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Effect of RGPP (Reactive Gas Pulsing Process) deposition parameters on physical properties and electrochromic performances of WO_x thin films

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Abstract

WO_x electrochromic films were deposited using an innovative method known as RGPP (Reactive Gas Pulsing Process) by varying the parameter t_{ON} which controls the duration of oxygen pulsing. This parameter has little influence on the chemical composition and physical properties but significantly affects their electrochromic performance, particularly the discoloration time and coloration efficiency. The deposited films are sub-stoichiometric (WO_{2.75} – WO_{2.89}) and transparent, with a refractive index ranging from 2.11 to 2.12 and a porosity from 15% to 16% as t_{ON} increases from 10 s to 40 s. The ion density and defects in the films vary slightly. The coloration times of films are very similar (12 s - 13 s), whereas the discoloration time varies significantly, from 71 s to 275 s for $t_{ON} = 10$ s to 40 s, respectively. The highest CE = 50 cm²/C was obtained for the film deposited with $t_{ON} = 30$ s.

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Introduction

The synthesis of WO_x films using the conventional sputtering deposition process can lead to instability phenomena. One possible way to limit instability phenomena, is to pulse the reactive gas (oxygen) flow rate into the deposition reactor. This technique, which is a variant of DC magnetron sputtering, is known as RGPP (Reactive Gas Pulsion Process) and has been used successfully by Xu et al [1] and Caccuci et al. [2]. They were able to develop a wider range of WO_x films using rectangular pulses.

According to Martin et al. [3], the oxygen flow rate would be better controlled by using exponential pulses compared to rectangular signals. However, this technique (exponential pulses), with exponential pulses, has not yet been widely used to obtain WO_x films with electrochromic properties.

In this work, WO_x films were deposited by RGPP using exponential signals, by varying the t_{ON} parameter which controls the duration of oxygen pulsing from a lower to a higher flow rate into the deposit chamber. The t_{ON} is the time taken by oxygen flow rate to increase from $D(O_2)_{min}$ to $D(O_2)_{max}$ (s) in the deposit chamber. The objective is to study the correlation between the t_{ON} parameter and the evolution of the WO_x properties on one hand, and on the other hand, to investigate the correlation between physical properties and electrochromic performance of films.

Methods

For an exponential pulse, during the introduction of oxygen from $D(O_2)_{min} = 1.65$ sccm to $D(O_2)_{max} = 9.65$ sccm, the evolution of the oxygen flow rate over time follows the following equation [4]:

$$D(O_2)(t) = (D(O_2)_{max} - D(O_2)_{min}) \frac{1 - e^{-t/\tau_{mou}}}{1 - e^{-t_{ON}/\tau_{mou}}} + D(O_2)_{min} \quad \text{(Equation 1)}$$

With $D(O_2)_{max}$: maximum oxygen flow rate (Pa.m³.s⁻¹), $D(O_2)_{min}$: minimum oxygen flow rate (Pa.m³.s⁻¹), t_{ON} : time taken for oxygen flow rate to increase from $D(O_2)_{min}$ to $D(O_2)_{max}$ (s) and τ_{mou} : Parameter for setting the shape of the signal increasing from $D(O_2)_{min}$ to $D(O_2)_{max}$. In this study, $\tau_{mou} = 10$ s.

During the oxygen flow rate decreasing, the oxygen flow rate varies according to:

$$D(O_2)(t) = (D(O_2)_{max} - D(O_2)_{min}) \times \left(1 - \frac{1 - e^{-t/\tau_{des}}}{1 - e^{-t_{OFF}/\tau_{des}}} \right) + D(O_2)_{min}$$

(Equation 2)

With t_{OFF} : time taken for oxygen flow rate to decrease from $D(O_2)_{max}$ to $D(O_2)_{min}$ (s), τ_{des} : Parameter for setting the shape of the oxygen decrease signal from $D(O_2)_{max}$ to $D(O_2)_{min}$. In this study, $\tau_{des} = 10$ s.

The signals for one pulsing period $T = 40$ s are shown in Figure 1. Films thickness was about 500 nm.

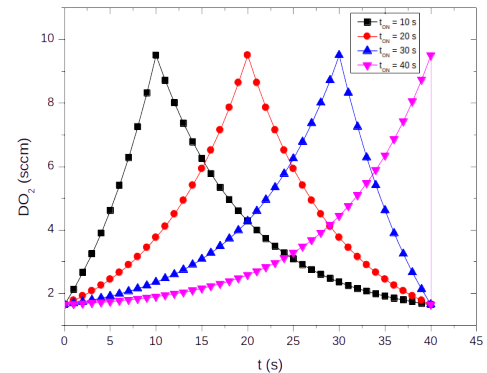


Figure 1 : Effect of t_{ON} on the oxygen flow rate during one pulse for a period $T = 40$ s, with $\tau_{mou} = 10$ s and $\tau_{des} = 10$ s for each pulse.

Results and discussion

- Films composition and physical properties

The influence of the t_{ON} parameter on the chemical composition of deposited films is illustrated in Figure 2.

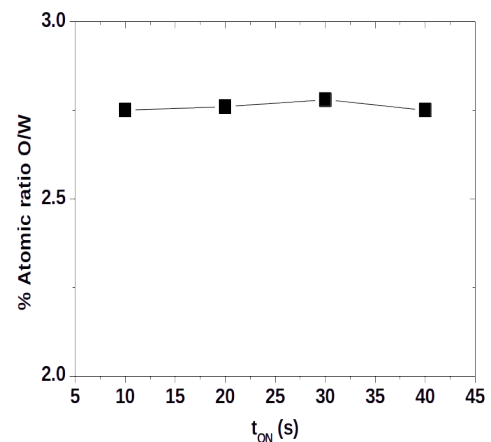


Figure 2: Evolution of % Atomic ratio O/W as a function of t_{ON}

Figure 2 reveals that all RGPP films are sub-stoichiometric with composition ranging from $WO_{2.75}$ to $WO_{2.78}$, indicating a limited influence of t_{ON} variation on films stoichiometry.

The effect of t_{ON} on optical properties such as optical transmittance, average refractive index and porosity [5] is shown in Figure 3.

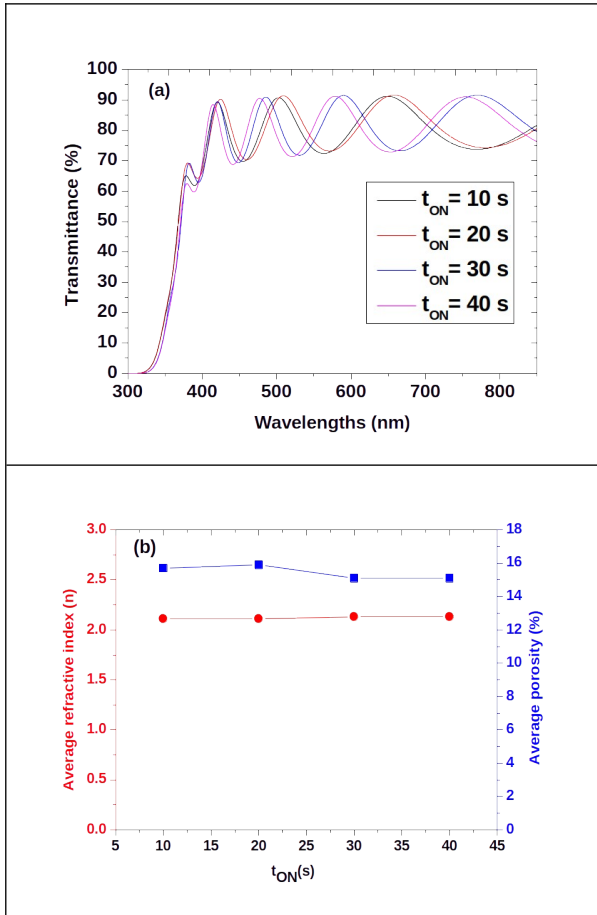


Figure 3: (a) Influence of t_{ON} on the optical transmittance and (b) on the average refractive index and porosity. The absolute error on optical transmittance was $\pm 0.05\%$.

Figure 3(a) shows that all films are transparent, with similar transmittance amplitude, irrespective of t_{ON} parameter. These films can be considered as potential candidates for smart windows applications. Additionally, the refractive index ($n \sim 2.1$) and porosity ($\sim 15\text{-}16\%$) are nearly identical for all films and do not appear to be influenced by the t_{ON} parameter.

Figure 4 presents electrical properties of films, including ions density (N_{ss}) and the average interface trap (or defects) density ($D_{it-average}$) in Metal Oxide Semiconductor (MOS) structures. N_{ss} and $D_{it-average}$ calculations are detailed in a previous work [6].

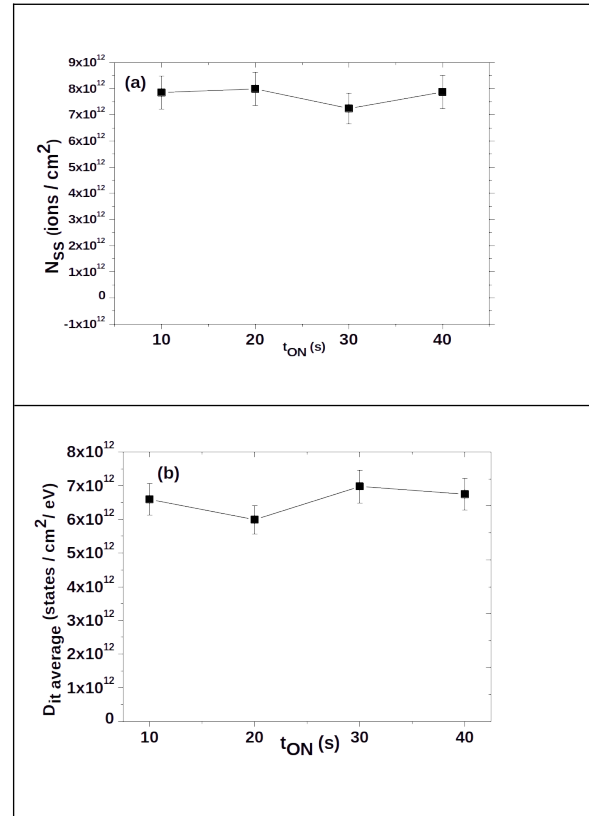


Figure 4: Effect of t_{ON} on (a) ions density (N_{ss}) and (b) interface trap density ($D_{it-average}$) on MOS structures.

Figure 4-a shows that N_{ss} varies only slightly with t_{ON} , which is consistent with the stoichiometric similarity observed among films. Positive N_{ss} values confirm the sub-stoichiometric nature of films, in agreement with the EDS analysis.

Figure 4-b demonstrates that t_{ON} has limited influence on defects evolution, consistent with the observed stoichiometric similarity across films. However, a slight increase in defects is noted for films deposited at $t_{ON} = 30$.

- Films electrochemical properties and electrochromic performances

The effect of t_{ON} on cyclic voltammetry of films is shown in Figure 5.

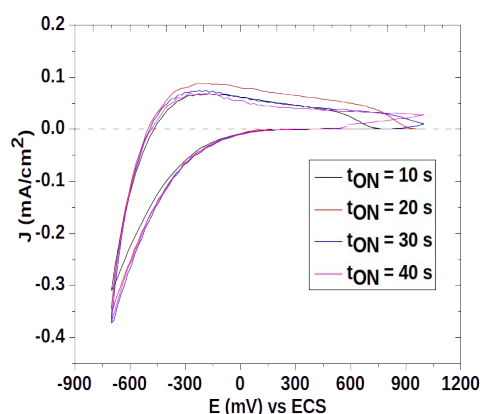


Figure 5: Effect of t_{ON} on cyclic voltammetry

Figure 5 shows that t_{ON} has a negligible influence on electrochemical curves during both reduction ($J < 0$) and oxidation ($J > 0$) cycles, consistent with the identical chemical composition confirmed by N_{ss} [6]. The ion insertion kinetics during reduction are nearly identical for all films. During oxidation, the peaks appear flattened and almost superimposed, indicating slow ion de-insertion kinetics, which can be attributed to the sub-stoichiometric composition and low porosity of films.

In future work, we plan to perform extended electrochemical cycling tests (up to several hundred cycles) to quantitatively evaluate the durability of the films and confirm their long-term electrochromic performance.

Films response times were determined from chronoamperometry measurements (Figure 6). The coloration time (t_c) was defined as the time required to achieve an optical density of $\Delta OD = 0.3$ at 632 nm, corresponding to a decay of 50 % of the transmission during coloration [7]. The bleaching time was identified as the time point when the current approached zero (Figure 6b) [8].

While all films exhibited similar current densities during the initial 5 s of coloration, slight variations emerged between 5–30 s. Nevertheless, the overall coloration times remained nearly identical across all samples.

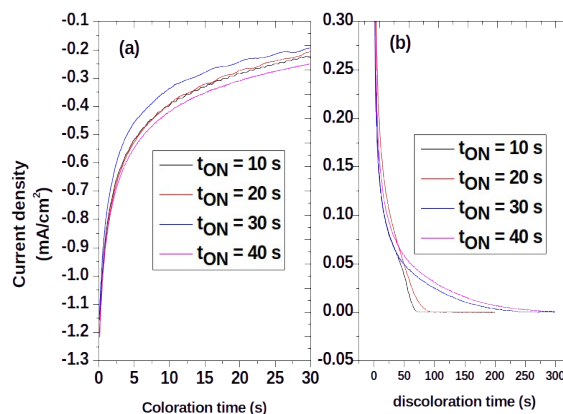


Figure 6: Effect of t_{ON} on the current density during (a) coloration and (b) bleaching.

In contrast, longer bleaching times can be observed (Figure 6b), especially for films deposited at $t_{ON} = 30$ and 40 s, likely resulting from combined effects of defect density and reduced porosity (see Figure 3b and 4b). The complete response time data are summarized in Table 1.

Table 1: Response time

t_{ON} (s)	t_c (s)	t_d (s)
10	13	71
20	12	86
30	13	225
40	12	275

As previously mentioned, the prolonged bleaching times reported in Table 1 can be partially attributed to the high density of defects in films, and are estimated between 6×10^{12} and 7×10^{12} states·cm⁻²·eV⁻¹, as shown in Figure 4b. These electrical defects can act as trapping sites for charged species (Li^+ , e^-) during de-insertion or during the bleaching process. According to our previous studies [5,8], a defect density below 5×10^{12} states·cm⁻²·eV⁻¹ is required to achieve relatively fast bleaching. A reduction in defect density can be expected through post deposition annealing of films.

Finally, the effect of t_{ON} on the coloration efficiency (CE) of deposited films is shown in Figure 7.

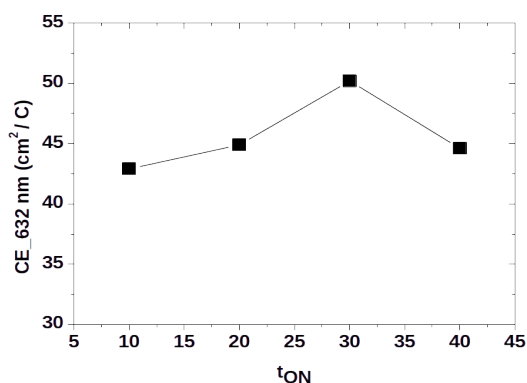


Figure 7: Effect of t_{ON} on the coloration efficiency at 632 nm.

It can be observed that the coloration efficiency (CE) is sensitive to the increase in t_{ON} . The highest CE value ($50 \text{ cm}^2\cdot\text{C}^{-1}$) is obtained for $t_{ON} = 30 \text{ s}$, which corresponds to a film exhibiting a slight increase in defects density. This result reveals that optimizing the defect density in WO_x films can enhance the coloration efficiency.

Conclusion

This study demonstrates that the t_{ON} parameter has a minimal influence on the main material properties, including chemical composition, optical transmittance (all films remained transparent), refractive index, porosity, and electrical characteristics such as defect density (Dit) and ion density (Nss). However, electrochemical analyses revealed a clear dependence on t_{ON} , particularly in coloration efficiency and bleaching kinetics. Optimizing the defect density and porosity through an appropriate control of t_{ON} can enhance the coloration efficiency. These findings highlight t_{ON} as a key parameter for tuning electrochromic performance while preserving the overall physical and chemical stability of WO_x films.

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