

Research Article

Effect of thermal treatment on thin films of NiO:WO₃ for optoelectronic applicationsK.S. Usha^{a,b,*}, Sang Yeol Lee^{a,b,*}, R. Sivakumar^c, C. Sanjeeviraja^d^a Department of Semiconductor and Electronic Engineering, Gachon University, Seongnam-si, Gyeonggi-do, 13120, Republic of Korea^b Gachon Advanced Institute of Semiconductor Technology, Gachon University, Seongnam-Si, Gyeonggi-Do, 13120, Republic of Korea^c Department of Physics, Directorate of Distance Education, Alagappa University, Karaikudi, 630003, India^d Department of Electronics and Communication Engineering, Alagappa Chettiar Government College of Engineering and Technology, Karaikudi, 630003, India

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ABSTRACT

Nickel oxide (NiO), a semiconducting metal oxide, with its exceptional optical, electrical, and magnetic properties make it highly sought after for use in optical, optoelectronic, and electrochromic devices. Recent advancements in NiO-optical devices relies on the optical parameters like intrinsic optical nonlinearities. The current study involves the deposition of NiO:WO₃ thin films utilizing radio frequency (RF) sputtering at various substrate temperature (T_s) of 100, 200, and 300 °C. An investigation was carried out to analyse the significance of T_s on the structural, optical, morphological, & vibrational characteristics. The X-ray diffraction investigation revealed the amorphous nature of the films. Scanning electron microscopy confirms the compact pinhole free surface of the films. The results of energy dispersive X-ray spectroscopy (EDS) spectra verified the existence of nickel (Ni), oxygen (O), and tungsten (W) components in the films. XPS analysis confirms the presence of both Ni²⁺ and Ni³⁺ states. The optical transmittance increased, and the band gap decreased with increase in T_s . The impact of T_s on various optical parameters such as refractive index, extinction co-efficient, dielectric constants, optical non-linear susceptibility, and dispersion energy parameters obtained by the Wemple-DiDomenico theory has been calculated and extensively investigated. The results indicate that NiO:WO₃ films can be used to fabricate electrochromic and optoelectronic devices.

1. Introduction

In the last two decades, semiconducting metal oxides (SMOs) have dominated the fields of technology, industry, agriculture, and medicine [1]. SMOs exhibit numerous remarkable electrical, optical, mechanical, and magnetic properties that render them appropriate for diverse applications in areas such as photocatalysis, solar energy conversion, optoelectronics, energy storage, light-emitting diodes, sensing, data storage, and biomedical devices [2–8]. Nickel oxide (NiO) is a superior material among many spinel metal oxides (SMOs) owing to its chemical stability, thermal stability, cost-effectiveness, and magnetic and electrical characteristics [1]. It is essential in several contemporary applications such as communications, supercapacitors [1], memory chips [9], solar cells [10], smart windows [11], LEDs [12], and gas sensors [13].

Nickel oxide is a wide bandgap material with a band gap ranging from 3.4 to 4.0 eV. Their extensive energy bandgaps render them

inappropriate for use as photocatalysts and visible light absorbers in solar cells. This problem may be addressed by using doping or by adjusting thin film deposition parameters such as substrate temperature, making it suitable for diverse optoelectronic and optical applications. Using the sol-gel technique, S. Zargouni et al. [14] investigated the thin films of NiO that were doped with ytterbium. Their results revealed an average transmittance over 80 %, as well as a band gap energy ranging from 3.86 to 3.92 eV. In addition, K.H. Kim [15] performed an investigation on NiO films which was fabricated with the sol-gel technique and then doped with copper. By introducing copper as a dopant, they achieved a significant reduction in resistivity, from 320 (Ω cm) - 23 (Ω cm). As well, the material exhibited an optical transmittance of about 80 percent and a little drop in bandgap energy values, from 3.73 to 3.69 eV. M. Touati et al. noted that incorporating cobalt into NiO films led to a substantial increase in transmittance, achieving values between 70 and 85 % in both the visible and near-infrared (NIR) spectra. The doping

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technique resulted in a decrease in the band gap value from 3.80 eV to 3.76 eV [16]. Furthermore, M.G. Althobaiti et al. [1] indicated that cobalt-doped NiO nanostructured films exhibited a decreased energy band gap, suggesting its potential use in linear and nonlinear optics as well as data storage.

The principal techniques used to fabricate NiO thin films were spin coating method [17], RF sputtering [18], electrodeposition [19], chemical bath deposition (CBD) [20]. RF magnetron sputtering is considered the most superior approach for developing NiO thin films as compared to other manufacturing methods. RF sputtering provides several significant benefits, including films with high purity and no pores, the ability to coat substrates that are sensitive to heat, precise control over the stoichiometry, structure, composition, have sturdy adhesion, economical, and have control over film thickness and possible deposition across large surface areas. The properties of the deposited materials can be enhanced by tuning the sputtering parameters such as the substrate temperature (T_s), chamber pressure, substrate to target distance, etc. Among these, the substrate temperature (T_s) is a crucial parameter for optimizing various aspects of inorganic semiconducting thin films. It has the potential to impact the surface roughness, the mobility (μ), the densities of charge carriers (n), the transmittance, the absorption coefficient (α), the extinction coefficient (k), and the bandgap (E_g) of deposited films. The optical properties of metal oxides like refractive index, and energy band gap elucidate the interaction of electromagnetic waves and the examined materials. The optical characteristics of solids elucidate lattice vibrations, energy band structure, excitons, localised defects, specific magnetic excitations, and impurity levels. An investigation of the optical characteristics of nickel oxide is essential due to its significant impact in the advancement of lasers, solar cells, light-emitting diodes, and electrochromic devices. Also, the intrinsic electronic excitation spectrum of a material is often represented by the frequency-dependent complex dielectric constant. The frequency-dependent dielectric constants in the Wemple–DiDomenico (WDD) single oscillator model represent the dispersion energy parameters [21]. These dispersion characteristics are crucial, since they are very beneficial for simple empirical laws applicable to a broad range of semiconducting materials [21]. Although these empirical principles vary significantly across different materials, this is abundantly proved [21]. The energy dispersion of optical characteristics plays a vital role in optical materials research, owing to its importance in optical communications and the development of novel devices for spectrum dispersion. By modifying the optical dispersion parameters, the efficacy of integrated optical devices such as monochromatic filters, electrical and optical switches, laser diodes, detectors, and amplifiers can be improved [22]. This enhancement is a common feature observed in both the crystal structure and the refractive index behaviour of semiconducting materials.

Investigating inorganic semiconductors like NiO with improved structural, morphological, vibrational, and optical characteristics might help achieve optimal and highly efficient optoelectronic devices. In light of this, in the present study, we fabricated nickel-tungsten oxide (NiO: WO₃) thin films with 85:15 ratio by means of RF magnetron sputtering technique. Currently, there is an inadequate comprehension of the detailed analysis about the optical characteristics for the NiO:WO₃ thin films due to the changes in substrate temperature. Hence, this work primarily aims to highlight the thermal effect on optical properties and the various optical parameters derived from that. In addition, the evaluation and detailed discussion of the thermal effect on dispersion energy parameters was carried out via the Wemple and DiDomenico (WD) approach. Further, a comprehensive analysis was conducted on the effect of temperature on structural, surface morphological, and vibrational characteristics, which play a crucial role in determining the efficiency of optoelectronic and electrochromic devices.

2. Experimental

An indigenously prepared nickel tungsten oxide target (NiO: WO₃) was used for the preparation of nickel tungsten oxide thin film via radio frequency (rf) magnetron sputtering. Ultrapure NiO and WO₃ chemicals were obtained from Sigma Aldrich. The NiO: WO₃ (85:15) target was prepared by adding a 15 % concentration of WO₃ chemical to 85 percent NiO. The target was positioned at a distance of 6 cm from the glass substrate. The sputtering chamber was first evacuated to a base pressure of 5×10^{-6} Torr. Subsequently, inert argon gas (sputtering gas) is introduced within the chamber. The operational pressure is upheld at 10 mTorr. To begin plasma, an RF power of 200 W is applied. The electrons present in the sputtering gas are pushed away from the nickel tungsten oxide target, resulting in collisions with adjacent Argon atoms. These encounters generate electrostatic repulsion which dislodges electrons from Ar atoms, leading to ionisation. Positively charged Ar⁺ ions are now directed towards the negatively charged electrode/target, leading to high-energy collisions with the target surface. These collisions dislodge atoms from the target, which emerge into the vacuum environment with necessary kinetic energy to access the surface of the substrate. The deposition proceeded at room temperature for 30 min. Similar deposition conditions were carried out with different substrate temperatures varied at 100 °C, 200 °C, and 300 °C.

The measurement of film thickness was performed using Mitutoyo SJ-301 by the technique of Stylus profilometry. The structural characteristic was examined using an X-ray diffractometer (XRD). Surface morphology was examined using Tescon Vega3 instrument. The optical characterisation was performed utilizing JASCO-V-670 & Varian Cary Eclipse spectrophotometers. The micro-Raman analysis was conducted using STR Raman spectroscopy.

3. Results and discussion

3.1. Structural analysis

The NiO: WO₃ thin films prepared at substrates temperatures (T_s) of 100, 200, and 300 °C had thickness of 1.16, 1.20, 1.23 μ m, respectively. The thickness of the films increases with increasing substrate temperatures. Consequently, films deposited at a higher temperature result in a thicker film than those deposited at a lower temperature. As the substrate temperature increases, the film's adherence increases as a result of an increase in nucleation sites, resulting in increased thickness [23]. Fig. 1 depicts the X-ray diffraction patterns of prepared films, which

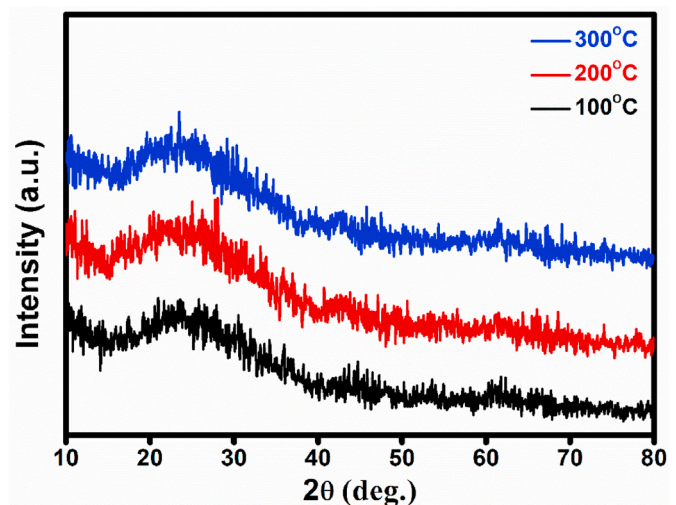


Fig. 1. X-ray diffraction pattern of NiO:WO₃ thin films prepared at various substrate temperatures.

evidently indicate the amorphous nature. Based on our previous study, undoped NiO film have a polycrystalline nature and possess a cubic structure [24]. As reported by M.M. El-Nahass et al. and M. Emam-Ismael et al. pristine NiO thin films possess polycrystalline face-centered cubic (FCC) structure [25,26]. From Fig. 1, it is evident that incorporation of WO_3 into the NiO matrix interferes with the crystallization process and promotes amorphization. S.V. Green et al. [27] reported that the sputter deposited $\text{Ni}_x\text{WO}_{1-x}$ thin films with $x = 1$ (pure nickel oxide) film was polycrystalline, and that W (16 %) addition led to an amorphous structure at $x \approx 0.84$. Amorphization upon W addition has been reported previously [28,29], and it was suggested that the W atoms weakened the long-range order in the Ni–O matrix. The ionic radius of W^{6+} (0.62 Å) is close to that of Ni^{2+} (0.69 Å), and it is hence likely that W^{6+} could substitute for Ni^{2+} . However, the high oxidation state of W (i.e., 6+) would induce a large perturbation to the lattice around a tungsten cation inserted in a site left free by nickel because of the large difference between the stable valence states, 2+ and 6+, respectively, and they seem to change the overall structure to a less dense state [29]. It is evident from Fig. 1 that the prepared films were amorphous in nature even at a substrate temperature of 300 °C. Similar observations were reported by Green et al. [28] that $\text{Ni}_x\text{WO}_{1-x}$ films, which were deposited at room temperature and subsequently annealed to a maximum of 700 °C, maintained their amorphous state even when $x = 0.75$. They become crystalline upon high-temperature treatment at 800 °C.

3.2. Surface morphological analysis

Morphological studies were undergone for the $\text{NiO}:\text{WO}_3$ (85:15) thin films coated at T_s of 200 °C and 300 °C. Fig. 2 (a, b) displays the SEM images of deposited films. Regardless of the substrate temperature, all the films exhibit a compact, homogenous, platelet-like structure with a smooth structure, indicating that the film is amorphous. Upon increasing

the substrate temperature, no cracks or holes were observed in the film, suggesting that the film exhibits a uniform and pinhole-free nature.

EDAX analysis of $\text{NiO}:\text{WO}_3$ (85:15) thin films coated at 200–300 °C was displayed in Fig. 2 (c). The atomic percentages for nickel, tungsten and oxygen were found to be 41.35 %, 3.42 %, and 55.23 %. The EDAX study validates the existence of nickel, tungsten, and oxygen, as well as the compositional purity of the deposited films.

3.3. XPS

Fig. 3 (a) shows the XPS survey scan spectra of $\text{NiO}:\text{WO}_3$ (85:15) thin films deposited on glass substrate at substrate temperature (T_s) of 300 °C. Furthermore, Fig. 3 (b) shows the deconvoluted core level spectra of nickel (Ni). The prominent peaks detected at 853.54, 855.65, and 859.74 eV correspond to the $\text{Ni } 2p_{3/2}$ levels. Furthermore, two peaks seen at 871.65 and 878.17 eV correspond to the $\text{Ni } 2p_{1/2}$ band levels. Also, the energy difference between $\text{Ni } 2p_{3/2}$ and $\text{Ni } 2p_{1/2}$ is determined to be 18.9 eV, in line with previous findings [30,31]. An evident minor peak at 855.65 eV coincides with the peak at 853.54 eV of Ni^{2+} , indicating the coexistence of Ni^{3+} with Ni^{2+} . As given in Fig. 3 (c) the distinctive peak at the core level of O-1s was seen at about 529.35 eV, which corresponds to the stoichiometric NiO (Ni^{2+} state) identified in the oxygen core level spectra [32]. A peak at about 531.18 eV, associated with Ni^{3+} , was seen in the fit core level spectra of O-1s [31]. The core level spectra of W-4f, Fig. 3 (d), show the doublets at the binding energies of 35.2 and 37.3 eV, corresponding to $\text{W } 4f_{7/2}$ and $\text{W } 4f_{5/2}$, respectively. Hence, the observed binding energy values of tungsten confirm the presence of six-valent tungsten (W^{6+}) state in the $\text{NiO}:\text{WO}_3$ film.

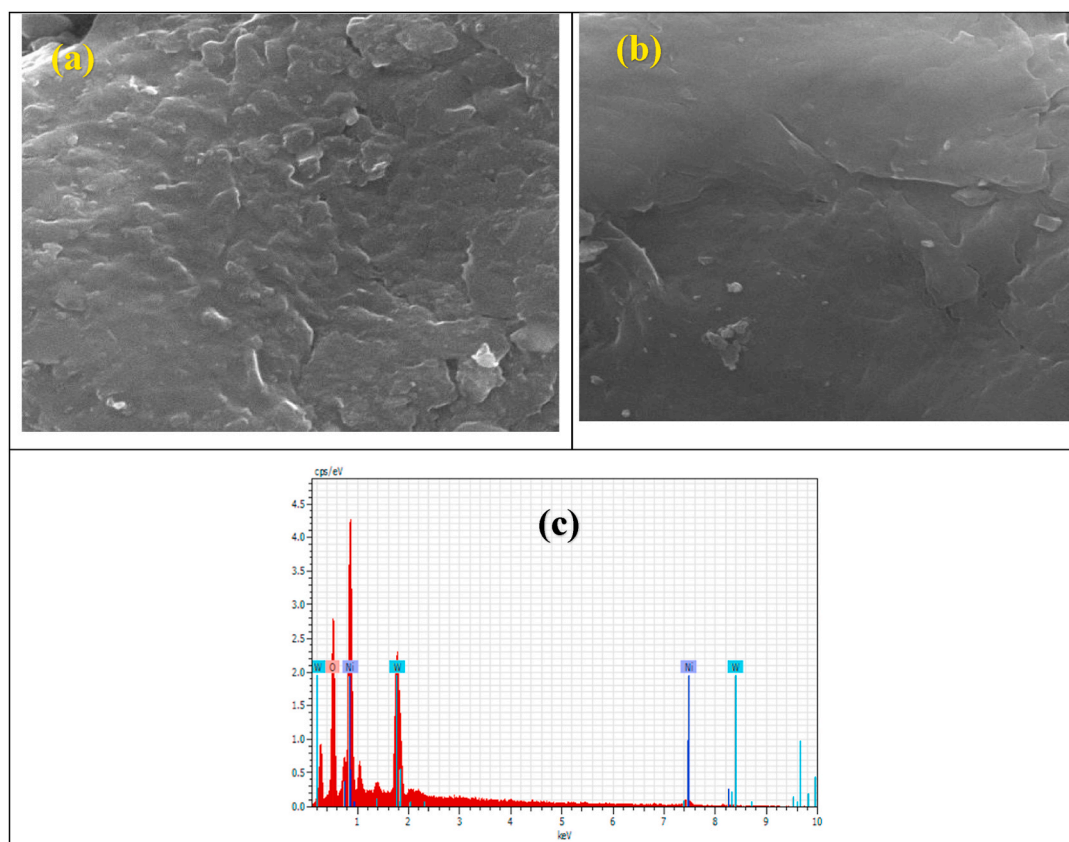


Fig. 2. SEM images of $\text{NiO}:\text{WO}_3$ thin films prepared at substrate temperatures of (a) 200 °C, (b) 300 °C, and (c) EDAX spectra of $\text{NiO}:\text{WO}_3$ thin films deposited at 300 °C.

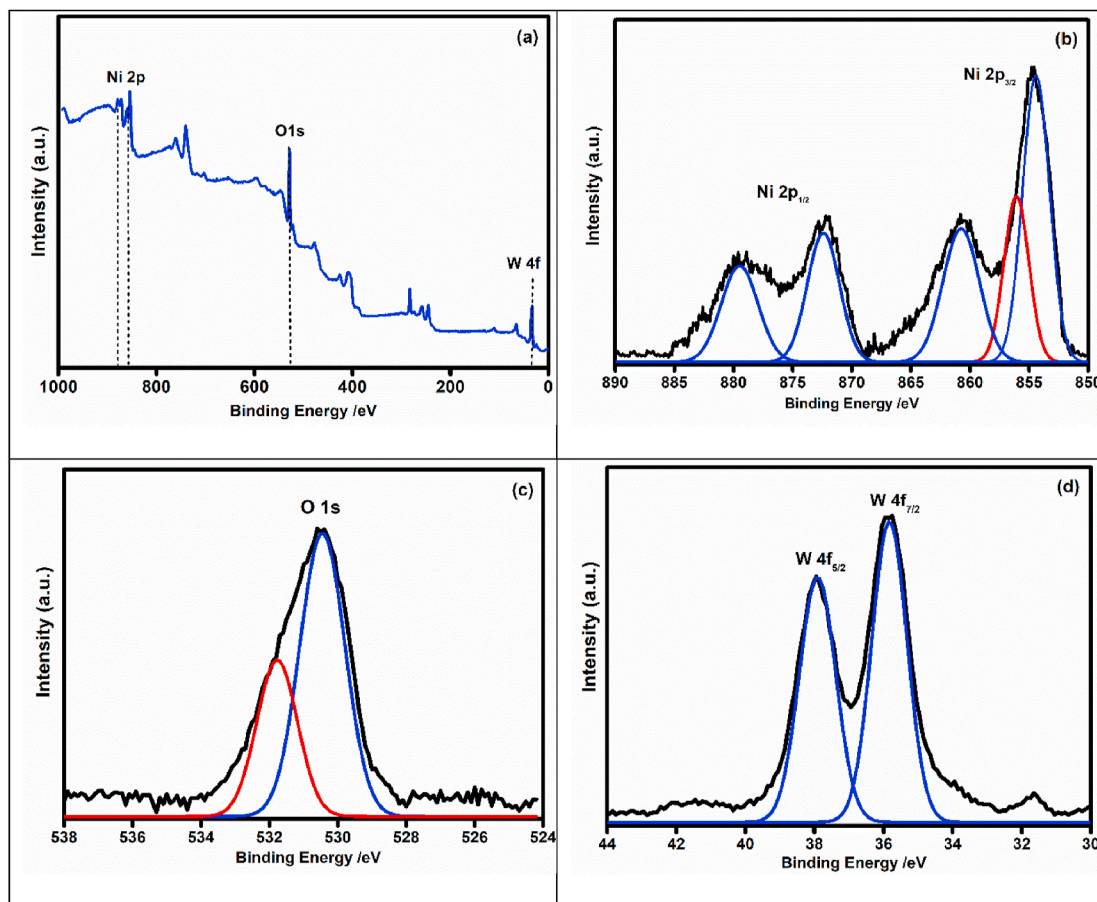


Fig. 3. (a) XPS survey scan spectra of NiO:WO₃ thin film deposited on glass substrate at 200 W- 300 °C; (b) XPS core level spectra of Ni; (c): XPS core level spectra of O; (d): XPS core level spectra of W.

3.4. Optical properties of NiO:WO₃ thin films

3.4.1. Optical transmittance

All the deposited NiO:WO₃ (85:15) films are visible-transparent. The films had an average transmittance of 73 %, 76 %, and 77 %, respectively. The interference fringes present in the transmittance spectra show the deposited films are homogeneous in nature. From Fig. 4 it is

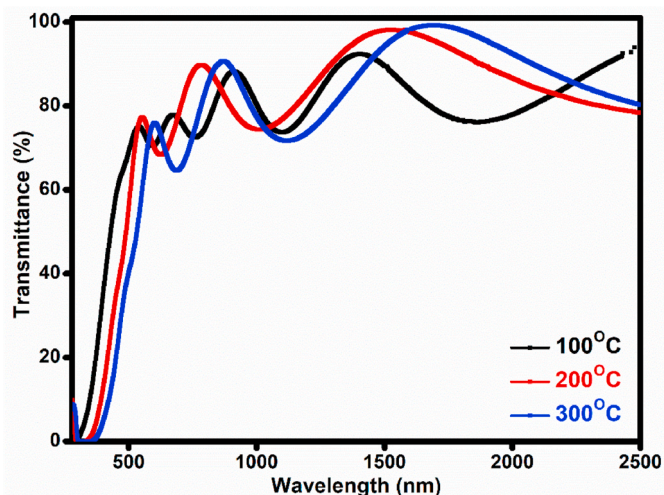


Fig. 4. Transmittance spectra of NiO:WO₃ thin films prepared at various substrate temperatures.

evident that the transmittance of the films increases with increasing T_s , which is attributable to the reduced free carrier absorption [24]. Furthermore, elevated substrate temperatures yield smoother film surfaces, leading to less scattering and hence an enhanced transmittance. Reddy et al. discovered the transmittance of sputtered Cu-doped NiO thin films, exhibited an increase in transmittance with increasing T_s [33]. In addition, H-L Chen et al. observed an increase in the transmittance of sputtered NiO samples when the T_s value increased [34]. This increase in transmittance is also associated with the presence of oxygen defects inside the structure, leading to the formation of Ni³⁺ ions & the creation of color centers [35]. Therefore, an increase in substrate temperature-induced transmittance can be attributed to reduced defect scattering (Ni³⁺). Also, as depicted in Fig. 4 the transmittance threshold shifts towards higher wavelength (red shift) indicating systematic drop in the band gap (E_g).

The absorption coefficient (α) may be determined using the following formula [36]:

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

Here, t represents the thickness. Fig. 5 displays the correlation between the measured optical absorption coefficient and the incident wavelength. The lower α values in the Vis-NIR range result from the films' lower absorption or higher transparency. Furthermore, the reduction of absorbance coefficient across the Vis-NIR correlates well to an upsurge in transmittance values.

An exponential relationship between photonic energy and absorption coefficients near the band edge can be derived from the following equation: [36],

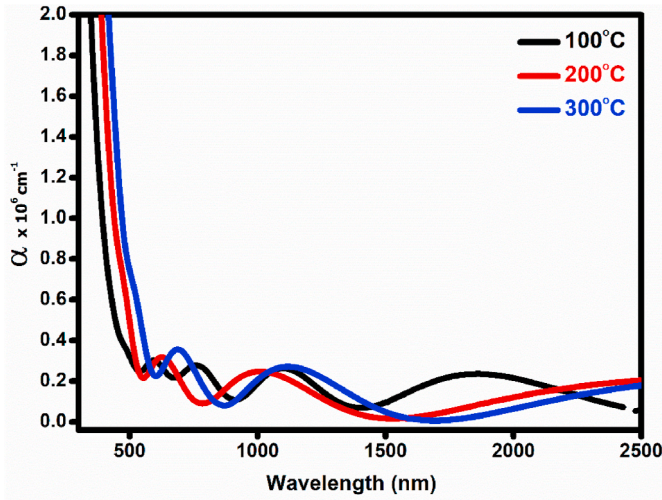


Fig. 5. Absorption co-efficient spectra of NiO:WO₃ thin films prepared at various substrate temperatures.

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_u}\right) \quad (2)$$

Here E_u , stands for Urbach energy, which indicates the magnitude of existing localized states band tail within the band gap, whereas α_0 denotes a fixed value. By plotting $\ln(\alpha)$ against $h\nu$, we can find E_u (not shown). The estimated E_u values are displayed in Table 1. Typically, in optical absorption, an electron located at the highest energy level in the valence band is stimulated to go to the lowest energy level in the conduction band, navigating the energy band gap. At this time, when disorder is present in the material this will create localized tail states, and because of this density of the electronic states in Valence and conduction band extends or tails into the energy gap. This tail is termed as Urbach tail and the energy associated with this referred to as Urbach energy. Hence, Urbach energy is indicative of disorder, amorphousness, low crystallinity, or poor crystallinity in a material, since localized tail state occupy their band gap [37]. When the substrate temperature rises, the Urbach energy increases due to an increase in defects (localized states).

According to Tauc model the optical gap (E_{opt}) for non-direct amorphous semiconductors, which describes the lowest-energy transition between the valence and conduction band can be determined using the following relation [30].

$$\alpha(E)h\nu \propto (h\nu - E_{opt})^2 \quad (3)$$

The variable ν represent frequency. Fig. 6 displays the Tauc plot for films deposited at various T_s , while Table 1 presents the calculated values of the optical gap (E_{opt}). These results indicate that elevated substrate temperature leads to a reduction in the optical absorption edge, and consequently resulting in modifications in the band structure. Normally, optical transitions of metal oxide are linked to the different energy levels inside the material. The primary transition is associated with the near band edge (NBE) located between the conduction band (CB) and valence band (VB). The rest of the transitions are associated with energy states that result from intra-band defects, like metal deficiencies or excessive

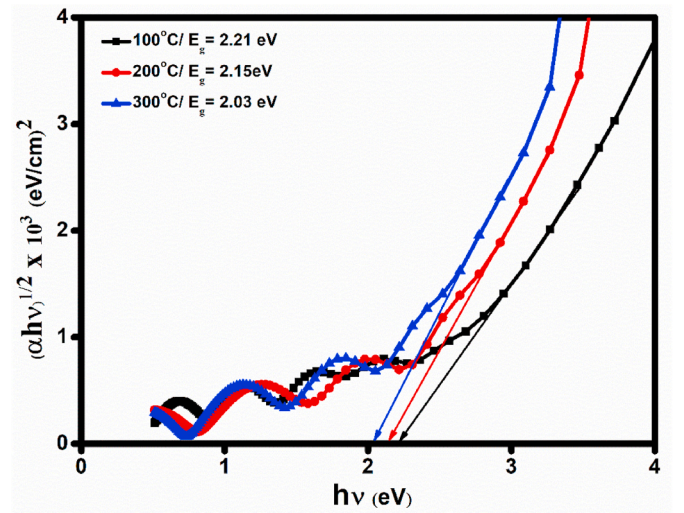


Fig. 6. Energy band gap of NiO:WO₃ thin films prepared at various substrate temperatures.

oxygen in p-type semiconducting metal oxides, or the formation of defect levels resulting from the incorporation of dopants. The shrinkage of E_g values is due to Moss-Burstein shift effect. Jonscher suggests that the reduction in the optical energy band gap might be attributed to the formation of localized states at the deep energy level [38]. The influence of substrate temperature results in the formation of localized states along the band edges of NiO:WO₃. Consequently, this leads to a modification of the energy gap of the film. This modification is probably related to the lowering of the conduction band and the simultaneous elevation of the valence band. Moreover, it is important to mention that the color of the deposited films is closely linked to the change in the transmission threshold, suggesting which the NiO:WO₃ films were well-suited for optoelectronics and ECD applications.

Since interference patterns have been identified in the prepared films, the refractive index (n) is assessed using the Swanepoel envelope technique [39].

$$n = \left[N + (N^2 - n_s^2)^{\frac{1}{2}} \right]^{\frac{1}{2}} \quad (4)$$

$$N = 2n_s \frac{T_M - T_m}{T_M T_m} + \frac{n_s^2 + 1}{2} \quad (5)$$

$$k = \frac{\alpha \lambda}{4\pi} \quad (6)$$

In this context, n_s represents the refractive index of the substrate used for the deposition of thin films; T_M and T_m are corresponding maximum and minimum enveloped transmittance; λ represents the wavelength of the incident wave. Using the experimentally calculated n values, Cauchy's fitting was done by the second order Cauchy dispersion relation ($n = a + b/\lambda^2$). Fig. 7 depicts the n data retrieved from Cauchy's fitting with respect to T_s . Fig. 7 shows a clear correlation between a rise in T_s and a drop in n , indicating a reduction in NiO:WO₃ (85:15) film density. A linear correlation between refractive index and packing density for Titanium-Doped Tungsten Oxide Thin Films was reported by C. V. Ramana et al. [40]. Hence, the decrease in refractive index with increasing T_s may be attributed to a reduction in the film's packing density. Comparable findings were documented by D. Mergel et al. [41], who also observed a decrease in the refractive index with increases in temperature. Based on his analysis, it can be inferred from the data that during rapid deposition, a certain quantity of point defects is incorporated into the thin film, resulting in development of energy levels at the band boundaries. This phenomenon results in additional absorption in

Table 1

Optical parameters of NiO:WO₃ thin films deposited at different preparative conditions.

Substrate temperature	E_g	E_u	ϵ_∞	n_o	$S_o \times 10^{13}$	λ_o
100°C	2.21	0.436	3.328	1.82	1.39	408
200°C	2.15	0.445	3.21	1.79	2.25	313
300°C	2.03	0.600	2.97	1.72	2.31	292

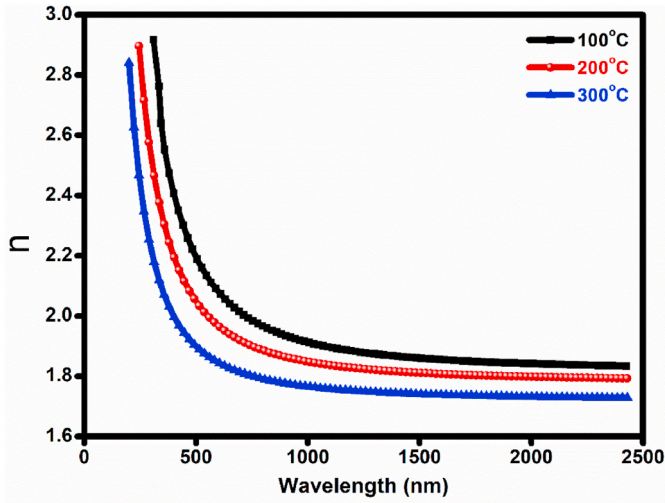


Fig. 7. Refractive index of NiO:WO₃ thin films prepared at various substrate temperatures.

the vicinity of the fundamental inter-band absorption and raises the refractive index within the visible spectrum range because of the Kramers-Kronig relationship. In our case, upon increasing the substrate temperature, the transmittance increases which decreases the absorption, which in turn decreases the refractive index.

Fig. 8 depicts the correlation between k and T_s . The observed extinction coefficient values along visible region is determined to be extremely small, around 10^{-2} , suggesting that the processed samples have a relatively uniform surface [42]. Fig. 8 suggests that the drop in the k value could be attributed to a decrease in the surface roughness. This reduction in roughness leads to lower scattering losses which in turn enhances the light transmission of the film. This conclusion supports our findings from the optical transmittance spectra, where we found an increase in transmittance as the T_{sub} value rose.

Figs. 9 and 10 demonstrate that as T_s increases, the value of ϵ_1 decreases because the speed of incident light in the material slows down. Additionally, the imaginary component, ϵ_2 , drops as a result of a decrease in the absorption of light photons resulting from the movement of dipoles in response to the electric field [43].

$$\epsilon_1 = n^2 - k^2 \quad (7)$$

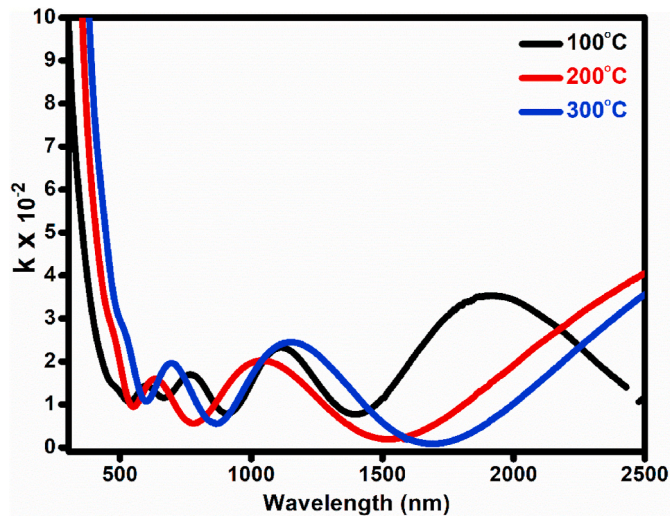


Fig. 8. Extinction coefficient of NiO:WO₃ thin films prepared at various substrate temperatures.

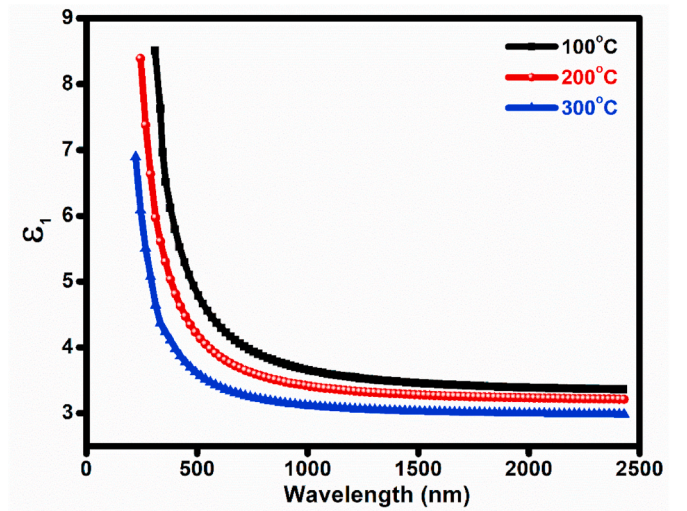


Fig. 9. Real part of dielectric constant of NiO:WO₃ thin films prepared at various substrate temperatures.

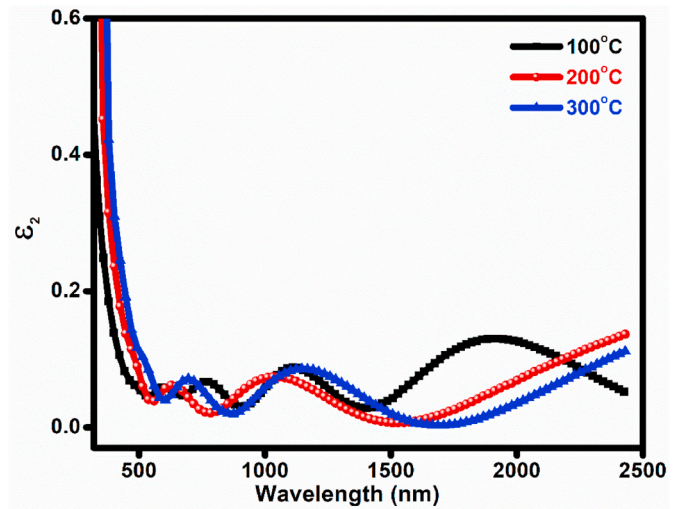


Fig. 10. Imaginary part of dielectric constant of NiO:WO₃ thin films prepared at various substrate temperatures.

$$\epsilon_2 = 2nk \quad (8)$$

The qualitative assessment of porosity can be transformed into quantitative data via the measurement of the optical property, namely the refractive index, of deposited thin film. The refractive index of a substance is inversely correlated with its porosity or directly related to packing density, as porosity increases, the refractive index decreases [44]. Packing density may be computed using the formula [45,46].

$$n^2 = \frac{[(1-p)n_v^4 + (1+p)n_s n_s^2]}{(1+p)n_v^2 + (1-p)n_s^2} \quad (9)$$

The formula includes the following variables: packing density (p), void refractive index/refractive index in vacuum ($n_v=1$), substrate refractive index ($n_s=1.5$), and NiO:WO₃ film refractive index (n). The optical packing density directly reflects the compactness of the deposited thin films. Fig. 11 illustrates the relationship between the packing density and the T_{sub} . Increased T_{sub} leads to decrease in packing density. One possibility for the decrease in packing density is the oxygen's out-diffusion from the lattice's interstitial location [47]. Generally, the film's density increases as the temperature increases. However, in

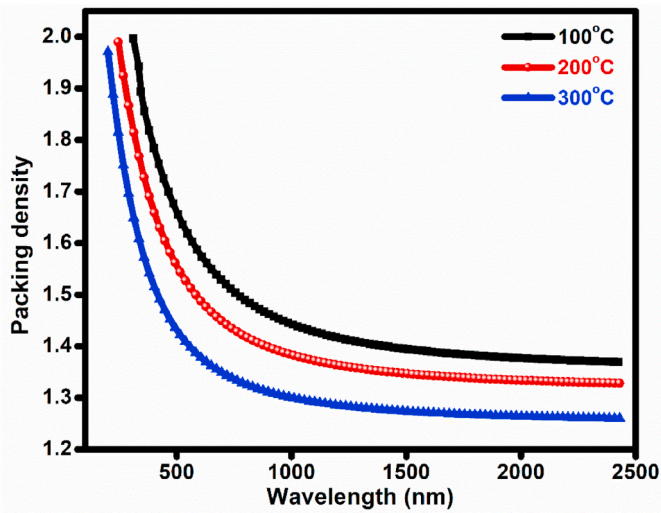


Fig. 11. Packing density of NiO:WO₃ thin films prepared at various substrate temperatures.

present case, the temperature is inadequate to enhance the movement of ad-atoms, causing them to bind together and raise the density of the deposited film. This results in a diminution in the measured film density value [24]. Our measured transmittance supports this interpretation.

Electronic polarizability is intricately connected to its use in the domains of optics and electronics. Electronic polarizability is a primary factor contributing to the nonlinear optical characteristics of materials when subjected to intense electromagnetic radiation. Therefore, it is essential to develop and fabricate efficient nonlinear optical materials grounded on the interconnections among nonlinear optical, optoelectronic, and electronic features that should be readily comprehensible and accessible. The electronic polarizability (α_p) of NiO:WO₃ thin films which gives the degree of the electronic response to the application of an electromagnetic field on the electron clouds may be estimated using Lorenz-Lorentz equation and Clausius Mossotti local field model: [35],

$$\left(\frac{n^2 - 1}{n^2 + 2}\right) = \frac{L\rho}{3M}\alpha_p \quad (10)$$

M, L, and ρ represent the molecular weight, Avogadro number, and density, respectively. Fig. 12 displays the electronic polarizability α_p as a function of substrate temperature. The polarizability of an atom is

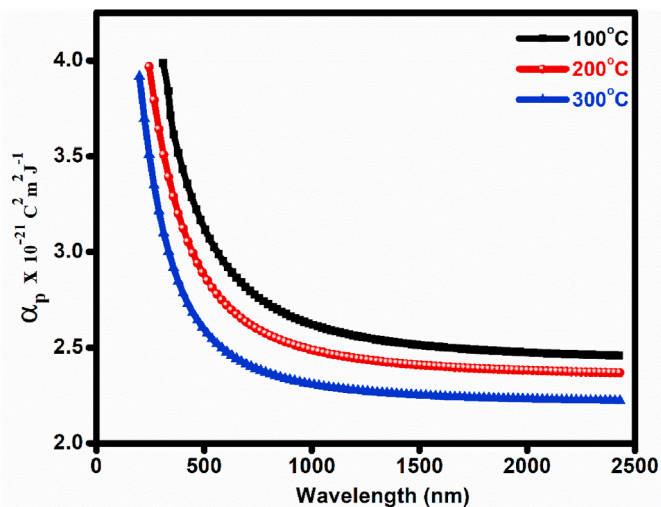


Fig. 12. Electronic polarizability of NiO:WO₃ thin films prepared at various substrate temperatures.

directly proportional to the number of electrons it carries. Larger atoms, which have a greater volume and more electrons, tend to have loosely bound electrons. In contrast, smaller atoms have tightly bound electrons. Here, as T_{sub} increases, NiO:WO₃ films exhibit reduced electronic polarizability, which may be attributable to a reduction in the electron volume. Also, electronic polarizability is directly related to refractive index. We can observe from Fig. 12 that the electronic polarizability follows the same pattern as refractive index. Hence the observed changes in α_p with increasing substrate temperature may be due to decrease in the refractive index.

The optical conductivity of a material is defined as its conductivity resulting from the absorption of incoming photons. In semiconductor materials, conductivity increases with incoming photons owing to the excitation of electrons from the valence band to the conduction band via absorbed photon energy. The real part of optical conductivity (σ_{op}), which represents the optical response of the manufactured films under the incident light may be determined by [36].

$$\sigma_{\text{op}} = \epsilon_0 \alpha n c \quad (11)$$

As seen in Fig. 13, it is evident that as the value of T_{sub} increases, the observed σ_{op} remains almost unaltered in the lower energy zone, while it increases over the higher energy region. This suggests that the free charges are easily accessible in this location with a low energy level. This property is advantageous for the fabrication of photovoltaic devices. Also, the reduced optical conductivity in the higher wavelength region is due to lower absorption. This corroborates well with our transmittance data. Moreover, when the substrate temperature rises, the optical conductivity escalates. This may result from the enhancement of crystal structure and the reduction of defect density. As the density of defects, which serve as recombination centers for optically emitted electrons, diminishes with an increase in substrate temperature, the σ_{op} rises. The value of optical conductivity that was obtained for all volume ratios is about 10^4 , which may be attributed to the excitation of electrons by photon energy.

The inelastic scattering process on a surface, including the transmission of energy quanta to or from the uppermost atomic layers of a solid, provides insights into potential excitations of a surface or interface, encompassing both electronic and vibronic excitations. The spectrum response of the material in an inelastic electron scattering experiment may be described by the dielectric theory known as the energy loss function. The energy loss function encompasses the whole energy spectrum, including valence inter band transitions and core level excitations. Two parameters, volume energy loss (VELF) and surface-

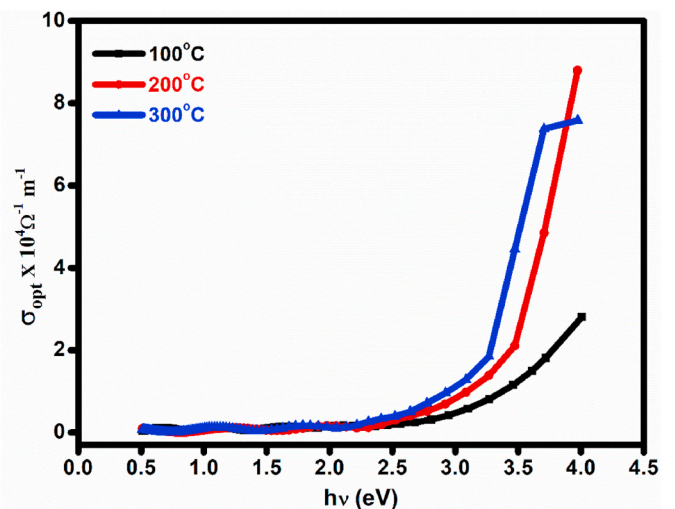


Fig. 13. Optical conductivity of NiO:WO₃ thin films prepared at various substrate temperatures.

energy loss functions (SELF), are often used to demonstrate the energy absorption by the material resulting from electron transitions. The initial parameter VELF elucidates the potential for rapid electrons to dissipate energy while traversing the bulk material. The second parameter SELF is defined as the condition under which an electron traverses the material surface. The following formulation may be used to estimate the VELF and SELF [36].

$$VELF = \frac{\epsilon_2}{\epsilon_1^2 + \epsilon_2^2} \quad (12)$$

$$SELF = \frac{\epsilon_2}{[(\epsilon_1 + 1)^2 + \epsilon_2^2]} \quad (13)$$

Figs. 14 and 15 show the variations in VELF and SELF of NiO:WO₃ films coated at varying T_{sub}. The measured results show that increasing T_{sub} decreases VELF and SELF values, indicating a decrease in electron energy loss. Also, at higher energy regions the values increase which may be attributed to the relatively larger penetration depth of electromagnetic radiation and interactions with more involved electrons.

The dielectric constant for a material under higher frequencies (ϵ_∞) could potentially determined by applying the equation shown below [36].

$$\frac{(n_0^2 - 1)}{(n^2 - 1)} = 1 - \left(\frac{\lambda_0}{\lambda}\right)^2 \quad (14)$$

The variables λ_0 , S_0 , and n_0 represent the mean wavelength between bands, the mean intensity of oscillation, and the static refractive index, respectively. Fig. 16 illustrates the relationship between $(n^2 - 1)^{-1}$ and λ^{-2} in relation to T_{sub}. The point where the $(n^2 - 1)^{-1}$ axis intersects is given by $(n_0^2 - 1)^{-1}$. Consequently, the value of n_∞^2 at λ_0 is equal to ϵ_∞ .

The assessed n_0 values, contingent of the density as well as structure of material, decrease with a variation in T_{sub}. The result indicates an overall reduction in the density of the film, and it is consistent with observed packing density. In addition, the S_0 values may be deduced from equation (15) in the following manner:

$$S_0 = \frac{(n_0^2 - 1)}{\lambda_0^2} \quad (15)$$

Table 1 exhibits the assessed values of ϵ_∞ , n_0 , S_0 , and λ_0 . It has been shown that when the temperature (T_{sub}) increases, the dielectric constant at infinite frequency (ϵ_∞) falls. Moreover, the measured λ_0 and S_0 value was similar to those reported for NiO thin film deposited using different substrate temperatures [48].

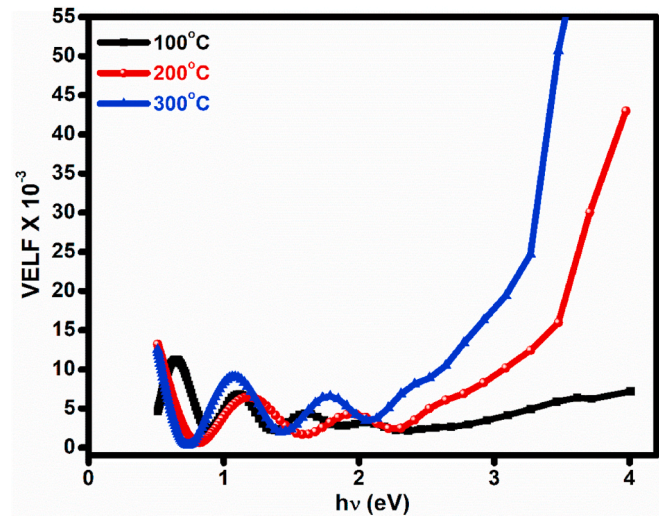


Fig. 14. VELF of NiO:WO₃ thin films prepared at various substrate temperatures.

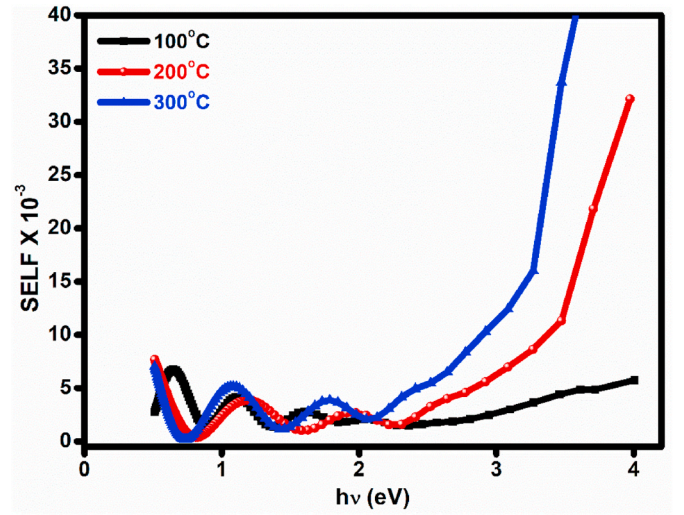


Fig. 15. SELF of NiO:WO₃ thin films prepared at various substrate temperatures.

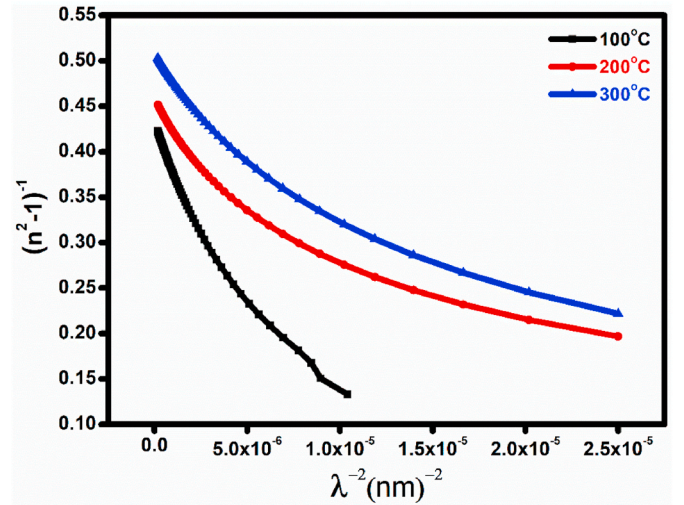


Fig. 16. $(n^2 - 1)^{-1}$ vs λ^{-2} plot of NiO:WO₃ thin films prepared at various substrate temperatures.

3.4.2. Parameters of dispersion energy

In order to attain a more comprehensive understanding of the role of nickel tungsten oxide films in the fabrication of optical devices, the dispersion energy components (E_0 and E_d) were determined by applying the Wemple and Didomenico (WD) simulation [49]. In this study, we examined the n values below the inter-band absorption threshold of material, and our findings are consistent with Sellmeier's formulae.

$$n^2 - 1 = \frac{E_0 E_d}{E_0^2 - (h\nu)^2} \quad (16)$$

The symbol E_0 represents the ^{mean} energy of the oscillator, whereas E_d represents the parameter for energy dispersion.

The component E_d is correlated to the valence of an anion, the effective number of dispersion electrons, the coordination of the nearest neighbour cation, & the ionicity. Fig. 17 depicts the relationship between the inverse of $(n^2 - 1)$ and the square root of $(h\nu)$. The E_0 and E_d variables are obtained from the slope and y-intercepts are shown in Table 2. The results of our study revealed a decrease in the E_0 value as the T_s increased, which may be attributed to a reduction in the energy band gap. The observed reduction in E_d values as T_s increases can be

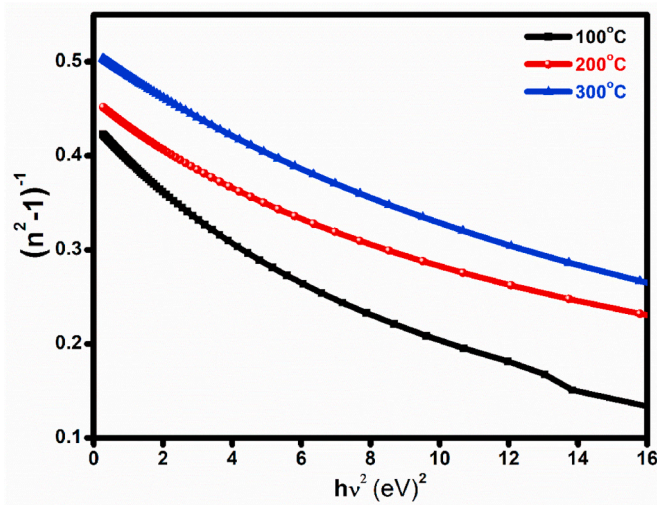


Fig. 17. $(n^2 - 1)^{-1}$ vs $h\nu^2$ plot of NiO:WO₃ thin films prepared at various substrate temperatures.

Table 2

Dispersion energy parameters of NiO:WO₃ thin films deposited at different preparative conditions.

Substrate temperature	E_o	E_d	E_o/E_g	M_{-1}	M_{-3}
100°C	3.55	8.41	1.48	2.40	0.196
200°C	3.44	8.06	1.47	2.34	0.197
300°C	3.39	7.73	1.49	2.28	0.198

related to the reduced atom coordination number. As previously mentioned, there is a relationship between E_o and E_g , where E_o is approximately 1.5 times E_g , as suggested by the WD model [49]. The relationship has been shown in Table 2, where the average ratio of E_o/E_g is around 1.5.

The fundamental relation with the E_o , E_d , ϵ_∞ , and moments associated with ϵ_∞ is represented as follows [36]:

$$E_o^2 = \frac{M_{-1}}{M_{-3}} \quad (17)$$

$$E_d^2 = \frac{M_{-3}^3}{M_{-1}} \quad (18)$$

As given in Table 2, the assessed M_{-1} value lies between 2.40 and 2.28, while the M_{-3} value ranges between 0.196 and 0.198 (eV)².

3.5. Photoluminescence study

Fig. 18 (a) shows the PL spectra of NiO:WO₃. According to Fig. 18 (a), we have observed UV emissions near 370 nm, accompanied by blue emissions near 420 nm. As depicted in Fig. 18 (b), upon excitation at 270 nm, the NiO:WO₃ undergoes photoexcitation, causing an electron to be elevated from the valence band, or VB, into the conduction band, or CB, while simultaneously creating hole present in the VB. At this time electron present in the CB rapidly undergoes relaxation. Subsequently, it promptly reconciles with the hole via radiative recombination, leading to the emission of photons at 370 nm. The emitted photons possess energy that matches or exceeds the energy of the band gap (E_g). This near band-edge emission (NBE) arises from the transition of Ni²⁺/Ni³⁺ ions [50]. In addition, some of these excitons originating from the CB combine with a hole through a non-radiative approach. This occurs when their energy is transferred to one or more phonons, resulting in the creation of “trapping” states within the nickel oxide lattice due to the inclusion of tungsten oxide. These trapping states are located between

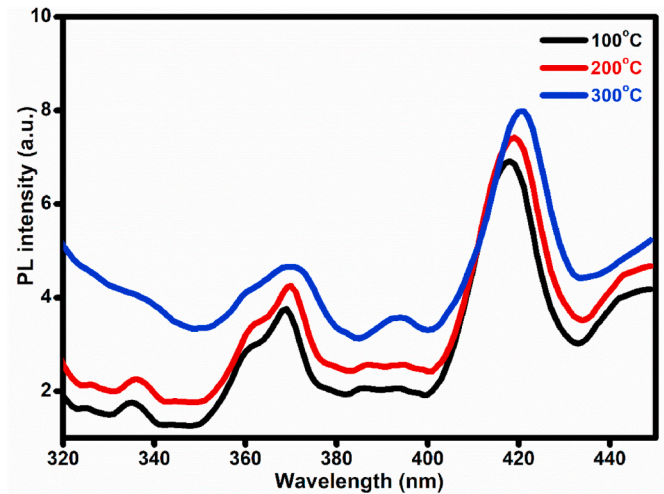


Fig. 18 (a). Photoluminescence spectra of NiO:WO₃ thin films prepared at various substrate temperatures.

the CB and the valence band (VB), and they contribute to the process of Shockley-Read-Hall recombination. Alternatively, the excitons may transfer their energy to another electron or to a hole through Auger recombination process. The non-radiative recombination mechanism results in the emission of a visible emission (VE) of blue wavelength at 420 nm [51]. The intensity of both NBE and VE increases with increase in substrate temperature, which is attributed to the increase in transition of Ni²⁺/Ni³⁺ ions and excess vacancies or oxygen interstitials. Furthermore, the emission peaks undergo a minor shift when the substrate.

Temperature increases, which is attributed to the decrease in its band gap. The notion corroborates the reported optical E_g results. Furthermore, as a consequence of this change in PL emission bands and the subsequent variations in the band gap, it came to light that NiO:WO₃ films might be used in optoelectronic gadgets as well as in ECDs.

3.6. Raman analysis

Fig. 19 depicts the investigation performed using micro-Raman imaging. NiO:WO₃ thin films coated with substrate temperatures of 100 °C and 200 °C exhibit a Raman band about 870 cm⁻¹, indicating the vibrational modes for W–O [52]. This confirms the presence of tungsten. When the temperature increased from 200 °C to 300 °C, along with W–O vibrational mode at 870 cm⁻¹, 1,2-phonon LO vibrational modes for Ni–O, at 570 cm⁻¹, & 1100 cm⁻¹ were detected. We can observe that the intensity of Raman band around 870 cm⁻¹ is higher than the other bands. Because, the Raman spectra of tungstate primarily originates from tungsten sub-lattices, whereas the nickel-containing environment shows less Raman activity [52]. Moreover, when the substrate temperature increases the intensity of 870 cm⁻¹ bands increases, which is attributed to the increased Raman vibrations from the tungsten sub-lattices. In addition, the wide spectrum of Raman bands might be attributed due to their amorphous nature [53], that fits in with our X-rd study.

4. Conclusion

The current study investigated the optical constants and dispersion parameters of sputtered NiO:WO₃ thin films as a function of substrate temperatures, viz 100, 200, and 300 °C. X-ray diffraction analysis confirmed that the films were amorphous irrespective of the substrate temperatures. Scanning electron microscopy reveals that the films have a dense and smooth surface without any pinholes. The presence of nickel (Ni), oxygen (O), and tungsten (W) components in the films was

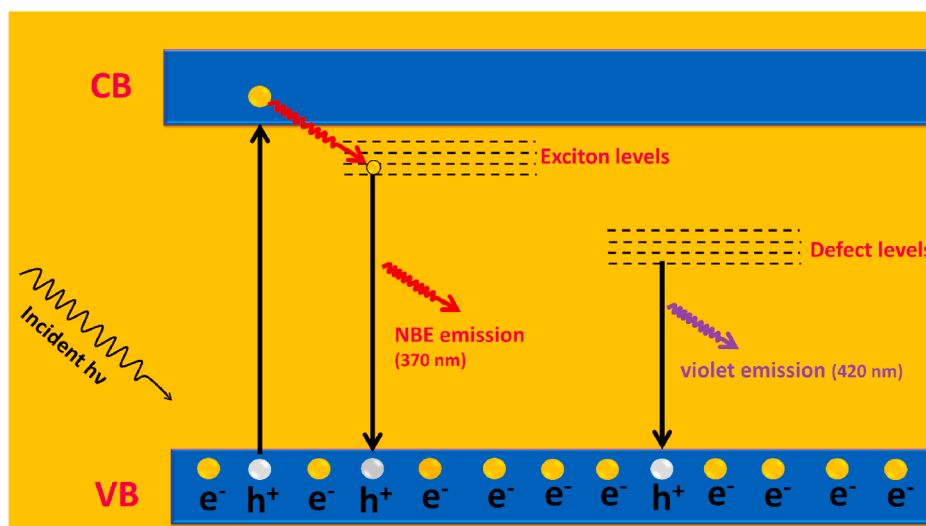


Fig. 18 (b). Schematic representation of NBE and visible emission in NiO:WO₃ thin films.

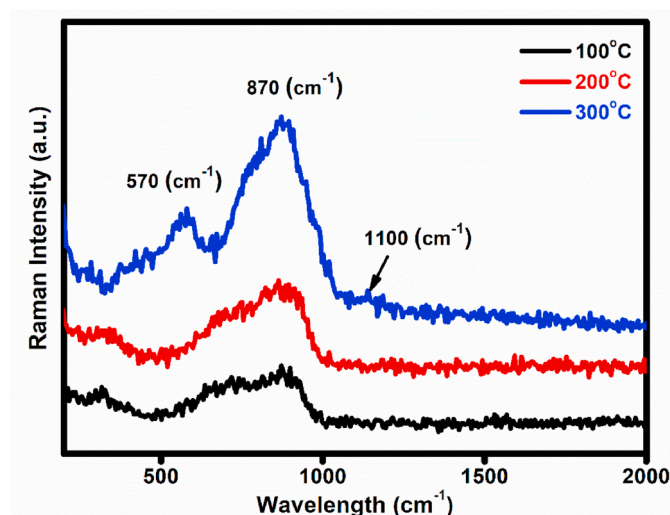


Fig. 19. Raman spectra of NiO:WO₃ thin films prepared at various substrate temperatures.

confirmed by XPS spectra. XPS analysis confirms the presence of both Ni²⁺ and Ni³⁺ states. Increasing the substrate temperature resulted in an increase in the average optical transmittance because of enhanced mobility of charge carriers. The red shift observed in the transmittance indicates a decrease in the band gap value. Also, the band gap in semiconductors decreases as the T_s increases, which is attributed to the Moss-Bursten shift. The refractive index decreases with increasing the T_s due to decrease in the packing density of the films. The decrease in the k value with T_s could be attributed to a decrease in the surface roughness. The diminution in packing density and electronic polarizability with T_s may be ascribed to a reduction in the n values. Increasing T_s decreases VELF and SELF, reducing electron energy loss. Higher energy regions have higher values owing to more electromagnetic radiation penetration and interactions with more electrons. The dispersion energy parameters E_o and E_d evaluated from WDD model indicated a decrease in the E_o value as T_s increased, possibly due to a reduction in the energy band gap, and a significant decrease in E_d values with increasing T_s which may be attributed to the reduced atomic coordination number. The nonlinear optical susceptibility increased with temperature, suggesting that molecules in nickel tungsten oxide thin film were more firmly bound. The PL spectra revealed NBE and visible emission. As substrate temperatures

increase, the Raman band at 870 cm⁻¹ corresponding to nickel tungstate amplifies due to enhanced Raman vibrations from tungsten sub-lattices. Based on the afore mentioned investigations, it is evident that sputter coated nickel-tungsten oxide thin films are ideal for the development of cost-effective optical devices such as optical switches, solar cells, photodetectors, lighting devices like Q-LEDs and Hy-LEDs, modulators, and electrochromic devices.

CRediT authorship contribution statement

K.S. Usha: Writing – review & editing, Writing – original draft, Data curation, Conceptualization. **Sang Yeol Lee:** Writing – review & editing, Supervision, Investigation. **R. Sivakumar:** Writing – review & editing, Validation, Investigation. **C. Sanjeeviraja:** Writing – review & editing, Validation, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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