Durability of VO_2-based thin films at elevated temperature: Towards thermochromic fenestration

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Durability of VO_2-based thin films at elevated temperature: Towards thermochromic fenestration

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Abstract. An explorative study was performed on sputter-deposited thermochromic VO_2 films with top coatings of Al oxide and Al nitride. The films were exposed to dry air at a high temperature. Bare 80-nm-thick VO_2 films rapidly converted to non-thermochromic V_2O_5 under the chosen conditions. Al oxide top coatings protected the underlying VO_2 films and, expectedly, increased film thickness yielded improved protection. Specifically, it was found that a 30-nm-thick sputter-deposited Al oxide top coating delayed the oxidation by more than one day upon heating at 300°C. The results demonstrate the importance of protective layers in thermochromic windows for practical application.

1. Introduction

Vanadium dioxide has a reversible metal–insulator transition at a "critical" temperature τ_c of about 68 °C [1]. Below this temperature, at $\tau < \tau_c$, VO_2 is monoclinic, semiconducting and infrared-transparent whereas it is tetragonal, metallic-like and infrared-reflecting at $\tau > \tau_c$. These properties imply that thin films of VO_2 exhibit thermochromism and can be of interest for windows and glass facades in order to control the inflow of visible light and solar energy into energy efficient buildings.

Thermochromic (TC) thin films of VO_2 have been discussed as adaptive coatings for glazing applications for several decades [2–5]. However, the progress towards practical applications has been disappointingly slow because of performance deficiencies such as a too high value of τ_c, too large luminous absorptance and too small modulation of the solar energy throughput [6]. However, recently there has been substantial progress towards the alleviation of all of these obstacles [7–9]. For practical implementation, the TC VO_2-based films must maintain their desirable properties for long times. This issue requires particular attention since the structure of VO_2 is not thermodynamically stable, and the material may be further oxidized and form non-TC V_2O_5 at high temperature and under humid conditions [10–12].

The most accurate method to test the durability of the coating is exposing it to the natural working conditions, but it is clearly very time-consuming to get satisfactory results. Instead, tests at high temperatures can be utilized to bring the aging time scale into a practical regime. Hence, accelerated aging tests are inexpensive and timesaving. In the present work we report on explorative studies of sputter-deposited VO_2 films subjected to temperatures up to 300 °C in dry air and demonstrate that thin sputter-deposited top coatings of Al oxide can provide good protection for TC VO_2. The present paper reports data that are complementary to those in an earlier study of ours [12].

2. Experimental

2.1 Film preparation

Thin films of vanadium dioxide, aluminum oxide and aluminum nitride were deposited from 5-cm-diameter vanadium (99.95% purity) and aluminum (99.99% purity) targets using reactive DC magnetron sputtering onto 1-mm-thick glass substrates. A detailed description of the film preparation can be found elsewhere [12].

In short, the VO_2 layer was first deposited at a power of 172 W in a mixture of argon and oxygen wherein the oxygen/argon gas flow ratio was kept at a constant value of 0.05 during the deposition process while the process pressure in the growth chamber was held constant at 1.2×10^{-2} mbar. The glass substrates were maintained at 450°C during deposition, as measured by a thermocouple. After deposition, the sample was cooled under vacuum.

The thickness of the deposited VO_2 films was kept constant at 80 nm; it was measured using a Dektak XT stylus profilometer. The deposition rate was 7 nm/minute.

A protective layer of Al_2O_3 was deposited onto the unheated VO_2 film by reactive DC magnetron sputtering from a pure aluminum target using an oxygen/argon gas flow ratio of 0.025 while the working pressure in the growth chamber was set at 4×10^{-2} mbar. The power on the target was 200 W and the deposition rate was 20 nm/minute.

Similarly to the aluminum oxide layer, an aluminum nitride layer was deposited onto the unheated VO_2 film by DC sputtering in a nitrogen/argon gas flow ratio of 0.025. The power on the target was 200W and the deposition rate was 25 nm/minute.

2.2 Accelerated aging test

To investigate the durability of the TC films, the samples were heated in a horizontal quartz-tube furnace. The temperature of the furnace center was kept at 300 °C under the flow of dry air at a rate of 100 sccm. After heating, the samples were cooled to room temperature in nitrogen atmosphere.

After each accelerated aging treatment, the optical transmission of the as-prepared and aged samples was recorded by a Perkin-Elmer Lambda 900 spectrophotometer. The transmittance was measured in the wavelength interval $300 < \lambda < 2500$ nm at room temperature and at an elevated temperature of 100 °C.

3. Results

Figure 1 shows spectral transmittance of a VO_2 film in as-deposited state and after treatment for one hour in air at 300 °C. Panels (a) and (b) refer to $\tau < \tau_c$ and $\tau > \tau_c$, respectively. The as-deposited film shows clear thermochromism and exhibits much higher infrared transmittance at room temperature than at 100°C.

Heat-treated films display very different optical properties, and no trace of thermochromism can be seen. The latter data are consistent with those expected for V_2O_5 [13], and it is evident that the vanadium-based film is fully oxidized.

Figure 2 reports analogous results of spectral transmittance for VO_2 films coated with a 10-nm-thick layer of Al nitride. These data indicate that the thermochromism has disappeared after 1 h.

This might be due to strain induced during the heat treatment process and thus the VO_2 film was stabilized in the metallic state. Therefore the Al nitride coating could not act as viable anti-oxidation layer for the thermochromic VO_2 films.

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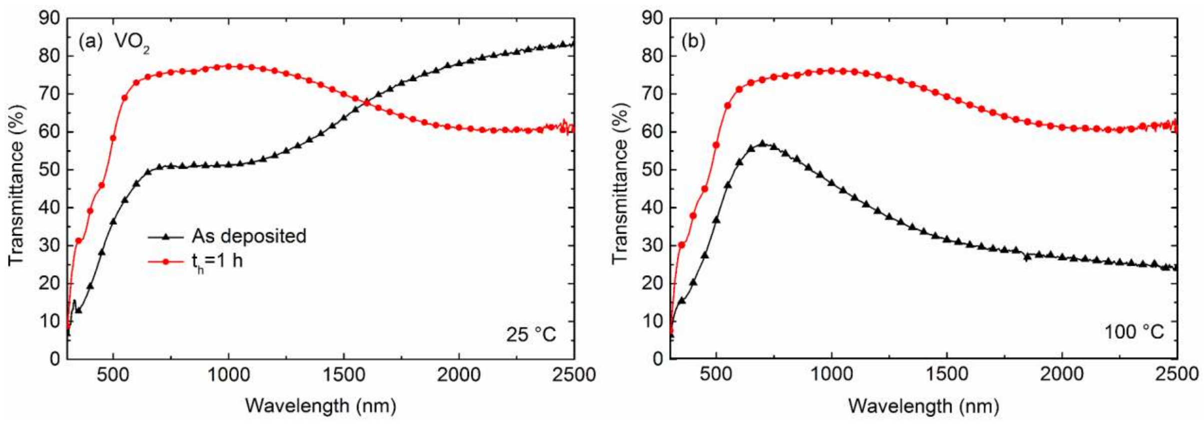

Figure 1. Spectral transmittance for an 80-nm-thick VO_2 film before and after heating at 300°C for one hour. Data were taken at $\tau < \tau_c$ (panel a) and $\tau > \tau_c$ (panel b). The results were reported also in earlier work of ours [12].

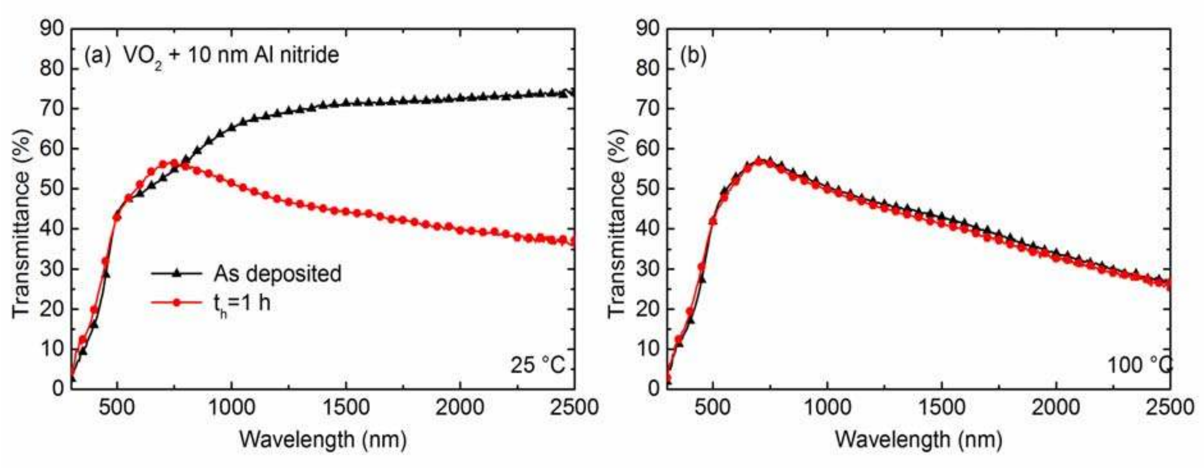

Figure 2. Spectral transmittance for an 80-nm-thick VO_2 film, coated with 10 nm of Al nitride, before and after heating at 300 °C for one hour. Data were taken at $\tau < \tau_c$ (panel a) and $\tau > \tau_c$ (panel b).

Figure 3 shows data for VO_2 films coated with Al oxide of the thicknesses 10 nm (panels a and b) and 30 nm (panels c and d) after heating in air at 300°C for the shown durations t_h.

Clearly the Al oxide prevents oxidation of the underlying VO_2, and the optical data are almost unchanged for the thicker Al oxide layer whereas the sample with the thinner top coating started to undergo some changes.

A minor increase in the spectral transmittance for t_h =30 h can be reconciled with a conversion of a slight amount of VO_2 to V_2O_5.

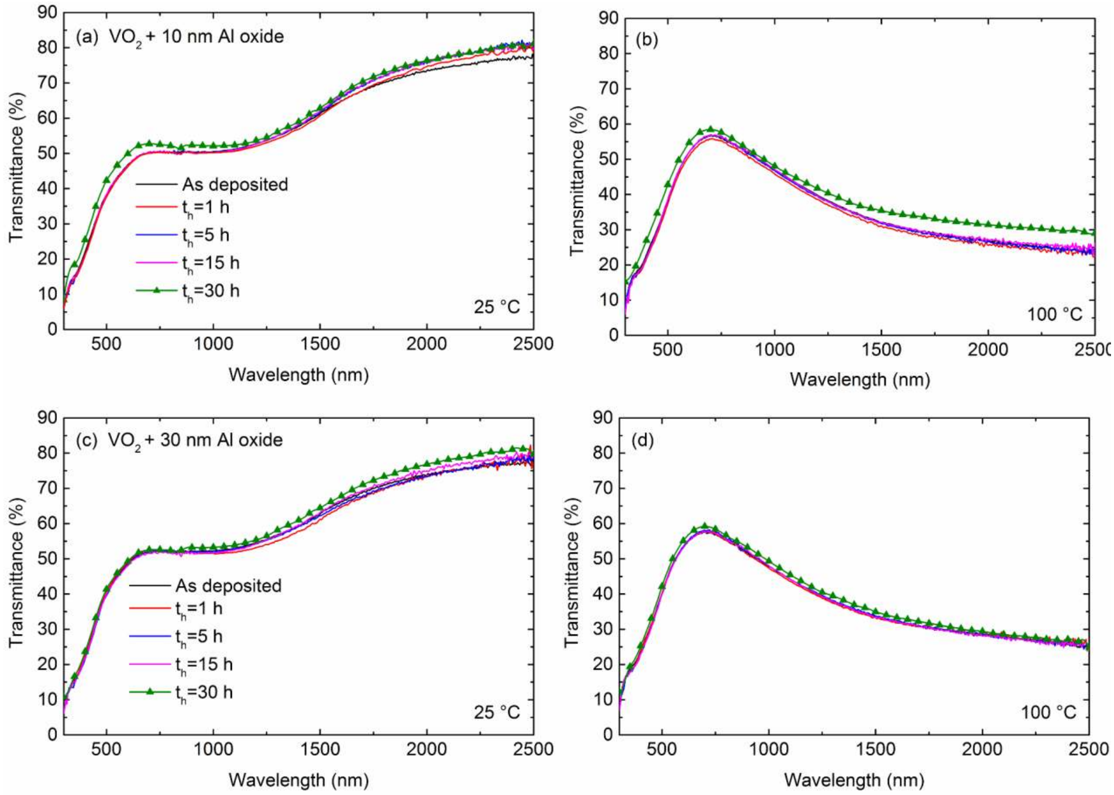

Figure 3. Spectral transmittance for 80-nm-thick VO_2 films, coated with 10 nm (panels a and b) and 30 nm of Al oxide (panels c and d), in as-deposited state and after heating at 300 °C in air for the shown durations t_h. Data were taken at $\tau < \tau_c$ (panels a and c) and $\tau > \tau_c$ (panels b and d). The results were reported also in earlier work of ours [12].

Further studies were conducted also for thicker Al oxide films, and figure 4 reports on a VO_2 film coated with 100 nm of Al oxide and heat treated in air at 300°C for 168 h. It is clear that essentially all of the thermochromism remains after this time, *i.e.*, after one week.

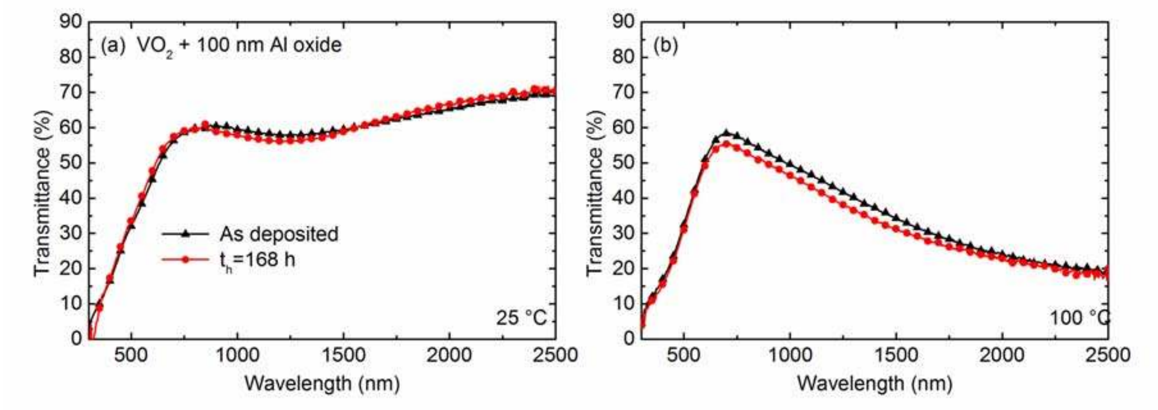

Figure 4. Spectral transmittance for an 80-nm-thick VO_2 film, coated with 100 nm of Al oxide, in as-deposited state and after heating at 300 °C in air for the shown durations t_h. Data were taken at $\tau < \tau_c$ (panel a) and $\tau > \tau_c$ (panel b).

4. Remarks and conclusion

A bare VO_2 film could not maintain its thermochromism under accelerated aging in dry air at 300 ºC. The oxidation mechanism might be that tetragonal VO_2 (β-phase, space group $P4_2/mnm$, at $\tau > 68$ °C) transforms progressively into monoclinic V_6O_{13} ($C2/m$ at $\tau > -124$ °C) and V_3O_7 ($C2/c$), until ultimately reaching orthorhombic V_2O_5 (*Pmnm*), as inferred from the equilibrium phase diagram of the oxygen–vanadium system [10,11].

A VO_2 film coated with 10 nm of Al oxide kept its thermochromism fairly well for heat treatment up to 30 h at 300 °C, and a thicker Al oxide coating of 30 nm yielded enhanced oxidation protection, as expected. A 10-nm-thick top layer of Al nitride yielded a radically different performance and could not offer a similar oxidation shielding under the chosen conditions.

The Al oxide top coating on thermochromic VO_2 films is not only working as an oxidation-preventing layer but can be used for anti-reflection purposes to enhance the luminous transmittance and thereby provide properties of interest for practical thermochromic fenestration [9].

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