



# Fast switching thermally treated nickel-tungsten oxide thin films for energy efficient smart windows

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## ABSTRACT

Anodic electrochromic (EC) materials like nickel oxide are vital as counter electrodes for smart window applications due to their distinctive optical characteristics during charge intercalation and deintercalation. The current research aims to explore the influence of substrate temperature ( $S_T$ ) on the electrochromic efficiency of RF sputtered nickel-tungsten oxide (NW) against room temperature (RT) fabricated NW films. Low temperature prepared films showed amorphous nature while crystallization commenced at high temperature. Surface roughness increased with  $S_T$ . Nickel vacancies decreased with increasing  $S_T$ . The grain size of the film increased with increasing substrate temperature. Favourable columnar nano structural morphology is observed. Raman analysis affirmed the existence of nickel defects. We discovered that low-temperature deposition (150 °C) enhanced the optical modulation to 65 % with the rapid switching speed of 0.89 s for bleaching and 1.0 s for colouring without permanent structural degradation. The advantageous amorphous structure, along with adequate nickel vacancies, facilitates the unobstructed rapid intercalation and de-intercalation of Li-ions, hence enhancing the device's efficiency. The study findings indicate that the prepared nickel tungsten oxide film is appropriate to be employed for the counter electrode in energy-efficient smart windows.

## 1. Introduction

Electrochromic (EC) materials which offer reversible color changes between black and transparent states are widely used in several commercial applications, such as switchable displays, energy-efficient windows, and electronic paper [1–4]. Recently, electrochromic smart windows with switchable electromagnetic waves have gained interest due to their potential application in skylights, architectural or vehicle windows, and internal partition applications [5]. Approximately 40 % of global energy use is ascribed to buildings. Over half of the total energy consumption in a building is attributed to the heating, cooling, and ventilation of that building. Considering this, implementing smart windows can help reduce energy consumption in buildings. Recent research has focused on further reducing the energy consumption in buildings by manufacturing self-powered electrochromic devices [6], self-rechargeable aqueous electrochromic energy storage devices [7], dual-functional electrochromic smart windows [8–10], electrochromic batteries [11], electrochromic supercapacitors [12], ITO free smart windows [13].

ECDs and sunglasses require transmissive, color-changing devices [14–17]. A range of smaller organic molecules [18–20], conjugated polymers [21–23], along with metal–organic frameworks [24,25], has been developed and synthesized as electrochromic materials to meet these criteria. Yet, these organic electrochromic materials generally exhibit inadequate chemical permanence in electrochemical cases and prolonged sunlight exposure [26], thereby restricting their application in everyday life. In comparison with organic electrochromic materials, inorganic electrochromic materials, like transition metal oxides [27] and the electrodeposited metals [28], exhibit stability in harsh environments.

Nickel oxide (NiO) & tungsten oxide (WO<sub>3</sub>) are inorganic EC materials, with NiO demonstrating anodic coloration and WO<sub>3</sub> showing cathodic coloration. NiO counter electrodes improve electrochromic device coloring efficiency when used with tungsten oxide [29]. In recent years, research initiatives have been designed at identifying a new counter electrode material with improved electrochromic characteristics. The efficiency of NiO ECD could potentially be improved through the incorporation of metals or alternative electrochromic compounds.

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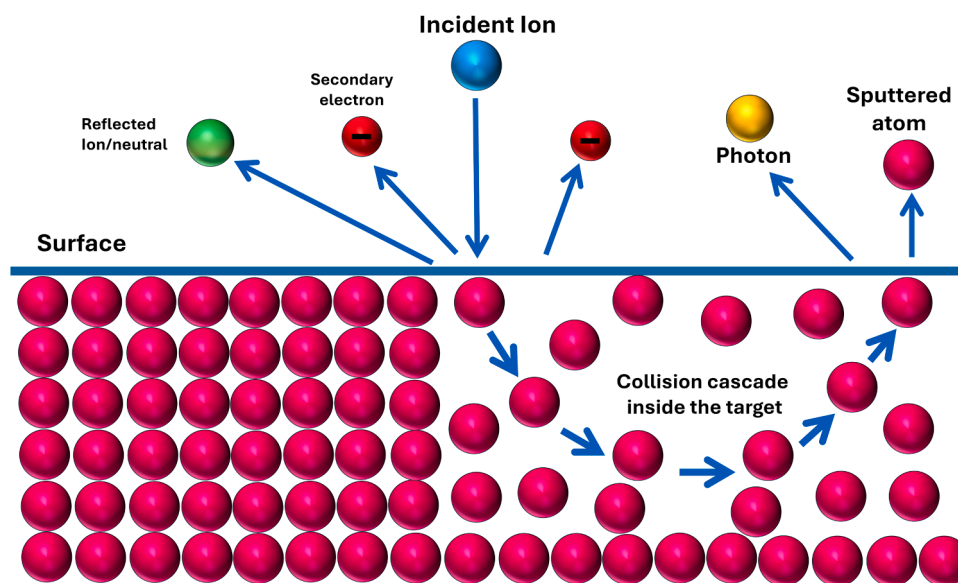


Fig. 1. Sputtering mechanism.

Zhan et al. [30] discovered that adding V-ions to NiO changed the crystal structure, increasing the redox surface area and ion transport to 81.9 % optical modulation. Also, Zhao et al. [31] demonstrated that the integration of 1D  $\text{CO}_3\text{O}_4$  with 2D NiO markedly improved electrochemical performance in comparison to their individual counterparts. The network structure, characterized by its porous, along with staggered design, significantly improves electrochemical performance by offering increased channels for the transfer of ions and electrons. The coloration efficiency of integrated  $\text{CO}_3\text{O}_4$  and NiO, surpassed that of NiO and  $\text{CO}_3\text{O}_4$ . Additionally, binary Ni-W oxides, like tungsten paired with NiO [32,33], or Ni incorporated into tungsten oxide [34], exhibit remarkable EC features. Lee et al. reported that NiO:  $\text{WO}_3$  films' lithium-ion intercalation rate exceeded those of NiO [35]. S.J. Lee et al. [36] noted that W-doped NiO thin films, designated as  $\text{Ni}_{1-x}\text{W}_x$  oxide, demonstrated enhanced electrochromic performance relative to pristine NiO.

The optimization of thin film deposition conditions is crucial for improving the efficiency of ECDs. Critical elements, including film deposition pressure, oxygen partial pressure, substrate temperature, and post-deposition treatments, play a significant role in influencing the structural, optical, and electrical properties of the films. Post-deposition annealing enhances crystallinity and minimizes defects, leading to improved optical transparency and electrical conductivity. Modifying the substrate temperature during deposition enhances the film's morphology and adhesion, offering uniform coverage across the substrate. The optimized parameters work together to enhance the performance of the deposited thin films by facilitating efficient ion transport, improving optical modulation, and increasing ECD efficiency [37]. Additionally, findings indicate that thermally treated film caused structural alterations that enhanced the efficiency of ECDs [37]. For instance, a study conducted by Xi Chen and colleagues revealed that thin films subjected to thermal treatment at 200°C demonstrated enhanced electrochromic performance, marked by an increased optical modulation and remarkable cyclic stability [38].

This research aims to boost the performance of ECDs through thermal treatment via substrate temperature. RF (radio frequency) magnetron sputtered nickel-tungsten oxide (NW) thin films were subjected to thermal treatment via changing the substrate temperature like RT, 150 °C, 250 °C and 350 °C (denoted as NW-RT, NW-150°C, NW-250°C and NW-350°C) during the deposition. We endeavored to provide a comprehensive analysis of the correlation between structural, morphological, vibrational, and electrochemical features and thermal treatment. The research findings suggest that low-temperature thermal

treatment at 150 °C generated nickel vacancies, which form many diffusion channels that allow the fast passage for ions and accept an enormous ion. The NW-150°C film exhibited exceptional electrochromic characteristics, achieving a visible transmittance modulation of 65 % @ 550 nm and a fast-switching rate of 0.89 s for the bleached state and 1.0 s for the coloured state. This study proposes that thermal treatments serve as an efficient technique to enhance the electrochemical efficiency of the nickel-tungsten oxide counter electrode.

## 2. Experimental details

Nickel-tungsten oxide thin films, referred to as NW films, were deposited on FTO substrates utilizing the RF magnetron sputtering method. The NW (94 %:6 %) target functioned as the cathode, while FTO substrates acted as the anode. Afterwards,  $5 \times 10^{-4}$  mbar of chamber pressure is achieved by means of the vacuum unit. A noble gas, namely Argon (Ar), is supplied into the chamber to enhance the deposition rate. The chamber pressure is decreased to  $5 \times 10^{-2}$  mbar and is sustained at this level during the deposition process. The negatively charged NW target collides with Ar atoms, leading to the release of electrons. The positively charged  $\text{Ar}^+$  ion attracts itself to the negatively charged target and collides against it at a high velocity. Fig. 1 demonstrates that the cathode emits atomic-scale fragments (comprising atoms & secondary electrons) during the process of sputtering. The expelled atoms are subsequently deposited as a thin coating onto the substrate. The deposition occurs at several substrate temperatures: room temperature (RT), 150°C, 250°C, and 350°C, for 150 minutes, utilizing 100 W RF power.

Structural as well as morphological analyses were conducted via the RIGAKU Smartlab X-ray Diffractometer, AFM Nanoscope:E, and Schottky type field emission scanning electron microscope (FE-SEM, SU-70, Hitachi)- Korea Basic Science Institute in Busan (KBSI, Busan). Micro-Raman investigations were performed using STR Raman spectroscopy. X-ray photoelectron spectroscopy (XPS: JEOL PS-9010 TR) was employed for elemental analysis. The electrochromic properties were analysed utilizing scanning potentiostat/galvanostat (CHI600E). (Carry 5000 UV-Vis-NIR, Agilent) was employed to investigate the optical properties.

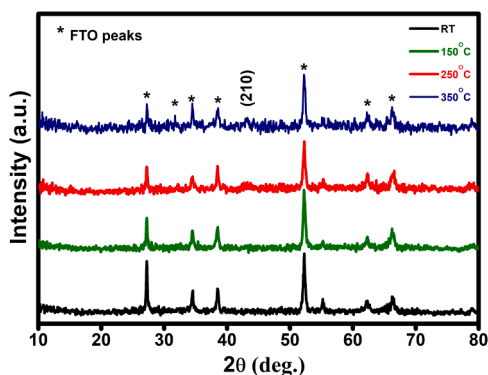


Fig. 2. XRD patterns for NW-RT, NW-150°C thin films.

### 3. Results and discussion

#### 3.1. Structural studies

Fig. 2 show the respective X-ray diffraction patterns of NW films coated on FTO at different  $S_T$ s like RT, 150 °C, 250 °C and 350 °C. XRD patterns show that films deposited at RT, 150 °C, and 250 °C are amorphous in nature. XRD patterns show that films are amorphous up to 250 °C. As reported in our previous study [39] undoped nickel oxide is polycrystalline in nature. The incorporation of 6 % of pure tungsten oxide into nickel oxide induces amorphization in the film. Evidently, the inclusion of tungsten causes the Ni-O matrix's long-range order to deteriorate. Because there is a huge difference among the stable valence states of  $2^+$  and  $6^+$ , tungsten ions with a high oxidation value ( $6^+$ ) would cause a significant disruption of the lattice surrounding a tungsten cation inserted into a nickel-free site, and they appear to alter the overall structure to a less dense state. Green et al. found similar findings for sputter-deposited nickel-tungsten oxide thin films [33]. At an elevated  $S_T$  of 350°C, crystallisation commenced in the film, as shown by the diffraction peaks found at  $42.7^\circ$ . The measured d spacing matches perfectly with monoclinic nickel-tungsten oxide (JCPDS Card No. 72-0480). The observed crystallization of the film at elevated  $S_T$  (350°C) may result from atoms migrating towards stable lattice positions, facilitating grain development in a favoured orientation [40]. At elevated  $S_T$ , the deposited atoms possess sufficient kinetic energy to provide an improved crystalline layer. The favoured alignment of films (210) may, however, result from the elevated thermal energy of atoms adhering to surfaces at increased substrate temperatures. It is notable that, in comparison to amorphous metal oxide films, high-crystalline metal oxide films exhibit poor electrochromic performance due to their ordered and dense structure, which hinders the intercalation and de-intercalation of ions [41]. As a result, the structurally modified amorphous films developed at low temperatures may offer multiple diffusion channels for swift movement of electrolyte ions in the electrochromic device, hence improving the device's efficiency [42,43].

#### 3.2. Morphological study

Fig. 3(a, b) shows AFM images of NW-150°C, and NW-350°C samples. As given in Fig. 3, both the films show uniform morphology with small cone-shaped grains on the surface. As the  $S_T$  rises, the values of surface roughness ( $R_{rms}$ ) increase from 0.352 nm to 0.658 nm. This indicates that the film surface becomes less smooth or rougher, possibly related to the initiation of the crystallisation at 350°C [44]. Fig. 3(c-f) presents the FESEM images for the NW-RT, NW-150°C, NW-250°C, and NW-350°C samples. The interaction that occurs with the sputter target & the substrate highly depends upon temperature. At higher temperatures, enhanced energy may alter collision dynamics and impact deposition properties, eventually influencing the morphology of the films. Also, the

diffusion rate of atoms over the substrate surface is affected by temperature; increasing the temperature provides increased atomic mobility, hence promoting coalescence and resulting in a more uniform film formation. On the other hand, re-evaporation and other material losses may occur at very high temperatures [45]. Therefore, the optimal  $S_T$  may enhance the development of the required morphology for the advantage of the electrochromic device. NW-RT sample showed a compact structure with an average grain size of 33 nm. Increasing the substrate temperature to 150 °C, the surface morphology showed small grains with an average grain size of 35 nm. Further increasing the substrate temperature, the NW-250°C, and NW-350°C samples showed average grain sizes of 45, and 54 nm. This shows that, increasing the substrate temperatures enables the surface atoms of the substrate to gain more energy, allowing them to migrate to appropriate nucleation sites, coalesce together and form larger grains. Moreover, the ions with low activation energy doped in the thin film may readily elude trap sites and migrate to nucleation sites [46]. In this study, the low activation energy of the tungsten oxide mixed in the NiO thin film leads to the increase in grain size with the increase in the substrate temperature. The thickness of the deposited NW films coated at different  $S_T$  like RT, 150 °C, 250 °C and 350 °C were found to be 320, 300, 280, and 250 nm as shown in Fig. 3(g-j). P. Cossari et al., reported that the intercolumnar structure significantly increased the contact area between the  $WO_3$  columnar structures and facilitated efficient mass movement across the film, resulting in advantages for ion intercalation and deintercalation kinetics [47]. According to M. H. Wang et al., the electrochromic  $WO_3$  thin film with a nanocolumnar structure has a higher lithium-ion diffusion coefficient, likely due to its extensive specific surface area and reduced channel length. The increase in the quantity of injected charges attributed to the nanocolumn architecture facilitates the facile movement in and out of lithium ions and electrons and causes rapid coloration/bleaching and displays fast reaction performance [48]. Hence, as shown in Fig. 3(g-j), the formation of columnar structure is advantageous for the electrochromic performance [49].

#### 3.3. Vibrational studies

The Raman spectra of NW films deposited at various  $S_T$  were deconvoluted using Shirley fitting and are shown in Fig. 4(a-d). The Raman spectrum is observed to exhibit three wide peaks: 1-phonon longitudinal optic (LO) mode beginning at  $565\text{ cm}^{-1}$  along with 2-phonon LO mode at  $1120\text{ cm}^{-1}$ , attributed to the vibrations between Ni-O bonds, and  $875\text{ cm}^{-1}$  corresponding to the W-O vibrational mode [50]. This validates the presence of NiO & W in the developed films. The detected signal at  $565\text{ cm}^{-1}$  indicates the presence of  $Ni^{3+}$  ions with  $Ni^{2+}$  ions, ascribed to the creation of vacancies in the Ni lattice [39]. Fig. 4(e), shows that the width (FWHM) of the Raman peaks decreases with an increase in  $S_T$ . The reason may be that NiO crystal lattice defects decrease with an increase in  $S_T$ . Particularly, the FWHM of the  $565\text{ cm}^{-1}$  Raman peak decreases with  $S_T$ , indicating the reduction in the nickel vacancies [51]. Also, the overall area of the peak as given in Fig. 4(f) is found to increase with increasing  $S_T$ , due to decreased lattice disorder in the film or the commencement of crystallization, validating the X-ray diffraction results [52]. Additionally, Green et al. [53] discovered that materials exhibiting a polycrystalline structure with bigger grains formed stronger Ni-O bonds, thereby weakening W-O bonds; conversely, amorphous materials and those with smaller grains had the reverse effect. These findings align with our current observation in which the intensity of Ni-O bonds becomes stronger than W-O with increasing  $S_T$ .

#### 3.4. X-ray photoelectron spectroscopic (XPS) study

Fig. 5 exhibits NW thin film XPS survey scan spectra deposited at 150°C and 350°C  $S_T$ . The XPS survey scan spectra only display the typical peaks for Ni, W, and O, so confirming the compositional purity of

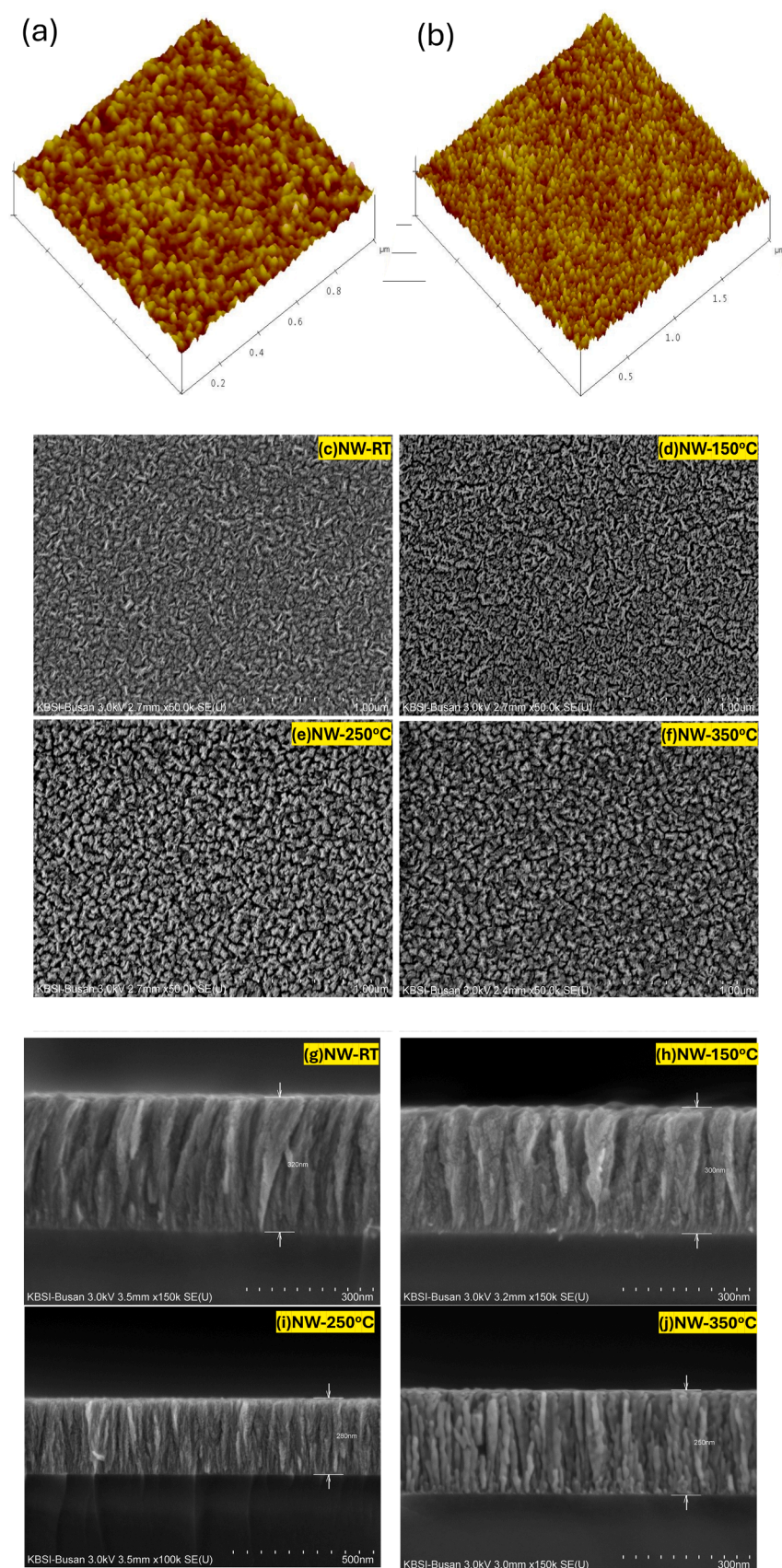


**Fig. 3.** (a) AFM image for NW-150°C, (b) AFM images for NW-350°C thin film. FESEM image for (c) NW-RT (d) NW-150°C (e) NW-250°C, and (f) NW-350°C thin film. Cross sectional image for (g) NW-RT (h) NW-150°C (i) NW-250°C, and (j) NW-350°C thin film.

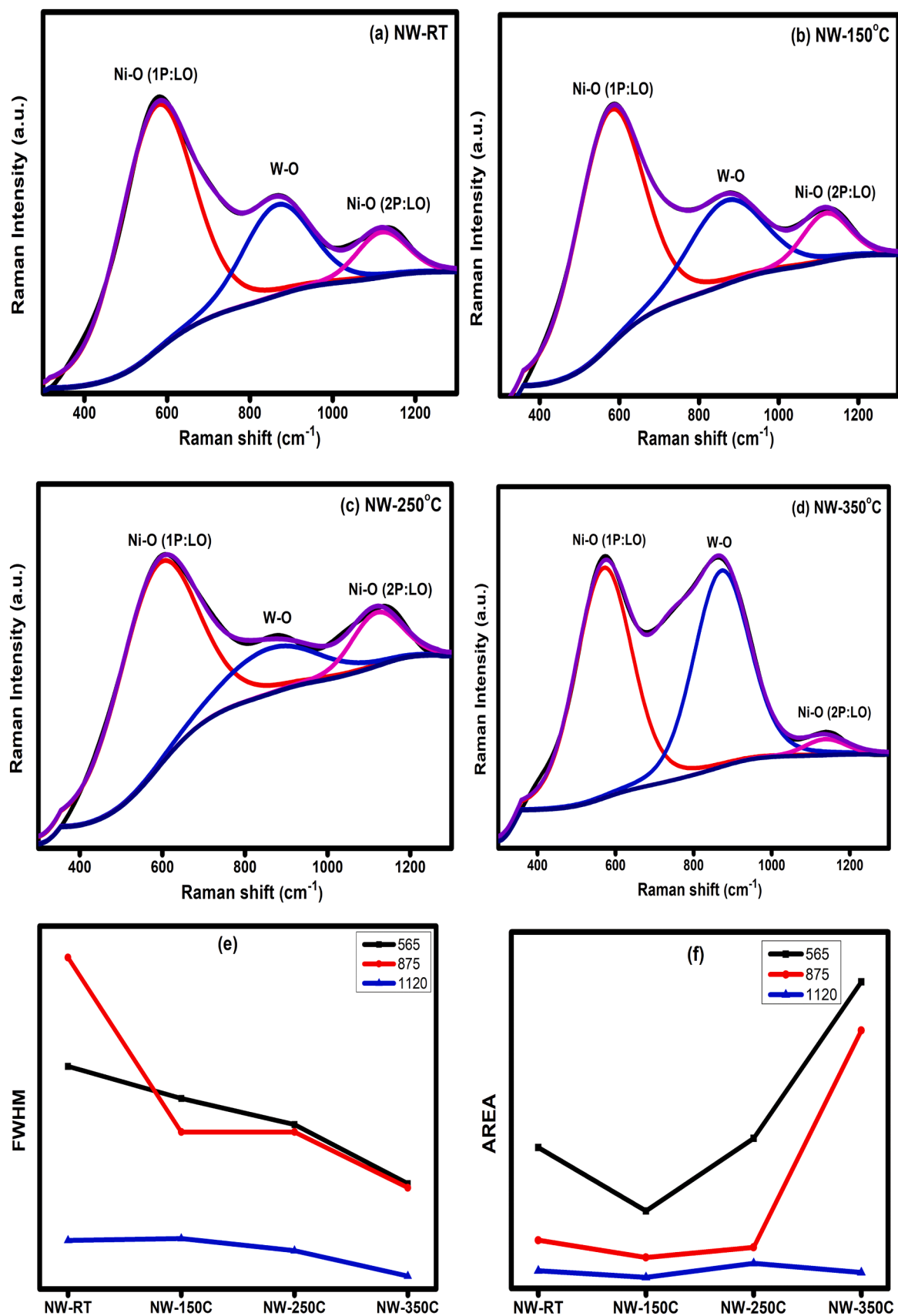


**Fig. 4.** Raman spectra for (a) NW-RT (b) NW-150°C (c) NW-250°C, and (d) NW-350°C thin film. (e) Variation of FWHM for NW-RT, NW-150°C, NW-250°C, and NW-350°C thin film. (f) Variation of Area for NW-RT, NW-150°C, NW-250°C, and NW-350°C thin film.

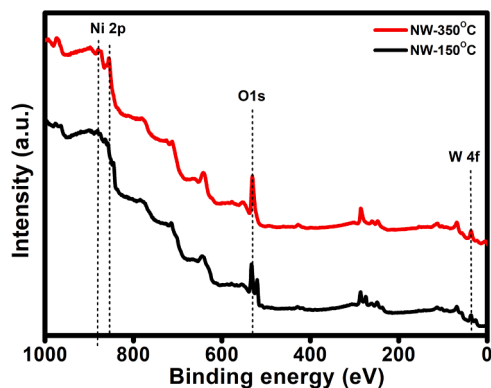
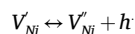
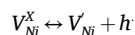
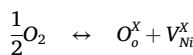


Fig. 5. XPS survey scan spectra for NW-RT, NW-150°C, NW-250°C, and NW-350°C thin film.

the deposited thin films. Fig. 6(a, b) illustrates the core level spectra of Ni-2p for films deposited at 150°C and 350°C, exhibiting peaks with binding energies of 853.77, 854.41, and 855.97 eV, representing Ni 2p<sub>3/2</sub>, along with their corresponding satellite peaks around 860.99,

863.42, and 865.06 eV, etc. Additional peaks identified at 870.52, 872.14, and 873.68 belong to the Ni 2p<sub>1/2</sub> level, with a satellite peak around 881.67 eV. The peaks detected at 855.97 eV, 863.42 eV, and 873.68 eV indicate the presence of Ni<sup>3+</sup> states [39]. A Ni<sup>3+</sup> ion is regarded to be equivalent to the acceptor as well as a nickel vacancy. Stoichiometric NiO must not have any Ni vacancies; yet, in thermodynamically typical cases, there will be a non-stoichiometric state of Ni vacancies, whereby the appropriate number of holes will be donated by Ni vacancies [54]. The defect equilibrium states for the creation of nickel vacancies are presented in the following equations.



The symbols O<sub>o</sub> and V<sub>Ni</sub> denote oxygen filling a lattice position and a nickel vacancy, respectively. The Kröger-Vink notation uses the following symbols to represent charges: x for neutral, ' for negative, '' for double negative, and • for positive. As depicted in Fig. 6(c) the nickel vacancy generates two holes, resulting in a doubly negative charged

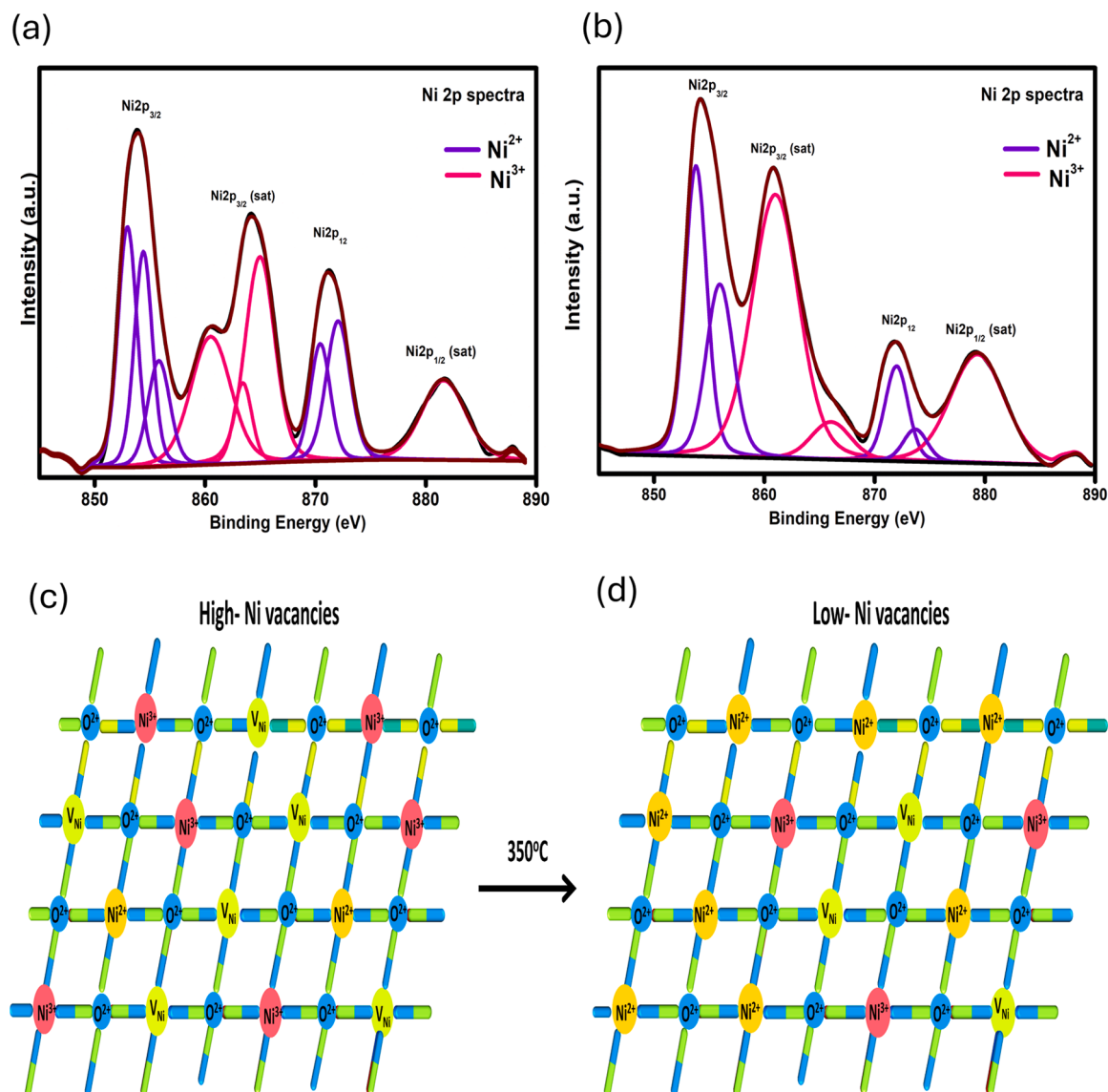


Fig. 6. (a, b) XPS core level spectra of Ni-2p for NW-150°C, and NW-350°C thin film. (c, d) reduction of nickel vacancies upon increasing substrate temperature.

**Table 1**  
Summary of the XPS results.

| Sample   | Ni <sup>2+</sup> (%) | Ni <sup>3+</sup> (%) | Ni <sup>3+</sup> / Ni <sup>2+</sup> |
|----------|----------------------|----------------------|-------------------------------------|
| NW-150°C | 71.21                | 28.79                | 0.40                                |
| NW-350°C | 79.49                | 20.51                | 0.25                                |

vacancies and transforming the material into p-type. Otherwise, each hole generated by a Ni vacancy may be seen as comparable to the generation of two Ni<sup>3+</sup> ions from every vacant Ni<sup>2+</sup> ion, since the release of a hole in the valence band corresponds to an electron from the 3d<sup>8</sup> orbital being excited to the acceptor level inside the band gap. Consequently, each doubly ionized nickel vacancy may be seen as comparable to the creation of two Ni<sup>3+</sup> ions [55]. Also, the substitution of W for Ni sites, leads to an increase in nickel vacancies (native defects), which induces increase in Ni<sup>3+</sup> ions, and a resulting increase of the hole concentration [39]. The concentration of Ni<sup>3+</sup> ions, Ni<sup>2+</sup> ions, and Ni<sup>3+</sup> / Ni<sup>2+</sup> ratio is given in Table 1. It is evident from Table 1 that compared to film deposited at 150°C film deposited at higher temperature (350°C) shows lesser quantity of Ni<sup>3+</sup> ions. As given in Fig. 6(c & d), and Table 1 increasing the S<sub>T</sub> decreases the nickel vacancies. Similar results were

observed by L. Ai et al. [54]. Fig. 7(a, b) displays the O 1s core level spectra of NW-150°C and NW-350°C. The peaks detected at 529.75 eV represents Ni-O (or) lattice oxygen. The peak that was identified at 531.20 eV belongs to the Ni<sup>3+</sup> state or Ni vacancies and oxygen defects that are generated across the surface of the film. The additional peak found approximately at 527.8 eV has been observed in the O 1s spectra. The lowest possible binding energy observed for O 1s (metal oxides) is often lesser than 528 eV [56]. Consequently, such signals were interpreted as evidence of a "double charge" phenomena. It can be observed that the Ni<sup>3+</sup> concentration or nickel vacancies decreased with increasing S<sub>T</sub>. Fig. 7(c, d) illustrates the core level spectra of W-4f for thin films for films deposited at 150°C and 350°C, displaying three different binding energy peaks of 35.47 eV (W 4f7/2), 37.53 eV (W 4f5/2), and 38.35 eV (W 5p3/2). The observed binding energies for tungsten indicate the presence of tungsten in its hexavalent state (W<sup>6+</sup>). Furthermore, the peaks detected at around 33.2 eV correspond to the W 4f7/2, indicative of the W<sup>5+</sup> state in WO<sub>3</sub> films [57]. The XPS analysis indicates that the prepared films are non-stoichiometric in nature consisting of Ni<sup>3+</sup> and Ni<sup>2+</sup> ions. The content of Ni<sup>3+</sup> ions or Ni vacancies decreased with increase in S<sub>T</sub>.

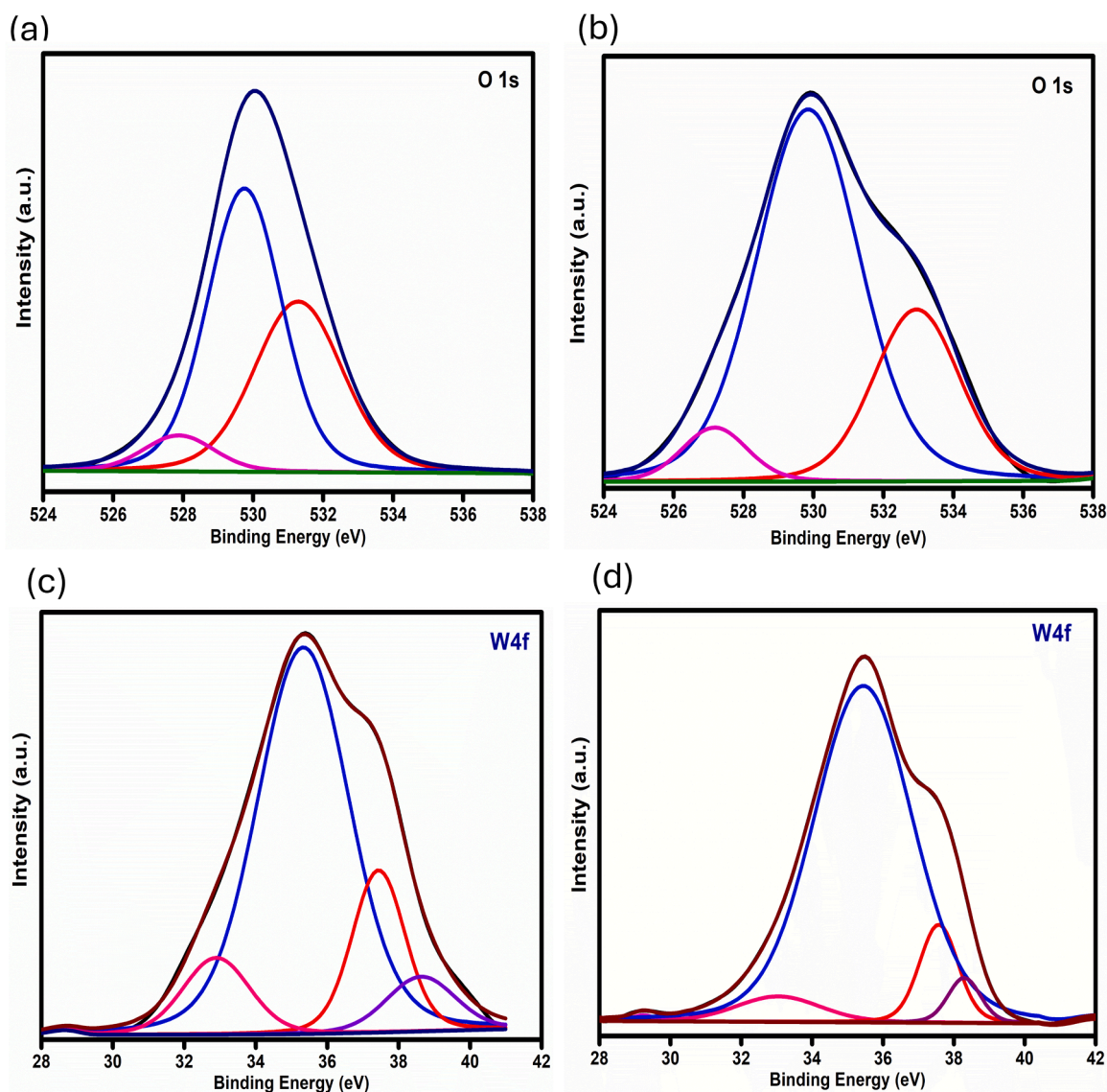


**Fig. 7.** (a) XPS core level spectra of O-1s for NW-150°C thin film. (b) XPS core level spectra of O-1s for NW-350°C thin film. (c) XPS core level spectra of W-4f for NW-150°C thin film. (d) XPS core level spectra of W-4f for NW-350°C thin films.

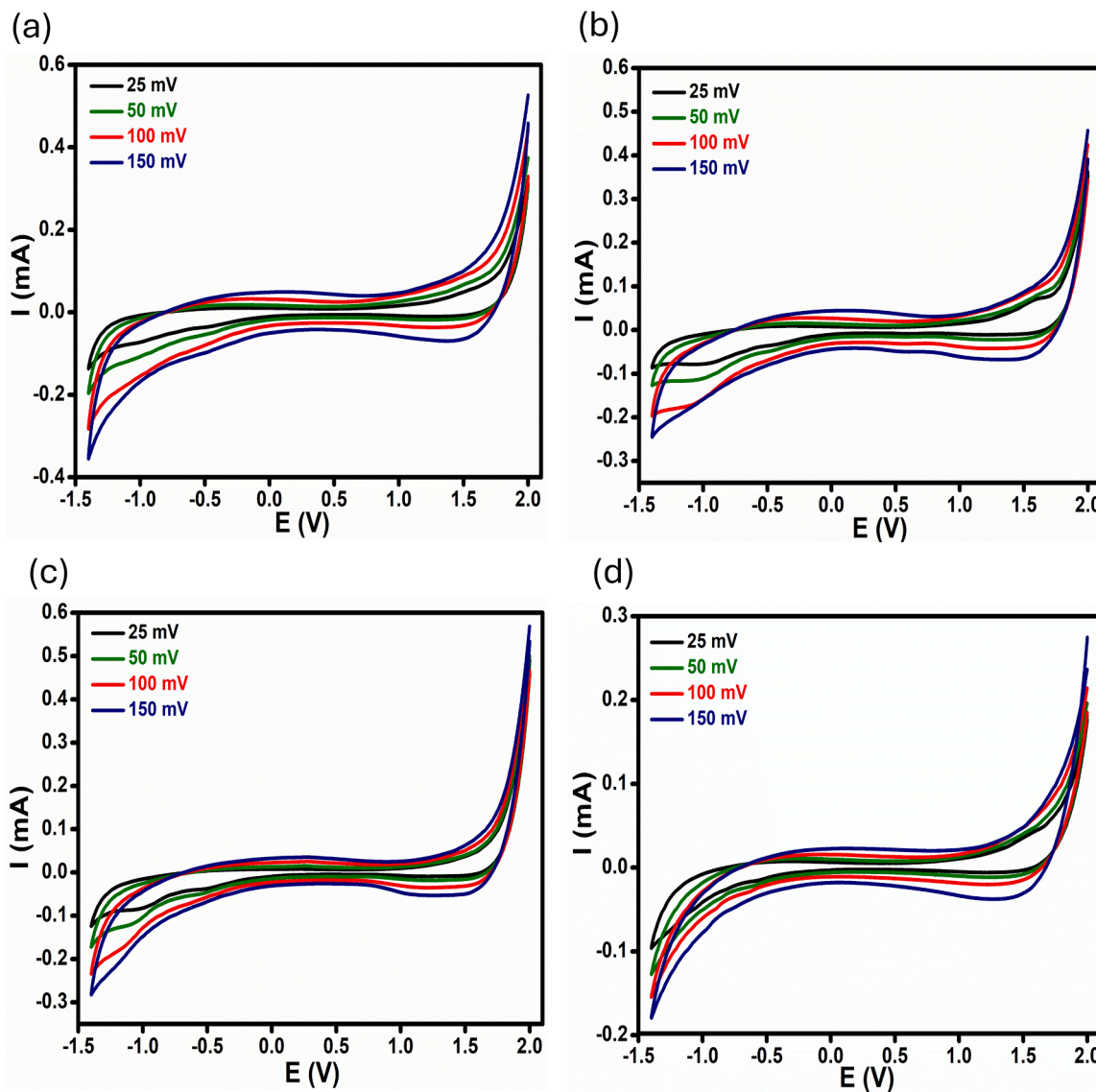


Fig. 8. CV studies for (a) NW-RT, (b) NW-150°C thin films.

### 3.5. Electrochromic studies on NW thin films

The electrochromic impact of the ECD is examined utilizing CV measurement. The CV measurements of NW thin films deposited on FTO substrates at various  $S_T$ , such as RT, 150 °C, 250 °C and 350 °C, were shown in Fig. 8(a, b, c and d), with scan speeds of 25, 50, 100, and 150  $\text{mVs}^{-1}$ . The cyclic voltammetry curves of NiO measured in 1 M  $\text{LiClO}_4$  (in propylene carbonate) over a potential scan between  $-1.4$  V and  $+2.0$  V display broad redox peaks, indicative of a conversion-type redox mechanism rather than a surface-confined process. The redox reactions involve lithium intercalation and deintercalation into NiO matrix. During the anodic process,  $\text{Ni}^{2+}$  is oxidized to  $\text{Ni}^{3+}$ , while  $\text{Li}^+$  ions are extracted from NW thin films. The film becomes dark brown (colored state) with its broader redox peak observed around 1.4 V. In the cathodic process,  $\text{Ni}^{3+}$  is reduced to  $\text{Ni}^{2+}$ , and  $\text{Li}^+$  ions are incorporated into the structure. The film reverts to its bleached form, and the associated redox peak is detectable at 0.99 V. The broader oxidation and reduction peaks of the respective anodic and cathodic scans were asymmetric in shape, due to the kinetic irreversibility of the redox scan or slower kinetics in non-aqueous electrolyte. Their corresponding redox reaction mechanism is as follows.

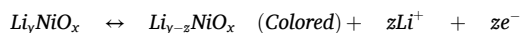
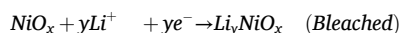


Fig. 9 shows an electrochromic device design. As depicted in Fig. 9(a, b) cathodic scanning around 2 and  $-1.4$  (V) transfers electrons &  $\text{Li}^+$  ions into films. The  $\text{Li}^+$  ions insertion creates localized energy levels around the valence band. Released electrons fill NiO thin film energy sites. More electrons fill energy states sequentially, raising the Fermi level. Electrical conductivity and optical characteristics changed with Fermi level. This reduces  $\text{Ni}^{3+}$  to  $\text{Ni}^{2+}$  and bleaches the film. As a result, the ECD fabricated using NW sample can allow both visible and NIR radiations. As depicted in Fig. 9(c, d) the anodic potential scan between 1.4 &  $-2$  (V) de-intercalates  $\text{Li}^+$  ions, shifting the fermi level down into lower levels of energy and oxidizing  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$ , causing brown colouring and partially allows visible radiation and blocks NIR radiation.

The electrochromic properties are substantially affected by ion diffusion inside the electrode. Diffusion coefficient can be utilized to measure the rate of ionic transport. Therefore, to examine the kinetics of reactions of  $\text{Li}^+$  ions, and diffusion coefficients were calculated with Randles-Servcik formula [42]:

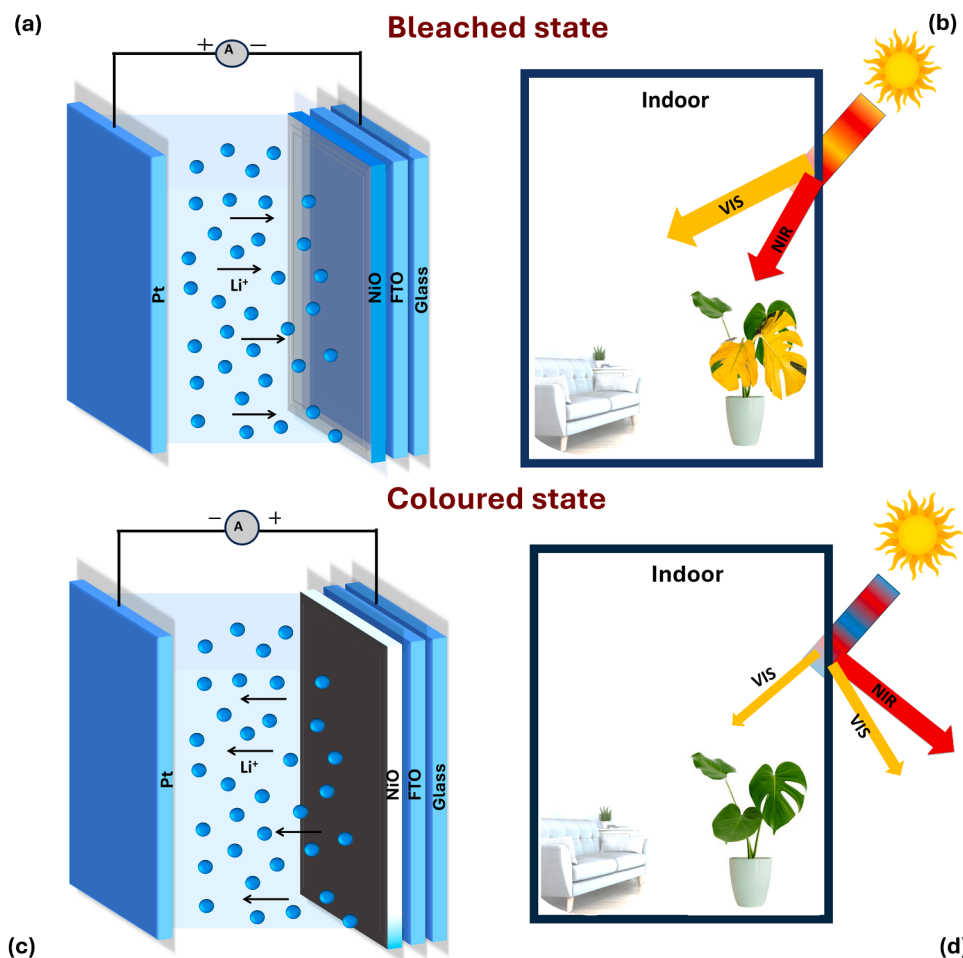


**Fig. 9.** a). The schematic illustration of electrochromic devices with NW electrode in the bleached state, (b) electrochromic window in transparent mode, (c) electrochromic device with NW electrode in the coloured state, and (d) electrochromic window in coloured state.

**Table 2**  
Electrochemical properties of NW thin films.

| Sample   | Diffusion Coefficient (cm <sup>2</sup> s <sup>-1</sup> ) × 10 <sup>-13</sup> | ΔOD @ 550 nm | Optical modulation ΔT = (T <sub>b</sub> -T <sub>c</sub> ) @ 550 nm | t <sub>b</sub> (s) | t <sub>c</sub> (s) |
|----------|------------------------------------------------------------------------------|--------------|--------------------------------------------------------------------|--------------------|--------------------|
| NW-RT    | 4.34                                                                         | 0.44         | 46                                                                 | 1.20               | 3.00               |
| NW-150°C | 8.84                                                                         | 0.60         | 65                                                                 | 0.89               | 1.00               |
| NW-250°C | 3.12                                                                         | 0.35         | 41                                                                 | 1.23               | 3.20               |
| NW-350°C | 2.37                                                                         | 0.28         | 30                                                                 | 1.30               | 3.40               |

$$D^{\frac{1}{2}} = \frac{i_p}{(2.69 \times 10^5) \times C_0 n^{\frac{3}{2}} v^{\frac{1}{2}}}$$

The equation variables are:  $D$  indicates diffusion degree,  $C_0$  indicates electrolyte cation quantity,  $n$  indicates amount of involved electrons, &  $v$  indicates scan rate. Towards obtain improved diffusion kinetics, it is important to make sure that there is a clear & unobstructed path for the Li<sup>+</sup> ions to travel across the films in either direction. As given in Table 2 when compared to NW-RT film the diffusion coefficient value is higher for NW-150°C film. Further increasing the substrate temperature showed decreased diffusion co-efficient values. It is evident that the diffusion of ions is highly influenced by the  $S_T$ . Madhavi et al. observed same findings, attributing the reduction in diffusion coefficient under higher temperatures due to the blockage of ion insertion sites [58]. Hsu et al. elucidated that despite the presence of a driving force obtained from the voltage being applied, the dense film structure formed at higher

temperature impeded the intercalation of Li<sup>+</sup> ions, therefore reducing the diffusion coefficient [59]. The NW-150°C thin film have a highly disordered amorphous structure, which might offer a large number of diffusion channels. This would allow electrolyte ions to move quickly and accommodate a large number of ions [60]. On top of that, as given in XPS results the presence of nickel defects or Ni<sup>3+</sup> ions might change this diffusion route & so affect the capacity of diffusion [61]. Thus, the increased Ni vacancies along with the favourable amorphous structure of fabricated NW-150°C thin films provides a distinct pathway for Li<sup>+</sup> ions, enhancing the device electrochromic efficiency.

Chronocoulometry (CC) yields quantitative data on the quantity of protons or ions intercalated or deintercalated upon the application of a double-step potential during a certain duration. Fig. 10 (a) illustrates the CC plot for the films subjected to cycling in 1 M LiClO<sub>4</sub> at a potential step ranging from + 2 to -1.4 V relative to Ag/AgCl. The quantity of charge interaction ( $Q_{in}$ ) increased when the  $S_T$  is increased from RT to 150 °C. Further increasing the  $S_T$  showed decreased  $Q_{in}$  values. The amorphous NW-150°C thin film, exhibiting enough nickel defects, promote the facile intercalation of Li<sup>+</sup> ions. Fig. 10 (a) shows that compared to  $Q_{in}$ , the de-inserted charges ( $Q_{din}$ ) are lower. This discrepancy results from some Li<sup>+</sup> ions being trapped within the film even after the process had been reversed.

The span of time it takes to reach 90 % of  $\Delta T$  is often referred to as response time, which is a critical characteristic of EC materials. The chronoamperometry curve cycled in 1 M LiClO<sub>4</sub> for 10 s at a potential step of + 2 to -1.4 V versus Ag/AgCl for Li<sup>+</sup> ions is shown in Fig. 10 (b). Table 2 shows the bleached ( $T_b$ ) and coloured ( $T_c$ ) switching time. NW-

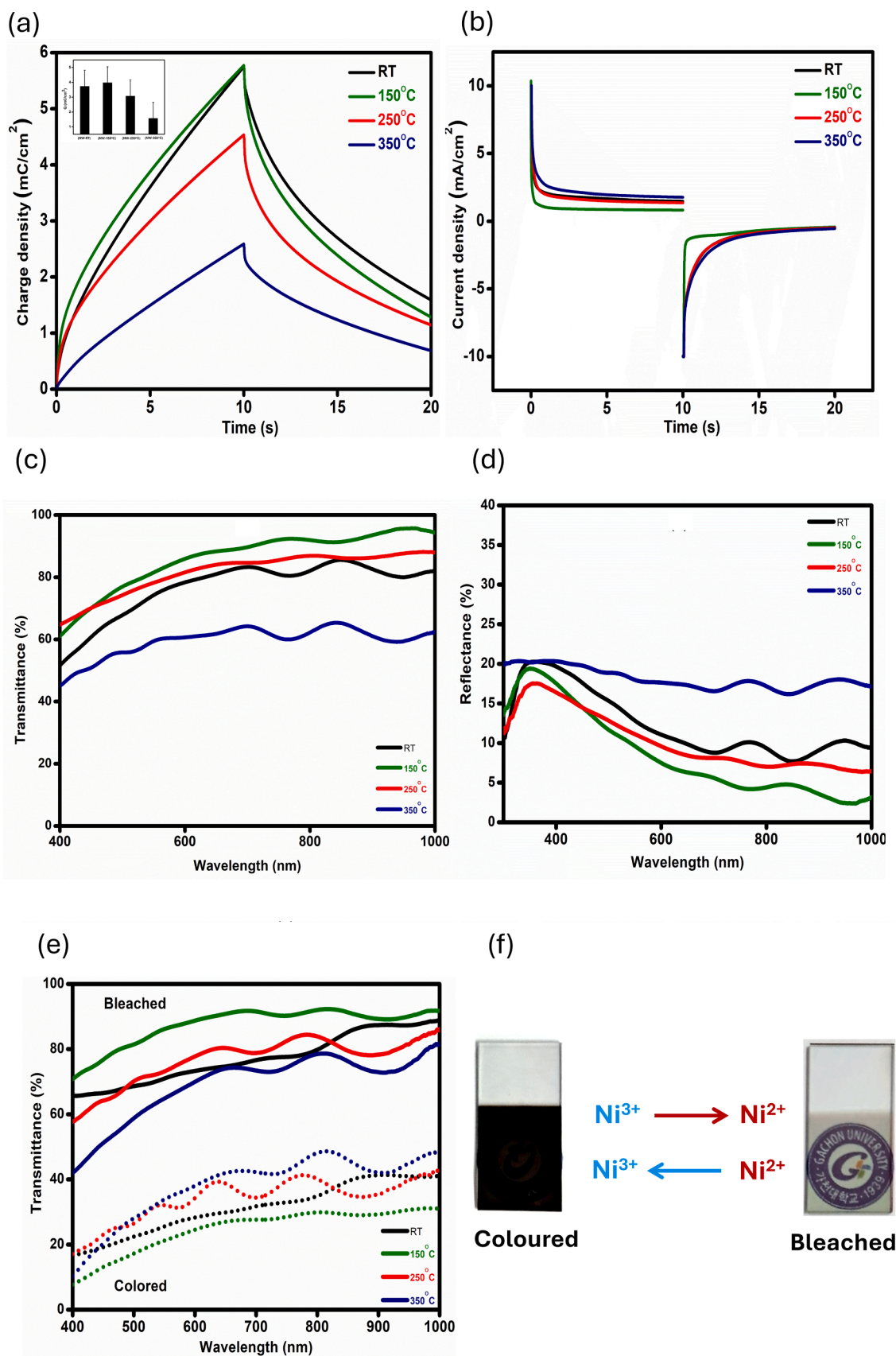


**Fig. 10.** (a) Chronocoulometry curve of NW-(RT, 150 °C, 250 °C & 350 °C) thin films. Inset shows the error bars. (b) Time response of the current density of NW-(RT, 150 °C, 250 °C & 350 °C) thin films. (c) Transmittance spectra for as-deposited NW-(RT, 150 °C, 250 °C & 350 °C) thin films. (d) Reflectance spectra for as-deposited NW-(RT, 150 °C, 250 °C & 350 °C) thin films.

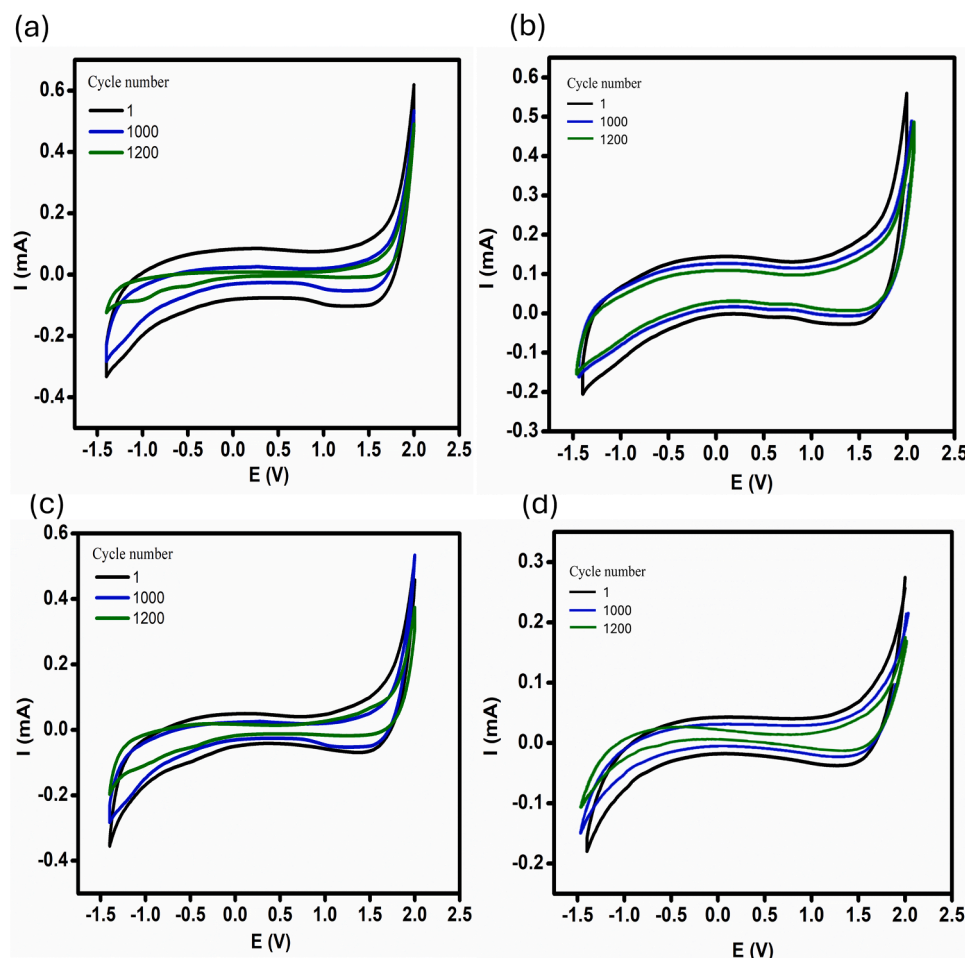


Fig. 11. Cyclic stability study for (a) NW-RT (b) NW-150°C (c) NW-250°C, and (d) NW-350°C thin film.

150°C thin film showed less  $T_b$  and  $T_c$  values. This decrease in switching speed is ascribed the enhancement of electron conductivity and the reduction of diffusion length [62].

As shown in Fig. 10 (c) the optical transmittance for the as-deposited NW-RT sample shows more than 60 % of transmittance in the visible spectrum. Increasing the substrate temperature to 150 °C the transmittance increased which may be due to decreased optical scattering of the film or decreased reflectance. Further increasing the temperature, the transmittance decreased, which may be due to changes in the optical scattering of the film and increase in reflectance. Reflectance Fig. 10 (d) of the samples initially decreased and then increased with substrate temperature. The critical parameters of electrochromic films for applications in devices are bleaching transmittance ( $T_b$ ) and coloring transmittance ( $T_c$ ). They need to exhibit significant opacity when colored and considerable transparency when bleached. The outcome is effective optical modulation ( $\Delta T = T_b - T_c$ ), which distinguishes  $T_b$  from  $T_c$ . Fig. 10 (e) shows the recorded optical transmission spectra of the NW films in the  $T_b$  and  $T_c$  states that spans from 300 nm to 1000 nm. NW-RT sample shows 71 % of transmittance in the bleached state and 25 % in the coloured state. As reported by S.H. Lee et al., the electrochromic Ni-W oxide exhibits a more rapid lithium insertion-extraction process compared to non-stoichiometric nickel oxide and may facilitate optical modulation by simultaneous coloring and bleaching with the working electrode. The shift from a p-type semiconductor to an intrinsic semiconductor due to the addition of tungsten led to a reduction in charge transfer resistance of Ni-W oxide films during lithium insertion. The augmentation of charge transfer density with addition of tungsten content in Ni-W oxide films is mostly attributable to the reduction of charge transfer resistance and the enhancement of the lithium diffusion

coefficient. The addition of tungsten into a base matrix of amorphous nickel oxide creates an open structure that primarily enhances the lithium diffusion coefficient [34]. Hence, addition of tungsten oxide increases the efficiency of ECD device. As the substrate temperature increased, the bleached and coloured transmittances were gradually reduced. But NW-150°C thin film showed high bleached transmittance of 86 %, very low coloured transmittance of 21 %, with the higher optical modulation (65 % at 550 nm). The digital image for NW-150°C film in coloured & bleached condition is showed in Fig. 10 (f). The reduction in colored transmittance and increased and bleached transmittance is directly correlated with the enhancement of  $\text{Li}^+$  ion intercalation and de-intercalation inside the NW-150°C films. At low temperatures, nickel oxide has a highly disordered amorphous structure, facilitating many diffusion channels for Li (ion) intercalation. Moreover, the slight increase of the substrate temperature to 150 °C reduces energy barrier & generates a significant quantity of defects, hence facilitating additional pathways for rapid Li-ion diffusion. However, as the  $T_f$  is further raised, the structure of the samples transforms to a denser form, obstructing the intercalation route of Li (ions). The fundamental need of electrochromic devices for practical applications is long-term cycle stability. As shown in Fig. 11 (a-d), the electrochemical stability of all samples was evaluated by conducting cyclic voltammetry for 1200 cycles at a constant scan rate of  $150 \text{ mV s}^{-1}$ . All the samples start to degrade slightly after 1000 cycles and further degrades at 1200 cycles. It is evident from Fig. 11 (b) that NW-150°C sample is highly stable up to 1000 cycles and starts to degrade slightly after 1200 cycles indicating the highly stable nature of the sample when compared to other samples. Table 3 demonstrates superior electrochromic performance for our sample in comparison to earlier studies [63–75].

**Table 3**

Comparison of our NW thin film's electrochromic performance with previous reported values.

| Material                          | Electrolyte     | Optical modulation ( $\Delta T$ ) % | Coloration time (sec)<br>$t_c$ | Bleaching time (sec)<br>$t_b$ | References |
|-----------------------------------|-----------------|-------------------------------------|--------------------------------|-------------------------------|------------|
| NW-150°C                          | Li <sup>+</sup> | 65.0                                | 1.00                           | 0.89                          | Our work   |
| NiO                               | OH <sup>-</sup> | 49.0                                | 2.50                           | 0.65                          | [63]       |
| NiO                               | Li <sup>+</sup> | 54.0                                | 7.30                           | 3.90                          | [64]       |
| NiO                               | OH <sup>-</sup> | 51.6                                | 4.20                           | 2.40                          | [65]       |
| NiO                               | Li <sup>+</sup> | 67.0                                | 14.90                          | 1.50                          | [66]       |
| NiO                               | OH <sup>-</sup> | 56.5                                | 11.0                           | 8.0                           | [67]       |
| WO <sub>3</sub> /NiO              | Li <sup>+</sup> | 46.0                                | 3.10                           | 4.60                          | [68]       |
| NiO-V <sub>2</sub> O <sub>5</sub> | Li <sup>+</sup> | 35.0                                | 8.00                           | 11.0                          | [69]       |
| NiO@W2                            | Li <sup>+</sup> | 61.5                                | 4.42                           | 1.40                          | [70]       |
| Ta-NiO                            | Li <sup>+</sup> | 43.5                                | 17.0                           | 8.0                           | [71]       |
| Li-Si-NiO                         | Li <sup>+</sup> | 37                                  | 2.4                            | 8.8                           | [72]       |
| Al-NiO                            | OH <sup>-</sup> | 43.1                                | 5.19                           | 2.51                          | [73]       |
| NiO                               | OH <sup>-</sup> | 51                                  | 2.60                           | 1.20                          | [74]       |
| NiO                               | Li <sup>+</sup> | 51.5                                | 10.10                          | 3.00                          | [75]       |

#### 4. Conclusion

In a nutshell nickel tungsten oxide counter electrodes were fabricated using the RF sputtering approach at various substrate temperatures: room temperature (RT), 150°C, 250°C, and 350°C. Low temperature deposited film showed amorphous nature. Crystallization of the film commenced at higher temperature. Surface roughness of the films increased with increasing substrate temperature owing to the crystalline nature. The FESEM analysis demonstrated that the grain size of the film increased with increasing substrate temperature. The formation of a columnar nanostructure facilitated efficient mass movement across the film, resulting in advantages for ion intercalation and deintercalation kinetics. The Raman study confirms the presence of Ni<sup>3+</sup> ions alongside Ni<sup>2+</sup> ions. The XPS examination reveals that the NW film is composed of Ni<sup>2+</sup> and Ni<sup>3+</sup> ions. The presence of Ni defects or Ni vacancies diminishes as the substrate temperature rises. The substrate temperature is crucial in improving electrochromic efficiency of NiO films, as it induces structural changes and generates nickel vacancies. The NW-150°C film demonstrated superior electrochromic performance, achieving an extremely high optical modulation of 65 % and a switching time of 0.89 seconds for bleaching and 1.0 seconds for coloring, and commendable cyclic stability up to 1000 cycles. The research results demonstrate that the developed nickel tungsten oxide film is suitable for use as a counter electrode in energy-efficient smart windows.

#### 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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