

Influence of Aging, Poisoning and Residual Charges on the Gasochromic Behavior of WO₃ Thin Films

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Abstract: Thin films of WO₃ were deposited in a mixed atmosphere of O₂ and Ar gas from a high purity target of 99.99 % tungsten using reactive DC-sputtering technique. Pt catalyst was sputtered on top of the WO₃ films from a high purity target of 99.99 % platinum in Ar atmosphere. Coloration takes place in hydrogen gas and bleaching in oxygen gas. During the Coloration/bleaching process several optical and electrical parameters were determined. The influence of the aging time and poisoning in air was investigated, and the residual charges resulting from the coloring/bleaching processes were discussed. It was found that gasochromic coloration velocity decreases with increasing aging time.

Keywords: WO₃; Pt-catalyst; Aging; Gasochromic; Electrochromic; Smart windows.

Introduction

Electrochromic materials are part of the transition metal oxides which have many interesting applications in science and technology (Granqvist 1995; Yaacob *et al.* 2009). WO₃ is one of the most frequently studied electrochromic materials due to its excellent electrochromic properties (Tahmasebi *et al.* 2013; Hakoda *et al.* 2013; Regragui *et al.* 2003; Yaacob *et al.* 2012; Granqvist 2000). The bi-layers gasochromic device is much simpler in comparison to the multi-layers structure of an electrochromic device (Xu *et al.* 2002). The gasochromic device consists of an electrochromic layer such as WO₃ and a very thin layer of a catalyst, such as Pt (Georg *et al.* 2000). Despite the intensive studies on the physical mechanisms of the electrochromic and gasochromic coloring/bleaching processes, they are still not completely understood and different models have been already proposed. According to one model, the change in the color of the electrochromic films is related to the double injection/extraction of ions and electrons in the films. For example in the case of WO₃ films, the W⁶⁺ is

reduced to W⁵⁺. This can be written in the simple form (Xu *et al.* 2002; Lee *et al.* 2001).



This model has attracted a large acceptance. According to another model, H₂ is dissociated on the Platinum, and transferred into pores or grain boundaries of WO₃ and subsequently creates water and an oxygen vacancy. The oxygen vacancy diffuses into the interior of the grain and water slowly desorbs from the film (Georg *et al.* 2000; Lee *et al.* 2001). The needed amount of the Platinum catalyst on top of the WO₃ films was previously investigated and optimized (Shanak *et al.* 2003).

In the present work, we have investigated the relation between the aging time, poisoning, and the residual charges and their influence on the coloration/bleaching processes of the WO₃ gasochromic films. To our knowledge there is a lack of information in literature dealing with the problem of aging of WO₃ films for gasochromic applications where only two studies exist (Georg *et al.* 2000; Ghosh *et al.* 2010).

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Experimental

Films of WO₃ were sputtered from a metallic W target (99.99 % purity). The sputtering was carried out at room temperature in a mixed atmosphere consisting of Ar and O₂ gas. The total sputtering pressure is 10 Pa, the sputtering voltage is 2.2 kV resulting in a sputtering power density of 1 W/cm². The Pt-catalyst was sputtered onto the top of the WO₃ films from a Pt metallic target of high purity (99.99 %) in Ar atmosphere. The best quantity of Pt to be used as catalyst was found to be 2.12-2.65 μg/cm² (Shanak *et al.* 2003). A film of WO₃ (about 8 cm² area and 200 nm thickness) was sputtered and divided into 4 parts, A, B, C and D (each part is about 2 cm² area). After the production, the Pt-catalyst was sputtered at the top of A and B samples. The other two samples (C, D) were aged in air for 22 days and then the Pt-catalyst was sputtered onto the surface. In order to investigate the effect of the aging time on the coloration/bleaching processes, optical and electrical measurements were performed after different times as shown in Table 1.

Table 1. Time in days between sputtering the different samples of WO₃ and the Pt-catalyst and the start of the measurements after sputtering the WO₃ or the Pt-catalyst

WO ₃ sample	Pt deposition onto WO ₃ film	Begin of measurements after WO ₃ deposition	Begin of measurements after deposition of Pt onto WO ₃
A	Immediately after preparation	1 day	Immediately after preparation
B	Immediately after preparation	16 days	After 17 days
C	22 days	22 days	Immediately after preparation
D	22 days	31 days	After 9 days

The optical transmittance was measured at a wavelength of 633 nm using a He-Ne laser and silicon photodiodes (Kitao *et al.* 2001). The coloration/bleaching processes were carried out in atmospheres of hydrogen and oxygen gas, respectively. To remove any impurities which may exist at the surface of the electrochromic films or in the atmosphere around it (e.g. humidity), we exposed the WO₃/Pt films to Ar gas at the beginning and as well between the switching from the coloration process with hydrogen to the bleaching process with oxygen

to avoid any external reactions between oxygen and hydrogen atoms. The optical transmittance as a function of time was measured at a wavelength of 633 nm using a He-Ne laser of 1-mW power and silicon photodiodes (Kitao *et al.* 2001). The absorption coefficient α was estimated using the equation $I = I_0 e^{-\alpha x}$, where I_0 is the intensity of the incident light, I is the intensity of the transmitted light and x is the thickness of the thin film. The optical density change (ΔOD) was obtained with the equation $\Delta OD = \log(T_b/T_c)$, where T_b is the transmittance of the fully bleached film and T_c being that of the colored film (Kitao *et al.* 1988; Trimble *et al.* 1999; Wang *et al.* 1996; Meda *et al.* 2002). The transmittance change ΔT was obtained by subtracting the minimum transmittance at the endpoint of the coloration process from the values of the maximum transmittance at the starting point of the coloration process.

The sheet resistance R_{\square} of the WO₃/Pt system was measured with a DMM (KEITHLEY 2000) by the use of the four point method. The measuring current was 0.1 mA or lower.

The coloration velocity was determined as the derivative of the optical density (OD) with respect to time at the start of the coloration (dOD/dt) (Salinga *et al.* 2002).

X-ray diffraction (XRD) measurements were carried out on the films with Cu K α radiation by the use of the Scherrer geometry. The measurements were performed with a resolution of 0.02 degree, with the measuring time per step being 20 s. A Perkin Elmer System 2000 spectrometer was used for ex-situ FT-IR spectroscopic measurements. For the IR measurements, as a substrate for the films, 100 silicon was used. To determine the baseline, the identical substrate material was measured and subtracted

Results and Discussion

Fig.1 (a,b) shows the XRD pattern of different WO₃ films sputtered with different O₂/Ar ratios onto glass and Si substrates. The values of the O₂ partial pressure in the sputtering gas significantly influence the microstructure of the WO₃ films. One can see from the same figure that the films sputtered with low O₂/Ar ratio (1%) are amorphous or nearly amorphous. The patterns of the films sputtered with higher O₂/Ar ratios (10% and 25%) were compared with the different known crystal structures of tungsten oxide. The peaks can be ascribed to the monoclinic structure, which is usually the structure of WO₃ at room temperature.

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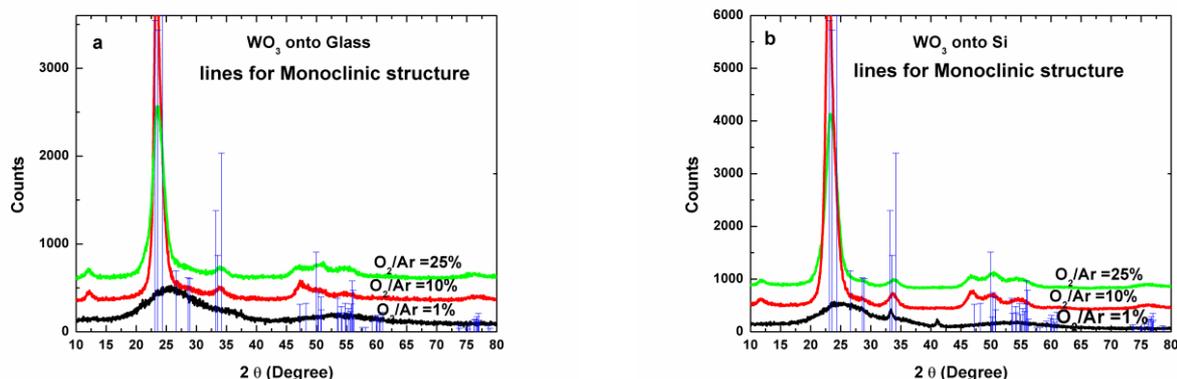


Figure 1. X- Ray diffractogram of WO₃ films with different O₂/Ar ratios; onto glass (a), and Si (b).

The normalized transmission T , versus the coloration/bleaching time for sample A is presented in Fig.2a, with the time of the aging process as parameter. From the Transmission values, it is possible to determine several optical parameters such as the absorption coefficient α , the change in the optical density ΔOD and the change in the transmission ΔT . Plotting these constants as a function of the aging time will clarify its influence of the coloring/bleaching processes. As shown from the same figure 2a, one can see that the transmission decreases faster to reach its minimum value (T_{min}) at the end of each coloration process when the aging time is short. When the aging time increases, the velocity of reaching T_{min} decreases continuously. Also, T_{min} increases continuously with increasing aging time. After the coloration, the sample was bleached again. With an increase of the aging time, a decrease of the values of the maximum transmission was found for the sample to reach. One possible reason

may be that not all the injected ions (H^+) which are used in the coloration process could be completely extracted in the bleaching process. Therefore, these small amounts of the non-extracted charges which stay in the films (residual charges), in addition to the poisoning of the surface of the films enforce the aging. This is due to the samples being aged in air (Kitao *et al.* 2001). It is possible that these residual charges may contribute with the oxygen ions to form OH or OHO bonds (Kitao *et al.* 2001). Fig. 3 presents the IR spectra during intercalation/deintercalation, which shows the W-O-H and H-O-H bonds at 1420 cm^{-1} and 1625 cm^{-1} , respectively. The behavior of the electrical sheet resistance R_{\square} , as a function of the coloration/bleaching time as it is shown in Fig 2b emphasizes the existence of the residual charges. In all cases after the coloration, the values of the maximum R_{\square} at the end of the bleaching case is lower than the starting value for the same cycle.

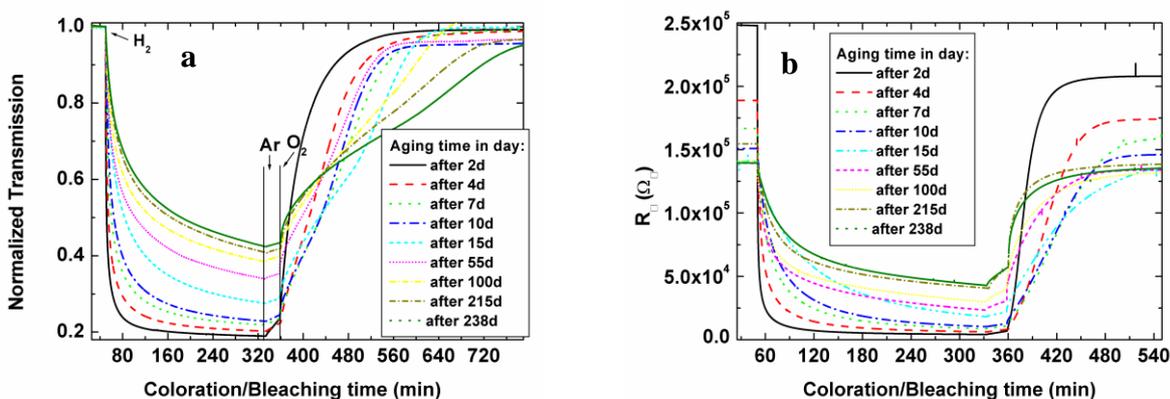


Figure 2. The normalized transmission (a), and the sheet resistance (b) as a function of the coloration/bleaching time for different aging times, sample A

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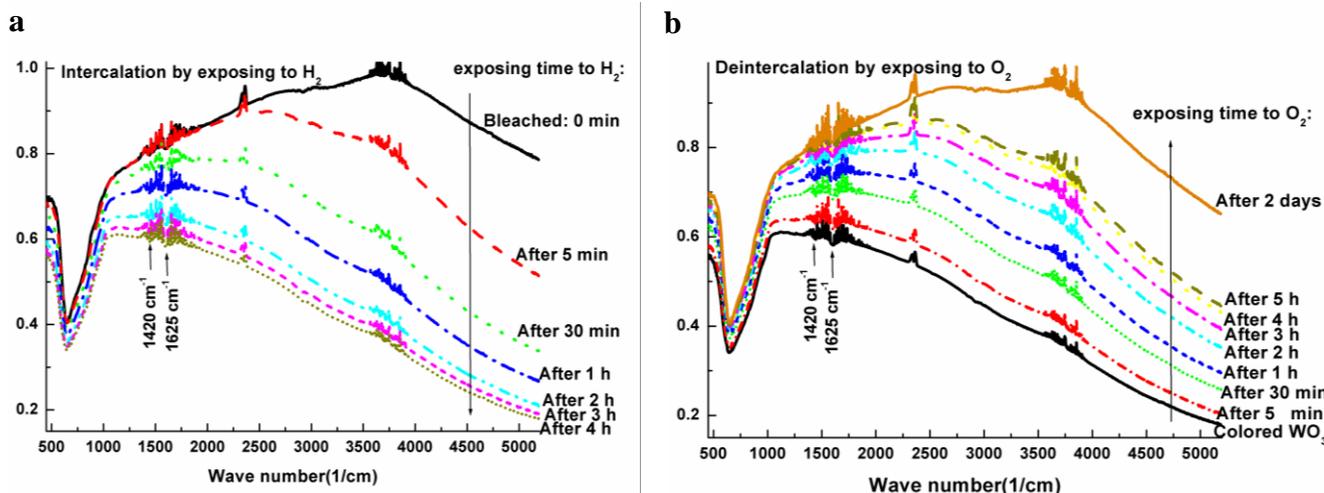


Figure 3. IR spectra of WO₃ film during coloration (a), and bleaching (b).

This means a continuous decrease in the maximum R_{\square} at the end of each bleaching case existed when the aging time and the cycling increased. In the bleaching case the sample was exposed to O₂ gas. The velocity of bleaching is faster at the beginning of the aging time. Later it decreases with increasing the aging time.

Fig 4 a and b present the transmission and the sheet resistance of the first cycle for the different samples A, B, C, and D. Not only does aging the samples of WO₃/Pt, where Pt is sputtered directly onto WO₃, decrease the coloration velocity as in case of A and B samples, but the aging between depositing the WO₃ and sputtering the Pt onto it also has an influence, as in case of C and D samples.

The optical and electrical responses of sample B are qualitatively the same as for sample A, but the differences are quantitative. The minimum values of the transmission at the end of the coloration

states are larger for B than for A. This is due to the longer period of aging time during which the sample B was kept in air before the measurements were started.

This increases the chance of poisoning of the WO₃ and the Pt. The presence of Pt catalyst on top of the WO₃ a long time before starting the measurements may cause change in the concentration of the oxygen vacancies (water content) in the WO₃ films. This may be the reason why the starting value of R_{\square} for sample B is much larger than for sample A as shown in Fig 2b, despite that both samples were sputtered at the same time and with the same boundary conditions. In addition, it was found that R_{\square} of the Pt-amount (here in the form of Pt-islands, no percolation) onto glass increases in air with the aging time and it is strongly dependent on the atmosphere (Georg *et al.* 2000; Shanak *et al.* 2003; Wilke and Scheffler 1996).

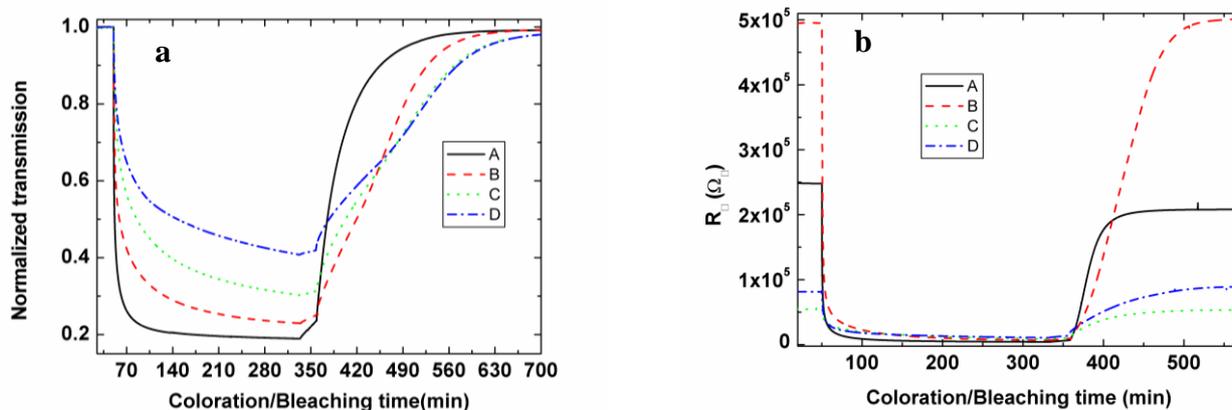


Figure 4. Normalized transmission (a) and sheet resistance (b) versus coloration/bleaching time for the different samples A, B, C, and D in the first cycle.

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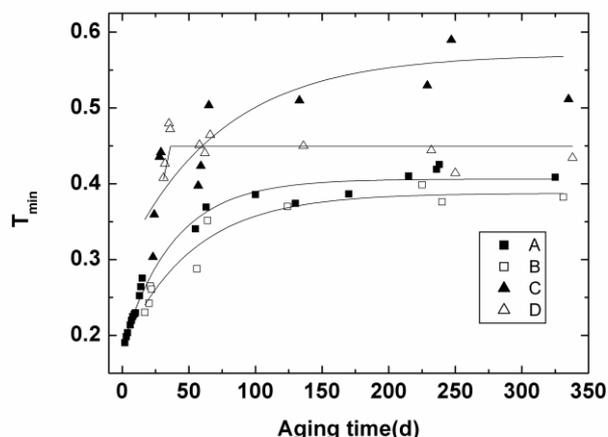


Figure 5. Minimum transmission T_{\min} versus aging time for the different samples.

The sputtering of the Pt catalyst onto the aged WO₃ films as in sample C, has a clear effect on the optical and electrical responses. Here the minimum values of transmission and R_{\square} were larger than in cases A and B. Furthermore, they were reached later than for A and B. This is due to the previous factors discussed for the cases of A and B such as poisoning and the concentration of oxygen vacancies. A further influence may come from the decrease in the degree of sticking (adhesion) between the Pt islands and aged WO₃, which may decrease the efficiency of the Pt catalyst.

In sample D, the Pt was sputtered onto the aged WO₃ and then the WO₃/Pt sample was aged before the measurements were carried out. There was more delay to reach the minimum values of transmission and sheet resistance at the end of the coloring states, and its minimum values are larger than in A, B and C.

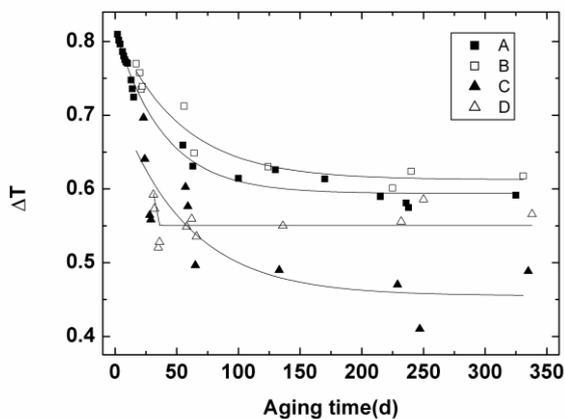


Figure 6. Change in transmission ΔT versus aging time for the different samples.

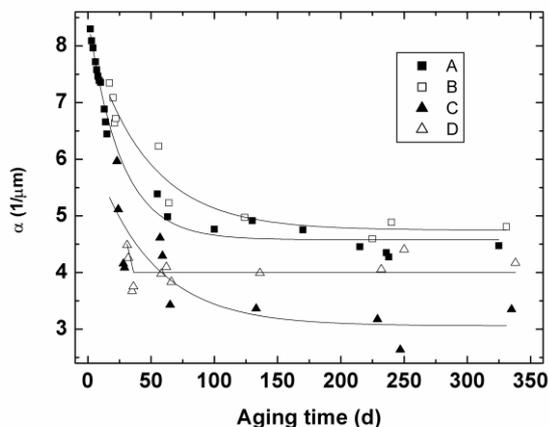


Figure 7. Absorption coefficient α versus aging time for the different samples.

The continuous increase in the minimum transmission T_{\min} versus the aging time was plotted in Fig 5 for all samples A, B, C and D. The continuous increase in T_{\min} equivalent to a continuous decrease in the transmission change ΔT between the bleaching/coloring cases as a function of the aging time is shown in Fig 6. The absorption coefficient α , and the velocity of coloration were plotted versus the aging time as presented in Fig 7 and 8 respectively. Similar values for these velocities were found in literature (Salinga *et al.* 2002). In Fig 8, the velocity of coloration is shown. It decreases strongly at the beginning of the aging time and then becomes nearly stable. In general, the behavior of the optical and electrical responses were explained by the aging time, poisoning, residual charges, in addition to the degree of sticking between the Pt islands and the WO₃ films. Another possible factor may come from the erosion that happens at the surface of the Pt island, which may cause a decrease in the efficiency of the Pt catalyst.

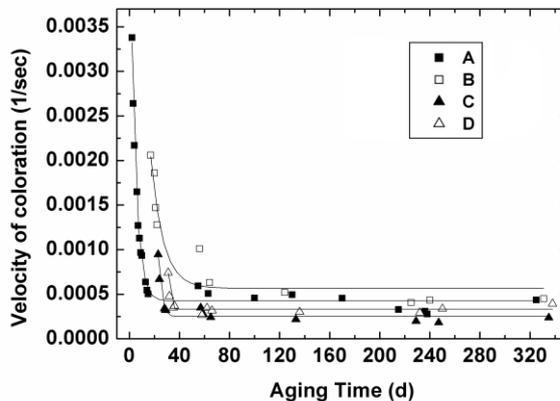


Figure 8. The velocity of coloration (dOD/dt) as a function of aging time for the different samples.

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From figures 6 and 7, one can see that ΔT and α continuously decrease and then become nearly stable after a period of time of about 40 days for samples A and B. For samples C and D, however, there is no reached real stability. The reason may be that the Pt catalyst is sputtered onto the aged WO₃ films, which may deteriorated the degree of sticking between the WO₃ and the Pt. Therefore there is a period of aging time at the beginning of the first few cycles where the change of the coloration/bleaching process is significant. Then a kind of stability and reversibility is found. We can call the aging before the stability to happen as a real or effective aging time. The results could be emphasized in Fig 8, where the velocity of coloration decreases in the real aging time and becomes nearly stable after the effective aging time.

Conclusion

Aging has a clear influence on both WO₃ films and Pt catalyst. It causes poisoning of the samples especially when they are stored in air. This will lead to a decrease in the coloration velocity and finally decreases the efficiency of the gasochromic behavior of the films. Therefore, the produced gasochromic devices should be tested directly after the production and should be always kept in a protective gas.

To reach a higher gasochromic efficiency (coloration/bleaching), it is preferable to deposit the Pt catalyst directly onto the WO₃ films and to avoid any aging time between the deposition of the WO₃ and the Pt catalyst.

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