

Rapid thermal annealing treatment on WO₃ thin films for energy efficient smart windows

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ABSTRACT

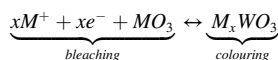
Electrochromic devices (ECDs) based on tungsten trioxide (WO₃) have garnered significant attention in the areas of smart windows, dynamic display, low-power displays, and in other advanced sectors. The electrochromic property of WO₃ is primarily influenced by both electron conduction and ion diffusion processes. This research investigates on the influence of rapid thermal annealing (RTA) on the electrochromic performance of RF sputtered tungsten oxide thin films, which relies on ion diffusion process. RTA treated film showed a mixture of amorphous and crystalline (monoclinic), heterostructure phase. Structural, compositional, electrical, optical, morphological, and electrochromic studies were carried out using various techniques. Based on the electrochromic analysis, WO₃ thin films, RTA treated at 300°C showed higher diffusion coefficient with larger optical modulation (ΔT) of 80 % due the formation of heterostructure with more oxygen vacancies. We hope that this research could propose the possibility for developing high-performance electrochromic smart windows.

1. Introduction

Global energy consumption is increasing almost every day, leading to an energy crisis. This energy crisis is as a result of increased industrial activity and technological advancements in both emerging and developed countries. Almost 40 % of global energy is consumed by commercial and civil buildings [1–3]. The energy supply from fossil fuels is estimated to endure just three to four decades. In this regard, it is imperative to develop energy efficient electrochromic devices (ECDs). Electrochromic devices have piqued the interest of researchers due to their ability to undergo reversible color change under low potential transformation. In contrast to other electronic devices, they require energy only during the switching process. They stay transparent/opaque once switched until disturbed by the application of a potential in the reverse direction [4]. Research indicates that smart windows, which are composed of electrochromic devices (ECDs), have the capability to regulate indoor lighting and temperature, which promotes energy saving [5,6]. Aside from smart window ECD has other potential applications like space craft thermal control, low-power displays, antiglare rearview mirrors, military camouflage, and energy storage systems [7].

Generally, highly efficient electrochromic smart window needs electrochromic materials with larger optical modulation, ultrafast

switching time, and superior cyclic stability. Among the various electrochromic (EC) materials, tungsten oxide (WO₃) stands out as one of the most significant due to its superior coloration efficiency, excellent optical modulation, and cost effective [8]. The electrochromic properties of WO_x, which are reversible upon double insertion of electrons and metal cations (such as Li⁺, H⁺), are significantly dependent on the composition and structure of the materials [9]. The coloration process can be explained using the following mechanism [10].



where M indicates alkali metals such as H⁺, Li⁺, K⁺, Na⁺, and so on, and the fractional number of sites occupied in the WO₃ lattice is determined by the subscript x in the general formula of the M⁺ intercalated compound M_xWO₃.

It is important to highlight that extensive research has been performed to enhance the electrochromic (EC) performance of WO₃ since its discovery. More importantly, earlier research has shown that the EC characteristics of WO₃ are strongly connected with its crystallinity [11–14]. It is reported that highly disordered or amorphous (porous) WO₃ exhibits excellent coloration efficiency with fast switching speed in the visible region [15]. For instance, W. Wei et al., improved the

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efficiency of the EC device by controlling the crystallinity of oxygen-deficient tungsten oxide on SnO₂ nanoflake arrays for advanced dual-band electrochromic smart window [16]. N.S. Pham et al., demonstrated that porous WO₃/NiO films prepared via triple pulse electrodeposition performs admirably, facilitating not only charge transfer and electrolyte penetration within the film, but also reducing WO₃/NiO film expansion during Li⁺ insertion and extraction [17].

However, lack of adhesion with the substrate's surface and the flexible amorphous matrix undoubtedly results in substandard long-term cyclic stability for the EC process [18]. In comparison to amorphous WO₃, crystalline or highly ordered WO₃ exhibits enhanced substrate adhesion and a more stable structure, thereby achieving the remarkable cyclic stability [19]. The structure and crystallinity of the WO₃ films are greatly influenced by the deposition parameters and post-annealing treatment. Particularly, post-annealing (thermal treatment) has a significant influence on the optical and microstructural characteristics of ECDs. Post-annealing under various temperatures will affect ion and electron transport in ECDs as it is highly dependent on the change in crystallinity of the WO₃ films [20]. Also, reports reveal that annealing-induced structural changes could improve the efficiency of ECDs. Y. Chen et al., have reported that, solvothermally prepared tungsten oxide EC films annealed at 250 °C shows large optical modulation (76.9 %) in the entire solar spectrum, reaching the largest value of 80.1 % in Vis region at 765 nm and 81.2 % in NIR region at 960 nm, fast responses (4.9 s for coloration and 6.0 s for bleaching) and a high CE of 86.4 cm² C⁻¹ [21].

According to a study by Xi Chen et al., the WO₃ films that were annealed at 200 °C exhibited superior electrochromic performance, characterized by a larger optical modulation (ΔT) and excellent cyclic stability [22]. Also, Kunyapat thumavichai et al., found that WO₃ films annealed at 350 °C had the best stability during the electrochromic analysis, with a 4 % increase in Li⁺ intercalation and a 12 % increase in deintercalation compared to the untreated WO₃ samples [23]. In addition, B. Wen-Cheun Au et al., observed a maximum optical modulation of 62 % for WO₃ thin films annealed at 100 °C [24]. Additionally, a report stated by C.-C. Liao et al., revealed that, WO₃ nanowire film annealed at 500 °C, provided better optical modulation of 64.8 %, and coloration efficiency of 61.3 cm² C⁻¹ [25]. However, the tightly packed and completely-ordered structure in crystalline WO₃ hinders the efficient insertion and extraction of ions, leading to a slower switching speed for coloration/bleaching [12,26]. Also, crystalline WO₃ films are not suitable for fabricating large-area devices owing to its non-uniform grain size. This limitation restricts WO₃ extensive application. Under these conditions, an optimum WO₃ heterostructure films combining the effects of amorphous and crystalline WO₃ would be of great benefit for fabricating highly efficient ECDs. For example, Her and Chang used a two-step hydrothermal process to prepare a crystalline/amorphous WO₃ core-shell heterostructure [27]. This innovative heterostructure exhibited an excellent optical modulation (of 44 % at 550 nm), with significant increase in colouring and bleaching (41.0 and 6.0 s), speed. Guo et al., used a two-step approach comprising hydrothermal treatment and spin-coating to fabricate hexagonal/amorphous WO₃ core/shell nanorod arrays, which exhibited excellent optical modulation (67.7 % at 660 nm) and CE (101 cm² C⁻¹ at 800 nm) [28].

Among various deposition techniques, magnetron sputtering is beneficial for fabricating uniform WO₃ films over large-area substrates. Post heat treatment like rapid thermal annealing (RTA) can favour the fabrication of heterostructure films. Even with the much shorter process time of RTP, the RTP-treated films show competitive or superior properties and uniformity to those annealed by furnace, which confirmed that the RTP system is a more efficient and effective annealing method than a furnace method [29]. In conventional annealing, high annealing temperatures are often required to allow the solvent to be removed from the film. However, conventional annealing at high temperatures transforms the films to crystalline nature which hinders the formation of heterostructure [30]. Also, crystalline tungsten oxide films are not

suitable for large-area devices because of its non-uniform grain size. Hence, it is possible to prepare high purity amorphous/crystalline WO₃ films using magnetron sputtering and rapid thermal annealing (RTA) techniques.

In the current investigation, RF (radio frequency) magnetron sputtering technique is adopted to fabricate WO₃ thin films. The manufactured films were subjected to rapid thermal annealing treatment, with temperatures ranging between 100°C- 400°C. An in-depth relationship between structural, optical, and EC characteristics and RTA treatment under nitrogen (N₂) atmosphere is analysed and reported. Performance of tungsten oxide electrochromic devices based on RTA treatment is reported for the first time.

2. Experimental

Thin films of WO₃ were fabricated with RF magnetron sputtering system KVS-2004 using ultra-pure (99.99 %) tungsten oxide target as shown in Fig. 1. Initially the sputtering chamber was evacuated to a base pressure of 5×10^{-6} Torr. Later inert Ar gas (sputtering gas) is inlet into the chamber with a flow rate of 30 sccm. The working pressure is maintained as 10 mTorr. In order to initiate plasma RF power of 60 W is applied to the WO₃ target. Now electrons present in the sputtering gas is propelled away from the WO₃ target, and creates collision with neighbouring Argon atoms. These collisions produce electrostatic repulsion, which 'knocks off' electrons from Ar atoms, resulting in ionization. Positively charged Ar⁺ ions are now propelled towards the negatively charged WO₃ target, resulting in high energy collisions with the WO₃ target surface. These collision knocks off atoms from the WO₃ target surface into the vacuum environment with sufficient kinetic energy to reach the ITO precoated glass substrate's surface (ITO/WO₃). The deposition was carried out at room temperature (RT) for 45 min. Later the prepared films were kept inside the RTA chamber as shown in Fig. 2. Initially the chamber was evacuated to a base pressure of 4×10^{-3} Torr, then N₂ gas with a flow rate of 30 sccm is let into the chamber. Then, the samples were subjected to RTA treatment with temperatures varying like 100°C (RTA-100°C), 200°C (RTA-200°C), 300°C (RTA-300°C), and 400°C (RTA-400°C) and, under N₂ atmosphere for 10 min.

The structural property of WO₃ thin film was analysed via X-ray diffraction study (RIGAKU Smartlab X-ray Diffractometer). The surface morphological property of the film was studied by Field emission

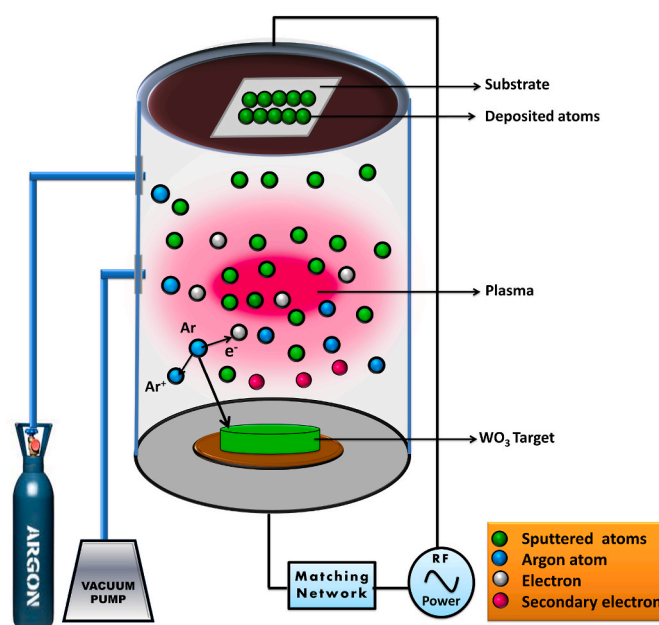


Fig. 1. Schematic illustration of sputtering unit with sputtering mechanism.

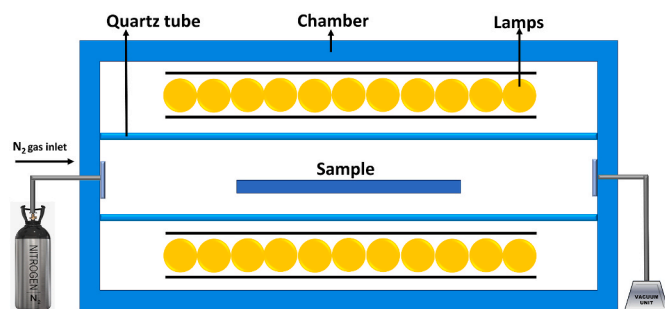


Fig. 2. Schematic illustration of rapid thermal annealing (RTA) system.

scanning electron microscopy (FESEM) equipped with energy dispersive X-ray analysis (EDX) (FEI QUANTA 250, Czech Republic). Fourier-transform infrared spectra was performed with JASCO FT/IR-4600 spectrometer. The electrical properties were measured using a 4-point Hall effect measurement system (HMS 3000, Ecopia). The optical property of WO_3 film was studied using UV–Vis–NIR spectrometer (Carry 5000 UV–Vis–NIR, Agilent) in the wavelength range of 300–2400 nm. Photoluminescence study was carried out using Dongwoo Optron. The elemental composition of the deposited film was studied by X-ray photoelectron spectroscopy (XPS: JEOL PS-9010 TR). Electrochemical measurements like cyclic voltammetry, chronocoulometry, electrochemical impedance spectroscopy (EIS) was done via VersaSTAT3 (VERSAtat3) in a three-electrode setup with WO_3 as the working electrode, Pt as the counter electrode and Ag/AgCl as the reference electrode immersed in 0.5 M of HCl electrolyte solution.

3. Results and discussion

3.1. XRD

The electrochromic performances of WO_3 films are greatly influenced by the crystal structure and chemical bonding. The X-ray diffraction (XRD) technique was used to examine the crystalline structures of WO_3 thin films deposited on ITO precoated glass substrate and then treated with rapid thermal annealing (RTA) at various temperatures (100 °C, 200 °C, 300 °C, and 400 °C), as illustrated in Fig. 3. WO_3 films deposited at room temperature (termed as RTA-RT), exhibit only diffraction peaks that correspond to the ITO glass [31], indicating the amorphous nature of the WO_3 films. WO_3 films treated with RTA-100 °C

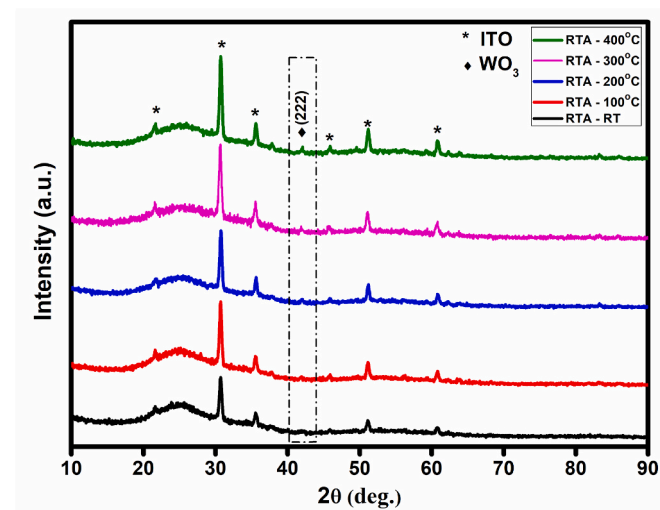


Fig. 3. XRD pattern of WO_3 films RTA treated at different temperatures (RT, 100 °C, 200 °C, 300 °C and 400 °C).

shows very mild diffraction peak at 41.89° corresponding to (222) plane of the monoclinic phase of WO_3 (JCPDF No. 83–0951) [23], indicating the mixed amorphous and crystalline nature of the film. Further increasing the RTA temperature to 200 °C, 300 °C, and 400 °C slightly increased the intensity of (222) plane indicating the improvement in the crystalline nature of the films. This indicates that the RTA treated films are not completely crystallized and confirms the successful formation of heterostructured (amorphous/crystalline) WO_3 films.

3.2. Morphological study

Surface and cross-section morphology of the as-deposited (RTA-RT) and RTA-300 °C WO_3 films deposited on glass substrate were shown in Fig. 4 (a, b, and c). As shown in Fig. 4 (a), the as-deposited WO_3 films exhibited a smooth, uniform, and crack-free appearance, revealing the low roughness of the thin film. The film exhibited smooth morphology with fine grains distributed evenly over the surface. This phenomenon might be attributed to the mobility of adatoms on the surface, which hindered the formation of the voided columnar microstructure. Limwichean et al. [29,32], obtained similar results for WO_3 thin films deposited using the HiPIMS approach. Furthermore, Besozzi et al., reported that low-pressure amorphous tungsten oxide deposition facilitated atom-by-atom development of the thin film, resulting in a compact and uniform surface and cross-section morphology, identical to the current work [33]. Fig. 4 (c) depicts the surface morphology of RTA-300 °C treated WO_3 thin films deposited on glass substrate which showed larger granular particles with disguisable particle boundaries. Similar morphology was observed by Yingming Zhao et al., for WO_3 thin films fabricated at a substrate temperature of 400 °C [34]. The surface exhibited granular voided structure which can facilitate the intercalation/de-intercalation of H^+ ions, which helps to enhance the electrochromic performance of the device.

3.3. FTIR

FTIR study was performed to investigate the bonding of oxygen to the metal ions in the M – O (Metal-Oxygen) structure. FTIR study was performed for the WO_3 films deposited on plane glass substrate. Fig. 5 shows the FTIR spectra of WO_3 for RTA (RT, 100 °C, 200 °C, 300 °C, and 400 °C) samples, recorded in the range of 200–2000 cm^{-1} . The broad peaks observed around 667, and 780 cm^{-1} are ascribed to the bending modes of vibrations for O–W–O in WO_3 [35,36]. The broad peak observed around 906 cm^{-1} corresponds to the stretching modes of W–O–W in WO_3 and the peak around 1390 cm^{-1} is attributed to the O–H bending vibration in W–OH [35,36]. This confirms the successful formation of highly pure WO_3 films.

3.4. XPS measurements

The X-ray photoelectron spectroscopy (XPS) technique was utilized in order to further investigate the chemical composition as well as the oxidation state of WO_3 films. The XPS survey spectra for RTA treated WO_3 samples reveal the presence of tungsten (W), oxygen (O), nitrogen (N), and carbon (C) elements (Fig. 6), confirming the successful fabrication of pure tungsten oxide thin films. Since the RTA treatment is conducted in the nitrogen (N_2) atmosphere, a small peak for N 1s is observed around 400 eV. As illustrated in Fig. 7 (a) and 7 (c), 8 (a), 8 (c), and 9 (a) the high-resolution W 4f spectra has spin-orbit peaks around binding energy levels of 35.5, 37.7, and 41.4 eV. These peaks correspond to the $\text{W } 4f_{7/2}$, $\text{W } 4f_{5/2}$, and $\text{W } 5p_{3/2}$ states, respectively, which represent the highest valence state of W^{6+} in WO_3 films [37]. Additionally, peaks observed around 33.8, and 36.5 eV, corresponds to $\text{W } 4f_{7/2}$, $\text{W } 4f_{5/2}$, which corresponds to W^{5+} state in WO_3 films [37]. The presence of W^{5+} peaks indicates that the as-deposited and RTA treated WO_3 thin films are all substoichiometric. In general, the ratio of $\text{W}^{6+}/\text{W}^{5+}$ can reveal the oxygen vacancy concentration level in the films. From Fig. 7(a) and (c),

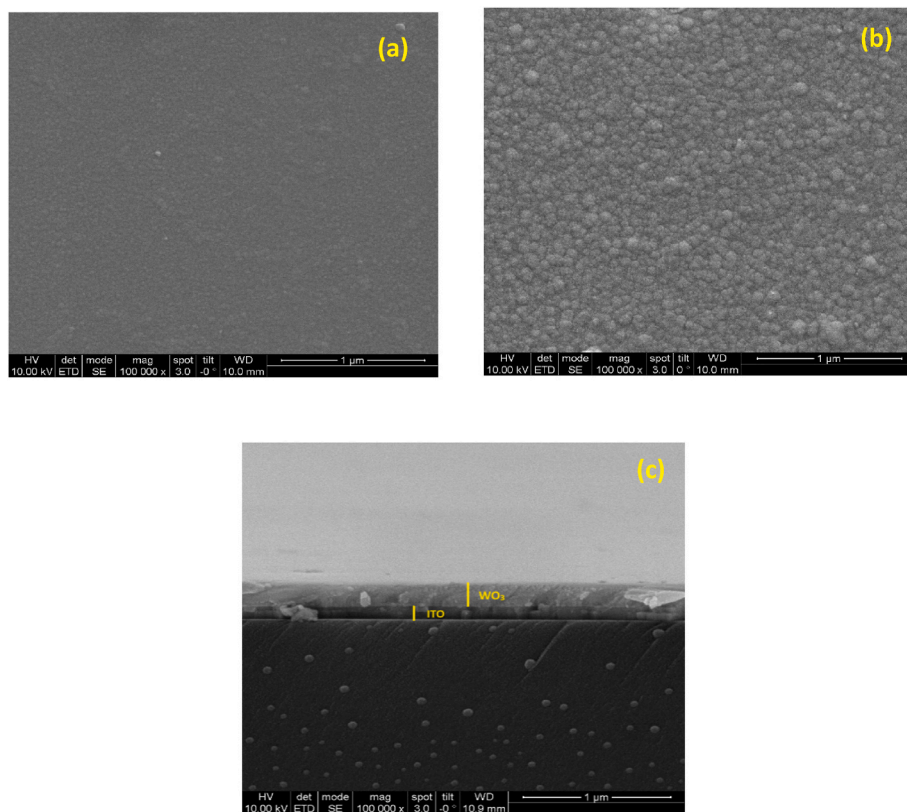


Fig. 4. SEM image of WO_3 films (a) RTA-RT, (b) RTA- 300 °C, and (c) cross sectional image of RTA- 300 °C.

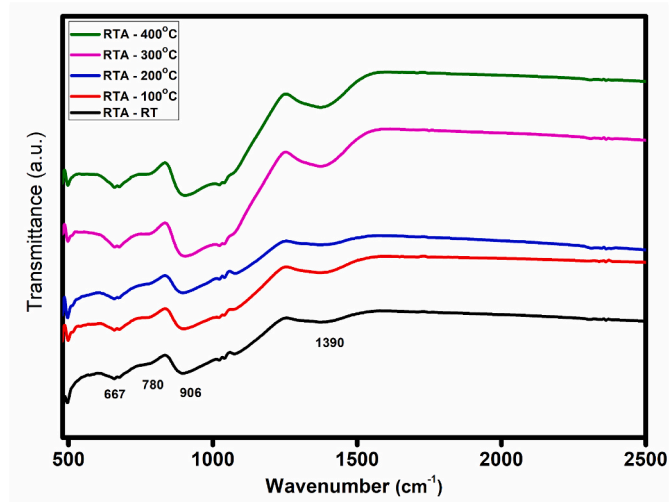


Fig. 5. FTIR spectra of WO_3 films RTA treated at different temperatures (RT, 100 °C, 200 °C, 300 °C and 400 °C).

8 (a), 8 (c), and 9 (a), we can observe that the W^{5+} signal increases with the increase in RTA temperatures, which indicates the increase in oxygen deficiency. Moreover, the high-resolution XPS spectra of O 1s can be deconvoluted into two peaks as shown in Fig. 7 (b) and 7 (d), 8 (b), 8 (d), and 9 (b), where the main peak at approximately 530.5 eV can be ascribed to the lattice oxygen of the W–O bond in the WO_3 , and the additional shoulder peak around 531.8 eV can be assigned to the adsorbed O on the surface, especially around the regions of oxygen vacancy [38,39]. Although XPS measurements have limited precision, it is however possible to carry out a semi-quantitative study of the relative O content trend in the deposited WO_3 films. The ratio of the adsorbed

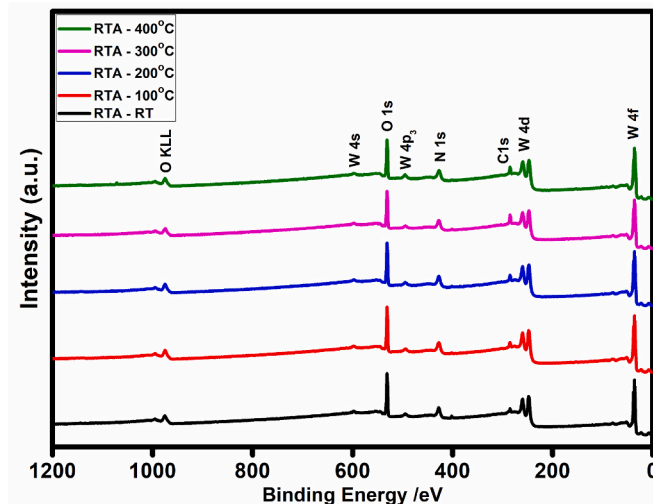


Fig. 6. XPS survey spectrum of RTA treated tungsten oxide thin films.

oxygen increases from 23.84 to 39.13 % due to the surface oxygen vacancies. This demonstrates the increase in oxygen vacancies with increase in RTA temperature.

In addition, we measured the atomic ratio of O/W with the high-resolution XPS spectra for W 4f and O 1s. As shown in Table 1, it can be observed that the O/W atomic ratios reduce from 2.24 to 1.92 with increase in RTA temperature. This decrease suggests an increase in the presence of oxygen vacancies. According to reports, the existence of oxygen vacancies in WO_3 films provides an enormous number of binding sites for H^+ ions, hence enhancing the optical modulation [40]. It also boosts the diffusion of H^+ ions into the WO_3 host for rapid electrochromic kinetics [41,42].

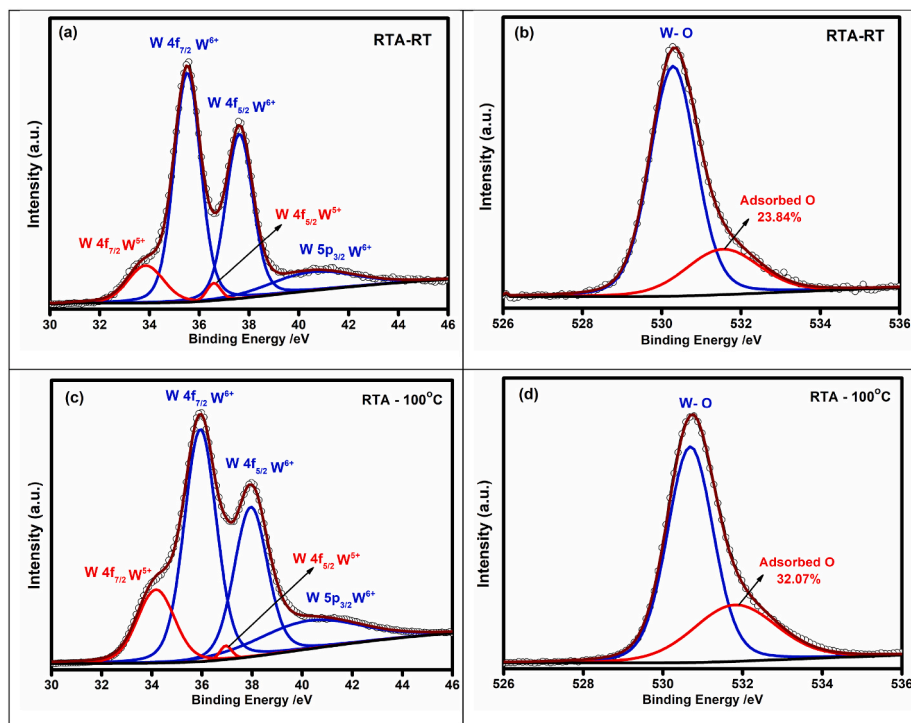


Fig. 7. XPS core level spectrum of tungsten oxide (WO_3) thin films. The black circles correspond to the experimental data. The brown curve corresponds to the fitting curves. Each black circles are resolved into different oxidation state: W^{6+} (blue curves) and W^{5+} (red curves). (a) W4f for RTA- RT (b) O1s for RTA- RT (c) W4f for RTA- 100 °C (d) O1s for RTA- 100 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

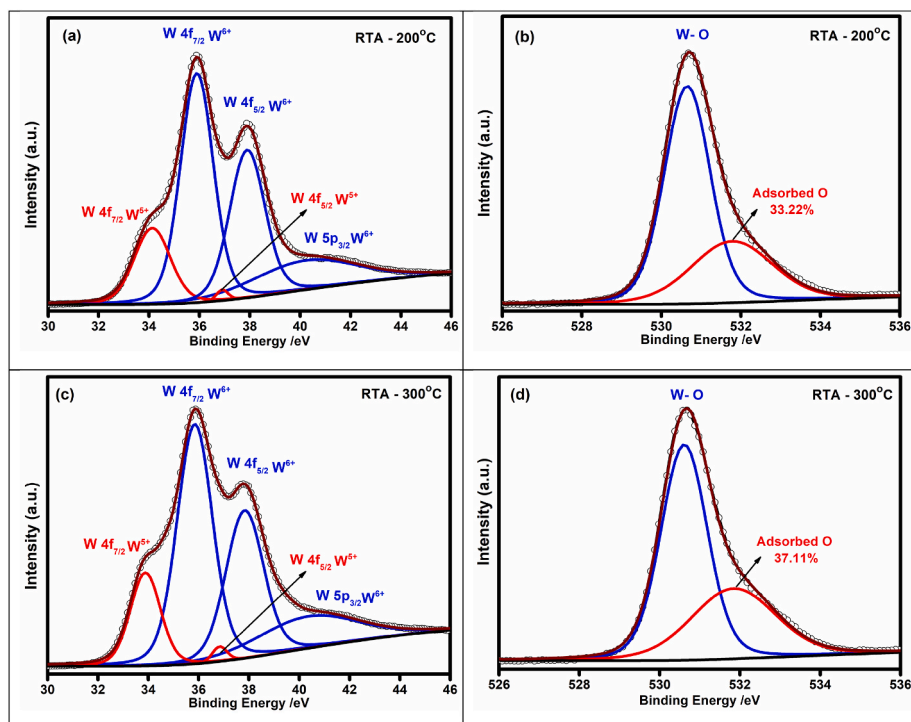


Fig. 8. XPS core level spectrum of tungsten oxide (WO_3) thin films. The black circles correspond to the experimental data. The brown curve corresponds to the fitting curves. Each black circles are resolved into different oxidation state: W^{6+} (blue curves) and W^{5+} (red curves). (a) W4f for RTA- 200 °C (b) O1s for RTA- 200 °C (c) W4f for RTA- 300 °C (d) O1s for RTA- 300 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.5. Electrical properties

The electrical properties of rapid thermal annealing treated WO_3 thin

films are listed in Table 2. The resistivity of the films decreased with increase in RTA temperature. The key reason for the reduction in resistivity was due to the heat treatment. With increase in temperature as

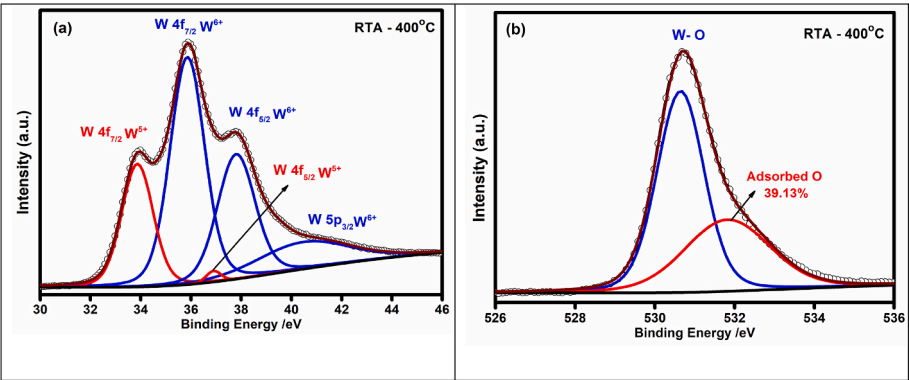


Fig. 9. XPS core level spectrum of tungsten oxide (WO₃) thin films. The black circles correspond to the experimental data. The brown curve corresponds to the fitting curves. Each black circles are resolved into different oxidation state: W⁶⁺ (blue curves) and W⁵⁺ (red curves). (a) W4f for RTA- 400 °C (b) O1s for RTA- 400 °C. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Summary of the XPS results.

Sample/RTA temperature	W (%)	O (%)	O/W
RT	69.16	30.84	2.24
100°C	68.67	31.33	2.19
200°C	67.88	32.12	2.11
300°C	67.77	32.23	2.10
400°C	65.69	34.31	1.92

given in Table 2 the energy gap between the conduction band and valence band decreases. When heat treatment is done, the valence electrons in the WO₃ gather enough energy to break the covalent bond and hop to the conduction band. This generates more charge carriers (as shown in Table 2). This increased concentration of charge carriers decreases the resistivity. As given in XPS results, increasing the RTA temperature increases the oxygen vacancies. Hence, both results (increased free-charge carrier concentration and decreased resistivity) are attributable to increased oxygen vacancy concentrations. These oxygen ion vacancies act as positively charged structural defects [43] and function as free-electron trap states, resulting in shallow donor states in the energy gap. The donor states overlap create a band as the concentration of the defect level rises, lowering the energy needed for carrier ionization. As a result, the thermally excited electrons partially occupy the conduction band, resulting in relatively strong n-type conductivity. Annealing under vacuum enhanced the amount of oxygen vacancies on the surface. As a result, RTA process reduced the electrical resistivity of the films. Similar observations were reported by M.F. Al-Kuhaili et al., for tungsten oxide thin films [43].

3.6. Optical properties

Fig. 10 depicts the optical transmittance spectra of RTA treated WO₃ films. The overall average transmittances were found to increase with increase in RTA temperature. This may be due to the reduction of absorption of free carriers and reduced scattering effect [43–45]. Similar results were reported in the literature also. Reddy et al., reported that for

DC magnetron sputtered thin films, transmittance increased as substrate temperature increased [45]. RTA -300°C WO₃ sample showed higher optical transmittance of 19 %. It can be observed from Table 2 that there is a marginal decrease in the energy bandgap (Eg) with respect to increase in RTA temperature. As given in XPS analysis increasing the RTA temperature increased the oxygen vacancy concentration. As per report an increase in oxygen vacancy concentration [46] will lead to a decrease in tungsten oxide bandgap. In addition, rapid thermal annealing (RTA) temperature also impacted the band gap of tungsten oxide [47]. In research by Castro-Hurtado's [48], it was observed that the band gap of the tungsten oxide film reduced as the annealing temperature increased. This can be attributed to the fact that the concentration of oxygen vacancies in the film increased with the increase in temperature [49].

The presence of oxygen vacancy concentration leads to form a defect

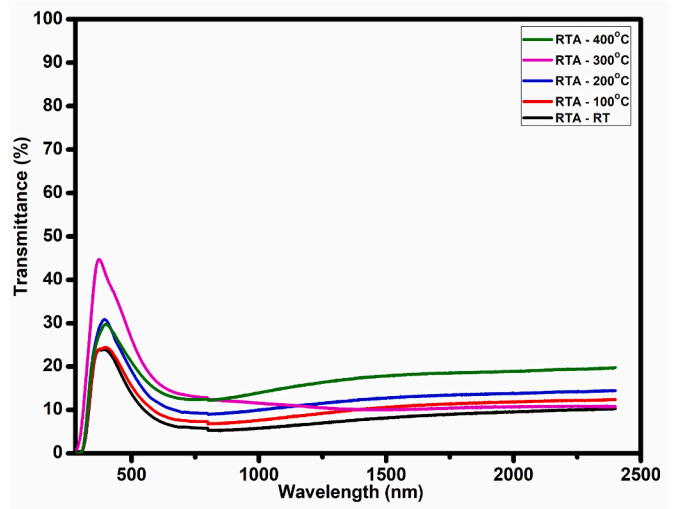


Fig. 10. Transmittance spectra of WO₃ films RTA treated at different temperatures (RT, 100 °C, 200 °C, 300 °C and 400 °C).

Table 2
Electrical and optical properties of WO₃ films.

Sample/RTA temperature	Resistivity ρ ($\Omega \cdot \text{cm}$) $\times 10^{-4}$	Charge carrier concentration N (cm^{-3}) $\times 10^{20}$	Mobility (μ) ($\text{cm}^2/\text{V} \cdot \text{s}$)	Transmittance at 550 nm T (%)	Eg (eV)
ITO	3.76	11.00	15.2	–	–
RT	10.1	3.00	19.4	10	3.12
100°C	9.14	3.63	18.8	11	2.95
200°C	8.13	5.87	13.1	13	2.73
300°C	7.87	6.50	14.4	19	2.96
400°C	6.86	8.00	11.4	17	2.70

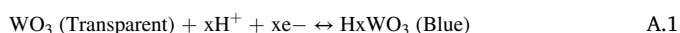
band below the conduction band and it extends into conduction band to form a degenerate semiconductor which results in a fermi level upshift. Therefore, the narrowing of E_g was attributed to increased oxygen vacancy concentration [50]. Also, these oxygen vacancies create low valence tungsten ion (W^{4+} or W^{5+}), which will provide unbonded electrons [50]. As the number of unbonded electrons increased, the bottom of the conduction band shrank, causing the E_g to decrease. RTA-300°C samples showed decreased energy bandgap when compared to film deposited at room temperature. WO_3 thin films having narrow band gap with continuous tunnel cavities are useful for enhancing its electronic conductivity and ion intercalation/de-intercalation [24]. This can favour the electrochromic device.

3.7. Photoluminescence

The photoluminescence spectra were recorded under the excitation wavelength of 325 nm at room temperature. As shown in Fig. 11 the characteristic peak appeared at 400 nm, near band edge emission (NBE), is the result of photons emitted by electron-hole recombination across the E_g of WO_3 [51]. The observed visible emission peaks (at 450 nm, 550 nm, and 720 nm) might be attributed to the presence of several luminous centers, like defect energy levels resulting from tungsten interstitials and oxygen vacancies, and also from dangling bonds in tungsten oxide thin films. PL intensities are significantly affected by surface defects [51]. Increasing RTA temperature leads to an increase in NBE and defect peak intensities as a result of the presence of a large number of defect densities.

3.8. Electrochemical analysis

In order to get a better picture of the RTA effect on electrochromism, the electrochemical and electrochromic properties of WO_3 thin films were first thoroughly investigated. The cyclic voltammetry (CV) and transmittance spectra of WO_3 films have been investigated using a three-electrode spectro electrochemical system in a 0.5 M HCl electrolyte. The electrochromic process of tungsten trioxide (WO_3) in the electrolyte based on hydrogen ions (H^+) may be explained as follows:



The CV measurements were carried out for RTA treated WO_3 films. Fig. 12 (a, b, c, d, e and f), represents the cyclic voltammetry of RTA treated (RT, 100°C, 200°C, 300°C, 400°C) tungsten oxide films at varying scan rates (10, 50, and 100 mV/s) in 0.5 M HCl electrolyte with a

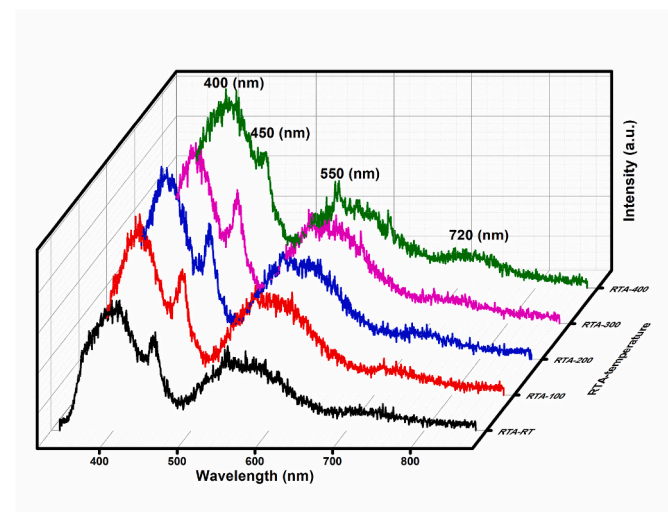


Fig. 11. Photoluminescence spectra of WO_3 films RTA treated at different temperatures (RT, 100 °C, 200 °C, 300 °C and 400 °C).

potential between -1 V and 1 V. A schematic illustration of WO_3 based electrochromic device is depicted in Fig. 13, in which ITO layer acts as transparent conducting layer, WO_3 film as electrochromic layer, and HCl as electrolyte. When cathodic scan was performed, the H^+ ions from the electrolyte gets intercalated into the WO_3 film, now the film turned dark blue as shown in Fig. 13 (a.), indicating the coloration of the film. As seen from XRD results, the room temperature deposited (RTA-RT) sample shows amorphous nature. It has been reported that the strong optical modulation of amorphous WO_3 is based on small polaron absorption caused by the insertion/extraction of H^+ ions and charge compensating electrons in the WO_3 lattice [52,53].

The injected electrons into the WO_3 films are located at W^{5+} sites, whereas the injected H^+ ions will be located in the center of the perovskite unit or form chemical bonds with interstitial oxygen atoms of the perovskite unit. In this case, a spatial separation will inevitably exist between the inserted H^+ ions and electrons, which accounts for the generation of small polarons [54]. Moreover, the formed polarons can absorb incident photon energy and jump back and forth between adjacent W^{5+} and W^{6+} sites [55,56]. Whereas, for RTA treated samples, the film attains crystalline nature slowly. The coloration process of crystalline RTA treated samples are generally considered to adapt to the Drude-mode-like free electron absorption theory [57]. Specifically speaking, ions and electrons will be simultaneously injected into crystalline WO_3 during the coloration process. While injected electrons are located at W^{5+} sites, injected H^+ ions sit at the above-mentioned position to maintain electrical neutrality. Eventually, crystalline WO_3 will undergo a transition from a semiconductor state to a metalloid state, leading to the formation of the tungsten bronze compound (HWO_3) [58]. This will cause an increase in the absorption across the spectrum.

Hence the coloration is due to the reduction of W^{6+} state to the W^{5+} state. Also, during anodic scanning, H^+ ions get de-intercalated from the WO_3 film, turning the film from blue to colourless as shown in Fig. 13 (b). This colour change is due to the charge transfer from W^{5+} to W^{6+} (oxidation). Throughout these reversible processes, the insertion and de-insertion of electrons from the electrode, and H^+ ions from the electrolyte, causes the coloured and bleached states of the films. Increasing the scan rates results in elevated peak (ip) currents, leading to an increased amount of charge flowing through WO_3 films. As shown in Fig. 12 (f), the RTA- 300°C treated WO_3 sample shows significantly higher current densities and larger CV areas when compared to other samples. This indicates that the structurally modified (heterostructure) WO_3 films with required amount of oxygen vacancies can provide more available sites for H^+ ions insertion/extraction [41,59], and hence improving the electrochromic device performance.

To further evaluate the RTA effect on the H^+ ion diffusion kinetics, the diffusion coefficients were evaluated using the following Randles-Servick equation:

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

where D is the diffusion coefficient, C_0 is the concentration of the cations in electrolyte, n is the number of electrons (taking the value of the valency of cations) and ν is the scan rate. As given in Table 3 the evaluated diffusion coefficient values increased with increasing RTA temperature. The increase in oxygen vacancies significantly increases the insertion sites for the H^+ ions, also it helps for the faster diffusion kinetics of H^+ ions [60]. For RTA- 400°C sample, the diffusion co-efficient value decreased indicating the blocking of H^+ ion insertion sites. RTA-300°C sample showed better diffusion co-efficient value, implying the enhanced H^+ diffusion process, compared to other samples. For efficient diffusion kinetics, it is crucial to have a clear and unobstructed pathway for the H^+ ions to pass through in both directions. The presence of defects in the crystalline structures can influence this diffusion pathway and consequently impact the efficiency of diffusion [22]. Hence, the presence of oxygen vacancies (defects), with heterostructure in the RTA-

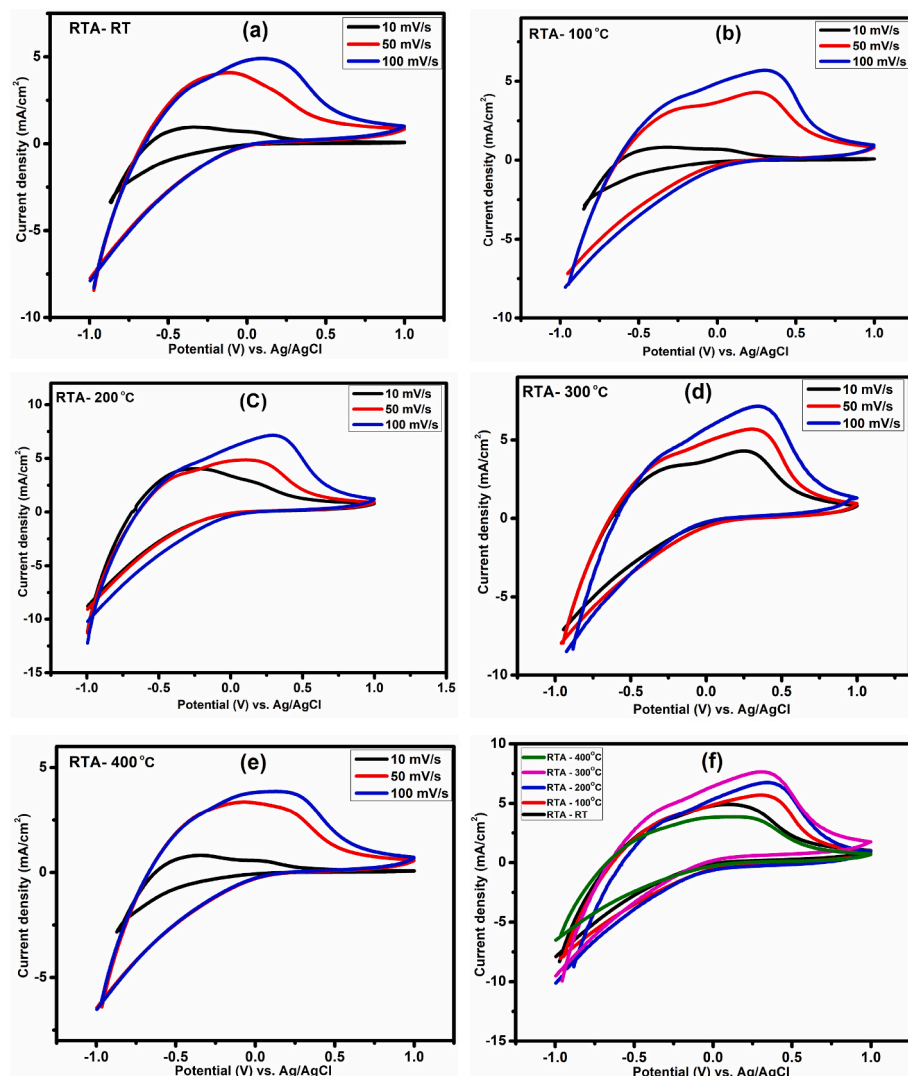


Fig. 12. CV curve for WO_3 film at different scan rates (10, 50, 100 mV/s) (a), RTA - RT (b) RTA - 100°C (c) RTA - 200°C, (d) RTA - 300°C, (e) RTA - 400°C, (f) CV curve for all WO_3 film at a scan rate of 100 mV/s.

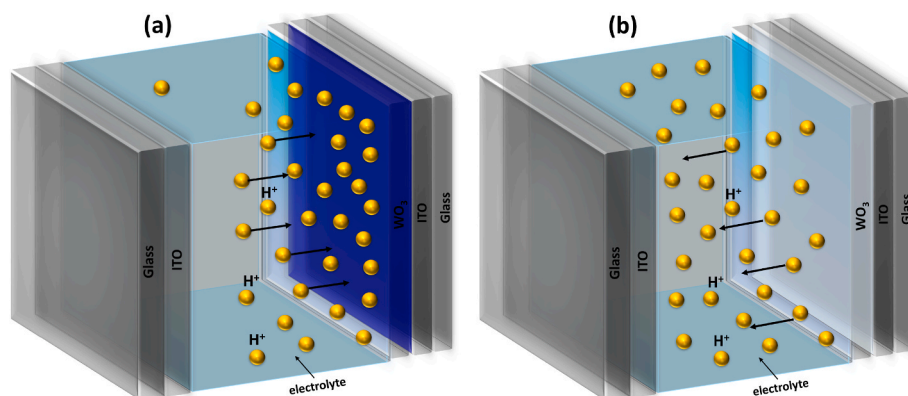


Fig. 13. Schematic illustration of WO_3 based electrochromic device (a) changing to dark blue color upon H^+ ion intercalation (b) color changing from dark blue to transparent upon H^+ ion de-intercalation. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

300°C sample provides a clear pathway for the H^+ ions, favouring the electrochromic device performance.

The optical transmittance in the range of 300 nm–2400 nm at coloured (T_c) and bleached (T_b) states is shown in Fig. 14 (a,b,c,d, and e)

and Table 3. Optical modulation (ΔT) is defined as the difference between the transmittances of coloured (T_c) and bleached (T_b) state. As given in Table 3, the ΔT of the WO_3 films increased with the increase of RTA temperature. Several investigations have indicated that the

Table 3Electrochemical properties of WO₃ films.

Sample/RTA temperature	Diffusion Coefficient (cm ² s ⁻¹) × 10 ⁻¹¹	Bleaching transmittance (T _b) (%)	Colouring transmittance (T _c) (%)	Optical modulation ΔT = (T _b - T _c)
RT	1.35	82	15	67
100°C	1.76	80	12	68
200°C	2.56	84	10	74
300°C	3.35	89	9	80
400°C	0.81	77	17	60

presence of larger amount of oxygen vacancies results in large optical modulation in WO₃ films [61–63]. Conversely, a decrease in oxygen vacancies leads to a reduction in optical modulation and no colouring is detected in almost stoichiometric amorphous WO_{2.98}. [62,64], which revealed the essential role of oxygen vacancy playing in the electrochromic capacity of WO₃ films. In the case of our experiments, the significant increase in the EC performance with RTA treatment is mainly owing to the decreasing level of O/W ratio, or increase in the oxygen vacancies as we have proved in XPS results. These oxygen vacancies create large amount of insertion sites and larger H⁺ ions get accommodated into the WO₃ thin films, and hence increasing the optical

modulation [60]. Further increasing the RTA temperature to 400°C decreased the optical modulation. The EC performance reduction can be owing to the increase of crystallinity after thermal treatment at little high temperature, which has a negative impact on EC properties of WO₃ films. According to reports, amorphous WO₃ film shows very high optical transmittance modulation with even little charge exchange due to the porous structures, whereas, with increasing crystallinity, EC properties can be drastically reduced in the visible spectral region and delay the switching kinetics [65–67]. RTA- 300°C sample, showed superior optical modulation of 80 %, which is owing to the heterostructure formation with large amount of oxygen vacancies.

Chronocoulometry (CC) provides quantitative data on the quantity of protons/ions that are intercalated or deintercalated with the application of a potential double step over a specific duration of time. To investigate the process of H⁺ ion intercalation/deintercalation over time, CC was performed in the range of -1 V–1 V versus Ag/AgCl for a duration of 10 s. Fig. 14 (f) displays the CC spectrum of RTA treated tungsten oxide films. The quantity of charge intercalated (Q_{in}) increased with increase in RTA temperature. Kunyapat thummavichai et al., reported that annealing successfully increased the kinetics of Li⁺ ions and enhanced the electrochromic performance of WO₃ films [23]. RTA-300°C sample, showed higher Q_{in} value, since the heterostructure WO₃

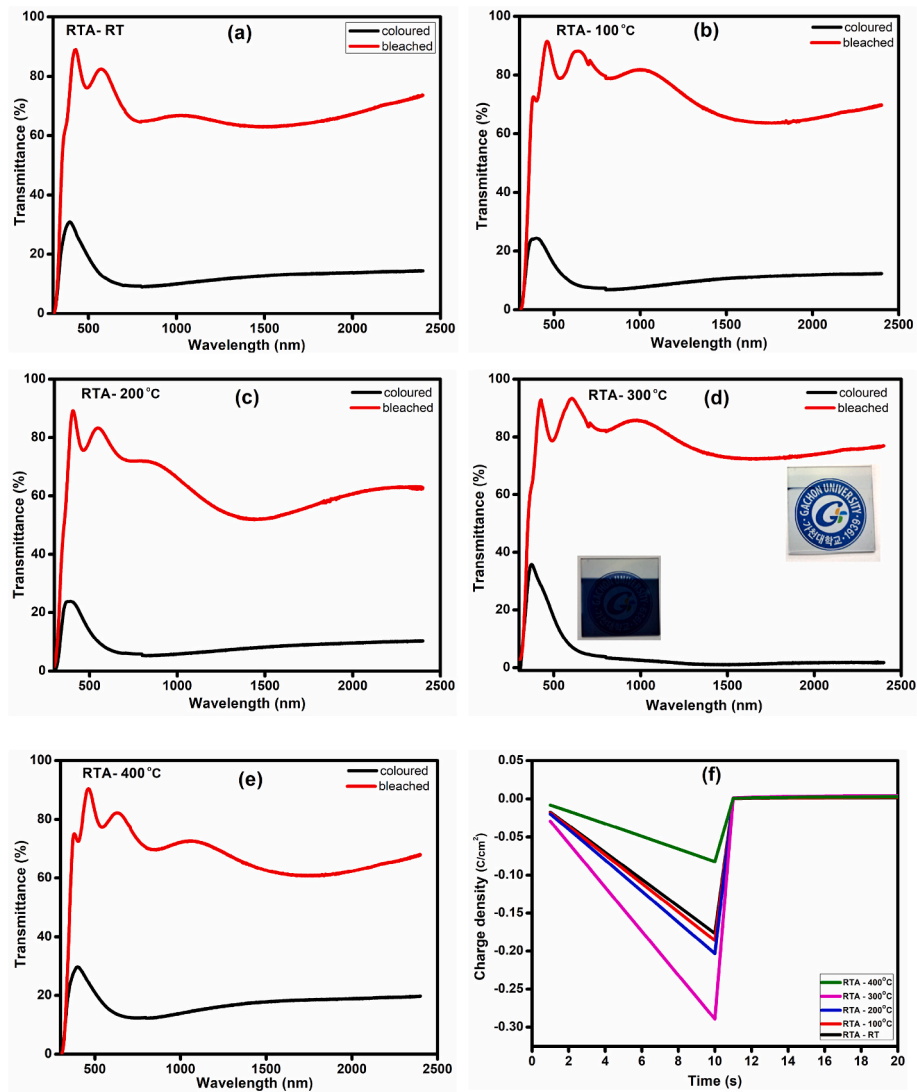


Fig. 14. Transmittance spectra in the coloured and bleached state for WO₃ films (a), RTA -RT (b) RTA -100°C (c) RTA -200°C, (d) RTA -300°C, inset (WO₃ films in their coloured and bleached states) (e) RTA -400°C, (f) Chronocoulometry curve for all WO₃ film.

with voided morphology favoured the easy intercalation of H^+ ions. Shengliang Zhang et al., reported that ECD fabricated using monoclinic oxygen-deficient tungsten oxide nanowires (m- WO_{3-x} NWs) showed a high optical modulation of the full solar spectrum, a high coloration efficiency, good cycle stability, and also had dual band independent control of NIR and VIS light [68]. Mingjun Chen et al., stated that oxygen vacancy modulated amorphous tungsten oxide films worked as excellent electrochromic energy storage smart window with fast-switching and ultra-stable dual-band [69]. According to Yingming Zhao et al., the RF magnetron sputtered WO_3 film with controllable crystallinity (mixed monoclinic and amorphous/less crystalline WO_3 film) exhibited superior electrochromic performance [34]. RTA- 300°C sample, showed better performance. Hence the hetero-structured RTA- 300°C WO_3 film with sufficient oxygen vacancy and granular voided morphology facilitated the H^+ ion intercalation. We further fabricated RTA- 300°C sample, in $3 \times 3 \text{ cm}^2$. The digital photograph of this device in the coloured and bleached state is shown in inset of Fig. 14 (d).

3.9. Impedance

Fig. 15 shows the Nyquist plot of WO_3 films with respect to RTA temperature. Fig. 15 clearly indicates the involvement of three different processes in the intercalation of H^+ ions into the WO_3 films, (i) The depressed semi-circular arc observed in the high frequency region represents the transport of H^+ ions at the interface between the electrode and electrolyte, (ii) The semicircle's middle frequency range corresponds to the charge-transfer process, and (iii) The slanted straight line observed in the low-frequencies area represents the diffusion of H^+ ions into the bulk of the electrode material, also known as Warburg diffusion. The steeper slopes of the Nyquist plots for the WO_3 films indicates faster H^+ diffusion kinetics [70], and the smaller semicircles mean lower charge transfer resistances [71]. The steepness of the tail increases with increasing RTA temperature indicating increased H^+ ion conductivity. Also, WO_3 sample treated with RTA-300°C shows steeper slope and smaller semicircle when compared to other samples. This result indicates that RTA treatment with appropriate choice of temperature can facilitate H^+ ion diffusion in the WO_3 host owing to the increase in conductivity and the decrease in diffusion barrier [59].

4. Conclusion

In summary, RTA treatment under nitrogen atmosphere were performed for RF sputtered WO_3 thin films in order to investigate the influence of RTA temperature on structural, compositional, morphological, electrical, optical, and electrochromic performance and discussed in detail. We have discovered that RTA treatment effectively accelerated the H^+ ion diffusion kinetics and boosted the electrochromic performance of WO_3 films. XRD revealed that film prepared at room temperature showed natural amorphous nature. With RTA treatment the film exhibited mixed hetero structure processing monoclinic and amorphous phase. XPS analysis revealed that the oxygen vacancies increased with increase in RTA temperature. The existence of these oxygen vacancies in WO_3 films provided an enormous number of binding sites for H^+ ions, hence enhanced the optical modulation and the efficiency of the electrochromic device. The SEM analysis showed that increase in RTA temperature showed granular voided morphology. Electrochromic performance of the films increased with increase in RTA temperature. The RTA-300°C WO_3 thin films demonstrated a superior optical modulation of 80 % at 550 nm. This work suggests that structurally modified WO_3 films with appropriate choice of RTA temperature improves the electrochromic performance of the device. Hence the fabricated electrochromic WO_3 can be applied in the field of energy efficient smart window.

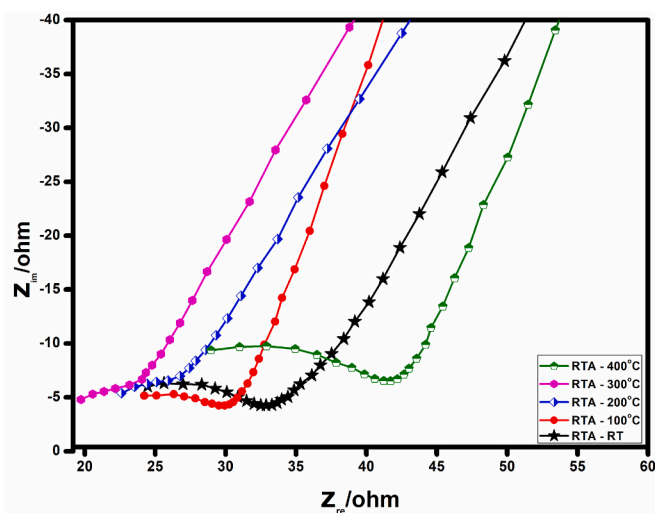


Fig. 15. Nyquist plot of WO_3 films RTA treated at different temperatures (RT, 100 °C, 200 °C, 300 °C and 400 °C).

CRediT authorship contribution statement

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

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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