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Durability of thermochromic VO₂ thin films under heating and humidity: Effect of Al oxide top coatings

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Abstract

An explorative study was performed on sputter-deposited thermochromic (TC) VO₂ films exposed to heat treatment under dry and humid conditions. The ambient conditions were harsh and 80-nm-thick VO₂ films rapidly converted to non-TC V₂O₅. It was found that a 30-nm-thick sputter-deposited Al oxide top coating provided good protection and delayed the oxidation for more than one day upon heating in dry air at 300 °C and that protection occurred for several days at 95 % relative humidity and 60 °C. The thickness of the Al oxide was important and, expectedly, increased thickness yielded enhanced protection. Our results are important for TC fenestration as well as for other technical applications.

Keywords: Thermochromism; VO₂; Durability

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1. Introduction

This paper shows that VO₂ films lose their thermochromic (TC) properties when exposed to heat and humidity, and that thermochromism can be retained by use of thin protective top coatings of Al oxide.

Vanadium dioxide exhibits TC properties and has a reversible metal–insulator transition at a “critical” temperature τ_c of about 68 °C [1]. Below this temperature, at $\tau < \tau_c$, VO₂ is monoclinic, semiconducting and infrared-transparent, whereas it is tetragonal, metallic-like and infrared-reflecting at $\tau > \tau_c$. These properties imply that, in principle, thin films of VO₂ are of interest for energy-efficient glazings and are able to admit solar energy at low temperature in order to provide indoor heating, whereas the same film can reject solar energy at high temperature and thus avoid excessive air conditioning. TC fenestration has been discussed for several decades [2–10], but practical implementation has been hampered by performance deficiencies such as a too high value of τ_c , too large luminous absorptance, and too small modulation of the solar energy throughput [11]. However, there has been substantial progress towards the alleviation of all of these obstacles, and it is well known that tungsten doping can decrease τ_c to room temperature [11,12], that luminous absorptance can be lowered by magnesium doping [13–16], and that solar energy modulation can be boosted by invoking VO₂-based nanoparticles rather than thin films [16–18]. Another obvious requirement for practical implementation of TC VO₂-based films and nanoparticles is that they must maintain their desirable properties during extended periods of time, which is far from obvious since V₂O₅, not VO₂, is the thermodynamically stable oxide [19,20].

Long-time durability of VO₂ films has received surprisingly scant attention in the scientific and technical literature, although it is known that top coatings of CeO₂ [21] and ZnO:Al [22] can serve as chemical protection barriers. In the present paper we report on explorative studies of sputter-deposited VO₂ films subjected to temperatures up to 300 °C in dry air and to ~80 °C under high humidity and demonstrate that thin sputter-deposited top coatings of Al oxide can impart good durability under both conditions provided that their thickness is sufficient.

2. Experimental

2.1 Thin film deposition

Thin films of VO₂ and Al oxide were prepared by reactive DC magnetron sputtering in a deposition system based on a Balzers UTT 400 unit. The targets were 5-cm-diameter plates of vanadium (99.95% purity) and aluminum (99.99% purity), and the substrates were 1-mm-thick glass plates. The target–substrate separation was 13 cm, and the substrates were rotated during the deposition to ensure even film thickness.

The system was evacuated to $\sim 10^{-5}$ Pa, and Ar was then introduced. The vanadium target was cleaned by pre-sputtering, and VO₂ films were prepared by sputtering in argon and oxygen (both with 99.997 % purity) at a discharge power of 172 W. The O₂/Ar ratio was set at 0.05 by mass-flow-controlled gas inlets, the gas pressure during sputtering was maintained at 1.2 Pa, and the substrate was heated by infrared irradiation to a constant temperature of ~ 450 °C as determined by use of a thermocouple. Films with thicknesses of 80 ± 5 nm, as recorded with a Bruker Dektak XT surface profilometer, were subjected to further study. The deposition rate was ~ 7 nm/minute. The deposition conditions were carefully monitored and kept since they are of crucial importance for reproducible formation of thermochromic VO₂ films, as discussed elsewhere [16,23,24].

Films of Al oxide were deposited onto unheated VO₂ films without breaking vacuum. After pre-sputtering, films were prepared at a discharge power of 200 W, an O₂/Ar gas flow ratio of 0.25, and a gas pressure of 4 Pa. Films with thicknesses in the 10 to 150 nm range were obtained at a deposition rate of ~ 20 nm/minute.

2.2 Equipment and procedures for ageing tests

Glass plates with films of VO₂, with and without Al oxide top layers, were subjected to two ageing tests. The first of these involved heat treatment in a conventional horizontal tube furnace (Heraeus D–6450). The oven temperature was stabilized at 300 ± 5 °C and samples, placed in a quartz boat, were introduced rapidly. Ambient air was circulated through the oven at 100 sccm; the relative humidity (RH) in the oven was estimated to remain below 0.1%

(referred to as “dry air” below). After heat treatment for a time in the range $1 < t_h < 30$ h, the samples were cooled to room temperature in nitrogen atmosphere.

More elaborate ageing studies were performed in a climate chamber (Vötsch Industrietechnik VC 4033 MH) which allows experiments at fixed values of temperature τ_h and RH. The tests were performed under two conditions: at $\tau_h = 60$ °C and RH = 95%, and at $\tau_h = 80$ °C and RH = 80%; the treatment time lay in the interval $24 < t_h < 168$ h (i.e., one day to one week).

Spectral optical transmittance $T(\lambda)$ of the various thin film samples was investigated by spectrophotometry in the $300 < \lambda < 2500$ nm wavelength interval by use of a Perkin–Elmer Lambda 900 instrument equipped with an integrating sphere. Data were taken at room temperature and at ~ 100 °C, i.e., well below and above τ_c for TC VO₂.

3. Results and discussion

3.1 Heat treatment in dry air

Fig. 1 shows spectral transmittance for a VO₂ film in as-deposited state and after heat treatment in dry air at 300 °C for one hour. Panels (a) and (b) refer to $\tau < \tau_c$ and $\tau > \tau_c$, respectively. The as-deposited film shows clear thermochromism and, in particular, the infrared transmittance at $\lambda > 700$ nm is much higher at room temperature than at 100 °C. Data of this kind have been shown many times before [2–9]. Heat treated films display very different optical properties with increased transmittance, except at room temperature and $\lambda > 1600$ nm, and no trace of thermochromism. These data are consistent with those expected for V₂O₅ [25–31], and it is obvious that the vanadium-based film is fully oxidized.

Fig. 2 reports analogous results for VO₂ films coated with Al oxide to the thicknesses 10 nm (panels a and b) and 30 nm (panels c and d). It is evident that the Al oxide prevents oxidation of the underlying VO₂ and the optical data are almost unchanged, irrespectively of t_h , for the thicker Al oxide layer, whereas a minor increase of $T(\lambda)$ can be seen for $t_h = 30$ h in the case of the thinner Al oxide. The changes in $T(\lambda)$ can be understood as the consequence of a conversion of a slight amount of VO₂ to V₂O₅.

3.2 Heat treatment in humid air

Fig. 3 shows data for $\tau_h = 60$ °C and RH = 95% at for an as-deposited VO₂ film and after treatment for three values of t_h . It is clear that noticeable changes have occurred for $T(\lambda)$ already at $t_h = 24$ h, and that prolonged heat treatment tends to further erode the thermochromism, which is essentially lost at $t_h = 120$ h.

The top coatings of Al oxide stabilize the underlying VO₂ film also for the present conditions, as apparent from Fig. 4 which reports data for 10 and 30 nm thick Al oxide top coatings in analogy with the presentation in Fig. 2. It is seen that the thinner Al oxide, reported on in panels (a) and (b), gives good preservation of the TC properties up to $t_h = 72$ h, and that further exposure to heat and humidity degrades the thermochromism. The 30-nm-thick Al oxide film gives better durability, and most of the TC performance prevails to $t_h = 120$ h, as apparent from Figs. 4(c) and 4(d).

Data were recorded also for $\tau_h = 80$ °C and RH = 80%, but otherwise as before. Fig. 5 shows results for VO₂ films coated with 10 and 30 nm of Al oxide under as-deposited conditions and after treatment for $t_h = 168$ h (one week). It is obvious that much, though not all, of the thermochromism is gone after this treatment. Some studies were conducted also for thicker Al oxide, and Fig. 6 reports data for a 150-nm-thick layer. It is clear that essentially all of the thermochromism now remains after one week. Some effects of optical interference are noticeable in $T(\lambda)$.

4. Conclusion and remarks

We carried out an explorative study on sputter-deposited TC VO₂ films subjected to heat treatment under both dry and humid conditions. The exposures were harsh, and 80-nm-thick VO₂ films rapidly converted to non-TC V₂O₅ under the chosen conditions. The oxidation mechanism may be inferred, schematically, from the equilibrium phase diagram of the oxygen–vanadium system [19,20]. Thus tetragonal VO₂ (β -phase, space group $P4_2/mnm$, at $\tau > 68$ °C) is expected to transform progressively into monoclinic V₆O₁₃ ($C2/m$ at $\tau > -124$ °C) and V₃O₇ ($C2/c$) until ultimately reaching orthorhombic V₂O₅ ($Pmnm$). The detailed influence of the ambient conditions—such as the water vapor content—is not known.

It was found that a 30-nm-thick sputter-deposited Al oxide top coating provided good protection and delayed the oxidation during more than one day for heating in dry air at 300 °C and that protection occurred for several days at 95% relative humidity and 60 °C. Expectedly, the thickness of the Al oxide was important and increased thickness yielded enhanced protection.

The ability to preserve the thermochromism in VO₂-based materials by a top coating is of great technological significance. It should be noted that such coatings may be desired not only for oxidation protection but for their optical functionality. Thus the top coating can provide anti-reflection and thereby enhance the luminous transmittance, which is advantageous for windows-related applications [11,16], and studies have been reported for anti-reflecting layers based on oxides of Si [32–37], Ti [36–42], Zr [43] and Al [37]. It is likely that some or all of these oxide layers are able to impart oxidation protection of the underlying VO₂. We also note that VO₂-based nanoparticles may be of considerable interest for TC fenestration [11,16–18]. Core–shell structures have been investigated recently with VO₂ cores surrounded by shells comprised of SiO₂ [44–48] or TiO₂ [49–51] and, again, the top layer may serve as oxidation protection.

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Fig. 1. Spectral transmittance for an 80-nm-thick VO₂ film in as-deposited state and after heating at 300 °C in dry air for one hour. Data were taken at $\tau < \tau_c$ (panel a) and $\tau > \tau_c$ (panel b).

Fig. 2. Spectral transmittance for 80-nm-thick VO₂ 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 dry 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).

Fig. 3. Spectral transmittance for an 80-nm-thick VO₂ films in as-deposited state and after heating at 60 °C in air with a relative humidity of 95 % for the shown durations t_h . Data were taken at $\tau < \tau_c$ (panel a) and $\tau > \tau_c$ (panel b).

Fig. 4. Spectral transmittance for 80-nm-thick VO₂ 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 60 °C in air with a relative humidity of 95 % 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).

Fig. 5. Spectral transmittance for 80-nm-thick VO₂ 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 80 °C in air with a relative humidity of 80 % for 168 h. Data were taken at $\tau < \tau_c$ (panels a and c) and $\tau > \tau_c$ (panels b and d).

Fig. 6. Spectral transmittance for an 80-nm-thick VO₂ films, coated with 150 nm of Al oxide, in as-deposited state and after heating at 80 °C in air with a relative humidity of 80 % for 168 h. Data were taken at $\tau < \tau_c$ (panel a) and $\tau > \tau_c$ (panel b).