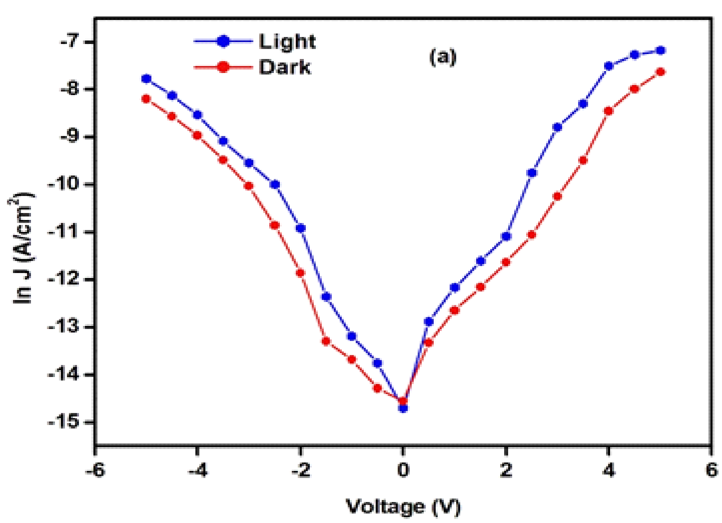


Fig. 8: I-V characterization of p-NiO/n-Si and p-WNiO/n-Si diode.



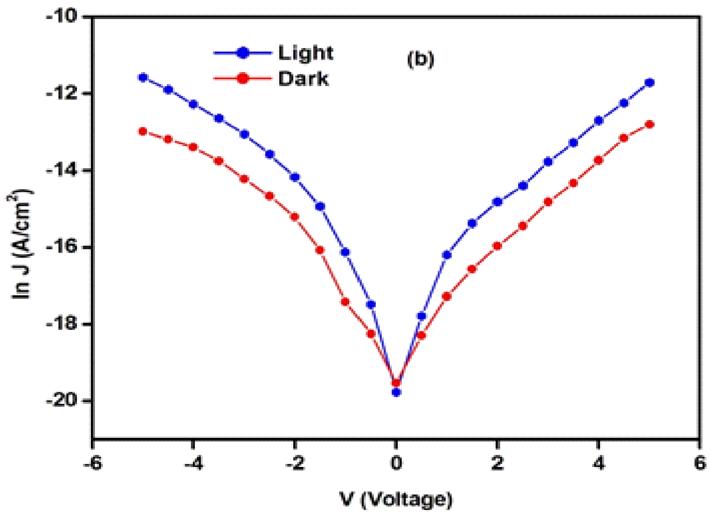


Fig.9: Ln J versus voltage of p-NiO/n-Si and p-WNiO/n-Si diode.

The calculated barrier height (Φb) and ideality factor (n) are shown table 1. From the table ideality value indicates more than one, it is due to the presence of a bias dependent barrier height, abnormalities of inorganic film thickness, non-uniformity of the interfacial charges and a wide distribution of barrier inhomogeneities. Therefore, the outcomes recommended the p-NiO/n-Si and p-WNiO/n-Si diode has potential device for optoelectronic applications.

Table 1: p-NiO/n-Si and p-WNiO/n-Si diode properties.

Diode		Ideality factor	Barrier height
p-NiO/n-Si	Light	3.6	0.77
	Dark	2.9	0.68
p-WNiO/n-Si	Light	2.1	0.60
	Dark	1.7	0.52

5 Conclusions

In summary, cubic phase with good conducting W-NiO thin films were successfully prepared by NSP pyrolysis technique with different doping concentrations of W. The effect of W doping on NiO thin films properties such as structural, optical, morphological and electrical properties are systematically investigated. XRD results revealed that the prepared films are polycrystalline nature with cubic phase and increase the W doping level with the predominant peak (222) shifted from 37.32° to 37.69°. The observed band gap value suggests the band gap value vary from 3.59 to 3.0 eV. The morphology results display the NiO surface is strongly disturbed by W doping and EDX spectra confirms the W-NiO film formation. The DC electrical conductivity results indicated the maximum conductivity of 7.60 X 10-6 S/cm was obtained from 7 wt% W doped NiO film. The fabricated p-NiO/n-Si and p-WNiO/n-Si diode results suggest the fabricated diode potential candidate for optoelectronic application.

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