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Stability of Thermochromic Vanadium Dioxide Thin Films in Harsh Environments of Temperature and Humidity

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Abstract

Stability of thermochromic VO_2 thin films against harsh environmental conditions, which is important if the films are to be used in practical smart windows, was investigated. The films were prepared on normal soda-lime glass substrates by reactive radio frequency magnetron sputtering of metallic vanadium target (99.95% purity) at a working pressure of $\sim 3.8 \times 10^{-3}$mbar, argon and oxygen flow rates of 76 and 1.4 – 3.0 ml/min, respectively, substrate temperature of 400 ˚C and sputtering power of 150 watts. After deposition, the films were exposed to extreme temperatures and relative humidity at 100 °C, 400 °C and 89%, respectively, for different time durations. Upon exposure, the films structural properties were investigated using the transmission electron microscope and the atomic force microscope, whereas the UV/VIS/NIR spectrophotometer was used to investigate the films' optical properties. The results showed some degradation in the first high-temperature exposure cycle (at t = ~ 100 ˚C) but were quite stable, and with sufficient thermochromism, after the subsequent cycles. Exposure of the films to extreme temperatures at 400 ˚C, resulted in complete loss of thermochromism. Exposure of the films to extreme humidity (RH ~ 89%) displayed a gradual increase in degradation with exposure time; however, the films retained sufficient thermochromism even after 3 weeks of exposure. Possible explanations for the degradation mechanism are discussed by correlating the observed effects in the structural and optical properties of the films.

Keywords: Vanadium dioxide; Thermochromism; Optical properties; Structural properties

Introduction

Vanadium dioxide (VO_2) undergoes a reversible structural phase transition across a critical temperature τ_c, from a semiconducting monoclinic phase for temperatures below τ_c to a tetragonal metallic phase for temperatures above τ_c (Granqvist et al. 2010, Shen et al. 2021). The phase transition is associated with sharp changes in optical and electrical properties making the materials suitable for many applications such as electrical switches (Pergament et al. 2018) holographic storage media (Nie et al. 2023), optical storage (Coy et al. 2010), thermal switches or sensors (He et al. 2023), and as a coating for energy efficient "smart" windows which of recent, has been an application of most interest for studies of the material (Granqvist et al. 2014, Cui et al. 2018, Shen et al. 2021, Haji et al. 2023a). Smart windows change their optical properties in response to external stimuli such as light, applied voltage or change in temperature and can provide dynamic control of solar energy throughput across a window for visual and thermal comfort in the building with little or no use of external energy (Zakirullin 2020). For VO_2, this entails being transmitting both in the luminous and

infrared parts of the solar radiation for temperatures below τ_c and highly infrared reflective but with insignificant change in luminous transmittance above τ_c (Mlyuka et al. 2009a, Haji et al. 2023b). For VO_2 films to be used for practical window applications, the transition temperature needs to be reduced close to room temperature, solar transmittance modulation and luminous transmittance need to be improved, and the durability of the film should be ensured so that they can last for decades (Mlyuka et al. 2009b, Li et al. 2012, Bleu et al 2023, Numan et al 2023). The first three issues have seen a lot of research efforts geared towards their improvements with techniques such as elemental doping with magnesium, tungsten, aluminium, zinc, zirconia, molybdenum, fluorine etc (Burkhardt et al. 1999, Mlyuka et al. 2009a, Lv et al. 2014, Lyobha et al. 2018, Mussa et al. 2018, Haji et al. 2023c), applying multilayer antireflection coatings such as those of TiO_2 (Mlyuka et al. 2009c) and use of nanoparticles (Li et al. 2010, Zhu et al. 2015). On the other hand, very few studies have reported on the issue of stability of the films (Ji et al. 2014). For practical use, the coatings will be exposed to different ambient conditions, important among which are temperature and humidity. In this paper, results on the degradation of the microstructure and optical properties of VO_2 films under extreme conditions of temperature and humidity are presented.

Experimental Procedure

VO_2 thin films were deposited by radio frequency magnetron sputtering of metallic V targets (99.9% purity) onto soda-lime glass substrates and on 3 mm carbon-covered copper grids using a Balzers BAE 250 coating unit. Before deposition, the films were thoroughly cleaned utilizing distilled water, ethanol and a ultrasonic frequency sweep cleaner following a standard substrate cleaning procedure as reported in (Sawa et al 2018). Thereafter the substrates were stored in dry airtight desiccator with silica gels placed inside to minimise humidity and other contaminants. Sputtering took place in argon and oxygen discharge with flow rates of 76 ml/min and 1.4 – 3.0 ml/min, respectively and a target substrate distance of 15 cm. The oxygen flow rate needed precise control to within ±0.05 of the optimum value of 2.2 ml/min for most of the sample depositions; however, it was necessary to regularly adjust the oxygen flow rate, to ensure stoichiometric VO_2 reproducibility since the optimum oxygen flow rate was affected by change of target, target to magnetron or target to chamber electrical resistance as well as target erosion (Rodriguez, 1999). Pre – sputtering, with the shutter to the substrate closed, was always necessary to remove target surface poisoning. The working pressure was controlled at $\sim 3.8 \times 10^{-3}$ mbar with the substrate temperature set at 400 ˚C through the PCU 101 radiant heater power controlling unit. The PCU 101 temperature scale was calibrated against the substrate's surface temperature utilising a Fluke 52 K/J thermometer. For all the samples, the rf sputtering power of 150 watts was used.

To investigate the effect of extreme environmental conditions on the VO_2 films, samples were exposed to temperatures of 100 ˚C in an oven for time durations of 12, 36 and 72 hrs. Some samples were exposed to a temperature of 400 ˚C for two hrs. For humidity, in absence of a humidity generator or climate chamber, a simpler and cheaper method was adopted to create and maintain desired relative humidity values as has been suggested by different authors (Madge 1961, Greenspan 1977). In this method, varied concentrations of either sodium hydroxide (NaOH) or calcium chloride ($CaCl_2$) solutions were kept in air-tight desiccators and gave different stable relative humidity values as per Table 1. The humidity was monitored by a standard hygrometer that was placed inside the desiccator. Samples were placed in the desiccator at 89% relative humidity for two, three and four weeks.

Table 1. Concentrations of NaOH and $CaCl_2$ solutions were used to maintain different values of relative humidity at a temperature of 29 ˚C.

NaOH (gm/100 ml water)	$CaCl_2$ (gm/100 ml water)	Percent Relative Humidity (%)
22.88	33.20	89
26.30	37.70	84
32.70	46.50	74
35.90	50.90	69

LEO 910 transmission electron microscope (TEM) was used to perform structural analysis, which entailed dark/bright field imaging for information on changes in grain size and boundaries, and the diffraction pattern for information of the degree of crystallinity and, using selected area diffraction (SAD), crystal orientations and lattice spacing. In this study, the accelerating voltage was fixed at 100 kV and magnification ranged from $12{,}500\times$ to $125{,}000\times$. Data from TEM was complimented by the 3D surface morphology analysis done using the Digital Instruments Nanoscope IIIa multimode atomic force microscope (AFM) operating in taping mode. 125 μm RTESP7 pyramidal silicon tips were used to scan the samples at scan rates and sizes of 1 Hz, 2 Hz and 1×1 μm, 2×2 μm, respectively. The UV/VIS/NIR Perkin–Elmer Lambda 9 spectrophotometer was utilised for near normal incidence transmittance measurements of the films in the wavelength range of $300 \leq \lambda \leq 2500$ nm at constant sample temperatures of 20 ˚C and 100 ˚C corresponding to semiconductor and metallic states of VO_2 films, respectively. The spectrophotometer was also used to determine the temperature dependence of transmittance at a wavelength of $\lambda = 2000$ nm, where the samples displayed maximum transmittance contrast after switching from a semiconducting state to metallic state.

Results and Discussion

Stability of VO_2 films at high temperatures in ambient air

Figure 1 shows the TEM bright field images (panels A and C) for the plan view of the grains size and morphology across the films and electron diffraction patterns (panels B and D) of fresh VO_2 thin films and those exposed to ambient air at 100 ˚C for 72 hours. The bright field images revealed increased porosity of the films (Figure 1 panel A) with long high-temperature exposure of the films in ambient air, as compared to the more compact (Figure 1 panel B) fresh, unexposed samples. Different levels of grey shade in the figures strongly suggest that the films are crystalline (Liao 2006, Pyrz and Buttrey 2008) for both unexposed and the exposed samples. The pores developed in exposed samples were probably due to the release of volatile components from the films, particularly adsorbed water (Li et al 2022) or the temperature induced irreversible expansion of the micro pores. The electron diffraction patterns did not reveal significant deviation in the degree of crystallinity and crystal orientation of the exposed compared to fresh samples, with both being highly crystalline. In both cases, the patterns display strong electron diffraction spots corresponding to the (220) and (022) planes in the $(1\,\bar{1}\,1)$ zone axis, with the observable slight difference likely due to the difference in sample orientation angle with the electron beam during TEM measurements (Sarney 2003), as it is generally difficult to orient the samples at exact the same angle with respect to the electron beam between electron diffraction TEM measurements. The indexed diffraction planes match well with those from XRD spectra of VO_2 films prepared in similar conditions that were matched with JCPDS data file no 43-1051 reported in our earlier work (Mlyuka 2010).

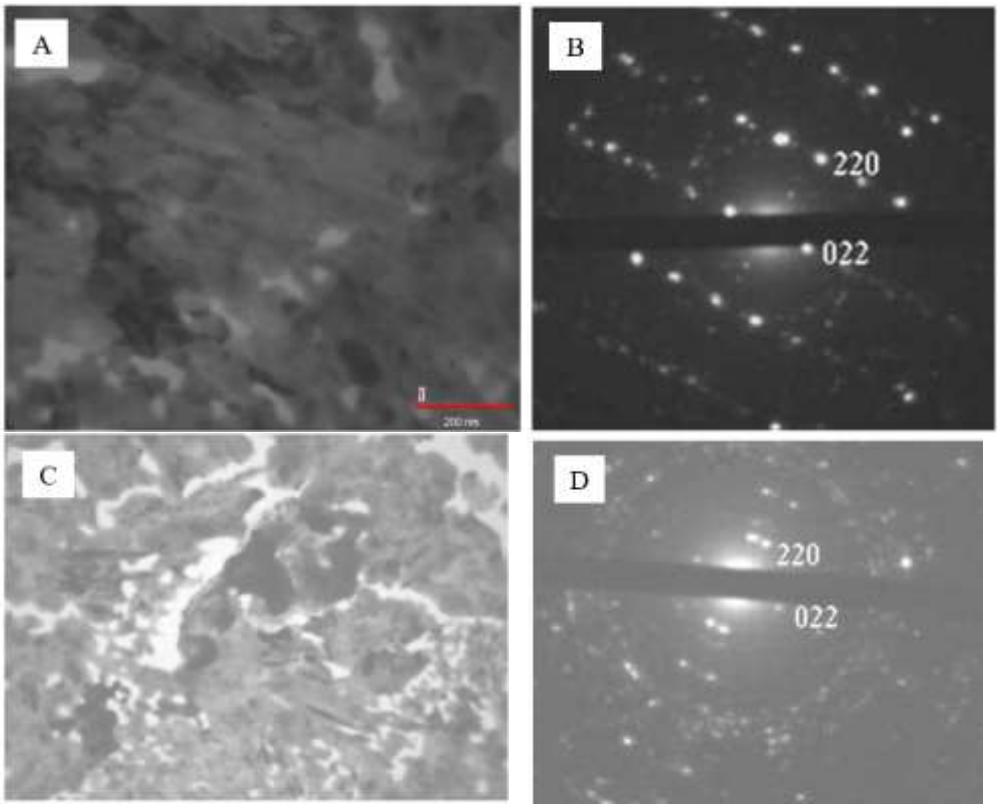

Figure 1: Transmission electron micrographs and electron diffraction patterns for (panels A and B) fresh and (panels C and D) aged VO_2 thin films subjected to a temperature of 100 ˚C in air for 72 hours.

Figure 2 (panels A, B and C) show three-dimensional AFM topographic images of fresh VO_2 films and those exposed to ambient air at 100 ˚C for 32 and 72 hours, respectively. Fresh samples displayed relatively more uniform grain distribution, whereas those exposed to high temperature in ambient air had a non-homogeneous grain distribution with a few seemingly larger grains together with many smaller grains. The figure also displays lower and wider valleys and higher and wider peaks for exposed samples compared to fresh samples. Analysis of the AFM images revealed an increase in roughness Ra from ~ 5 nm for fresh samples to about 10 nm after heat treatment. The grain mean sizes sharply decreased in the first heating cycle and thereafter remain almost constant for several cycles (Figure 2 panel D). An increase in surface roughness correlates well with the increase in porosity of the films with exposure as observed by the TEM bright field images and as has also been observed for other materials (Sakai and Nakamura 2005).

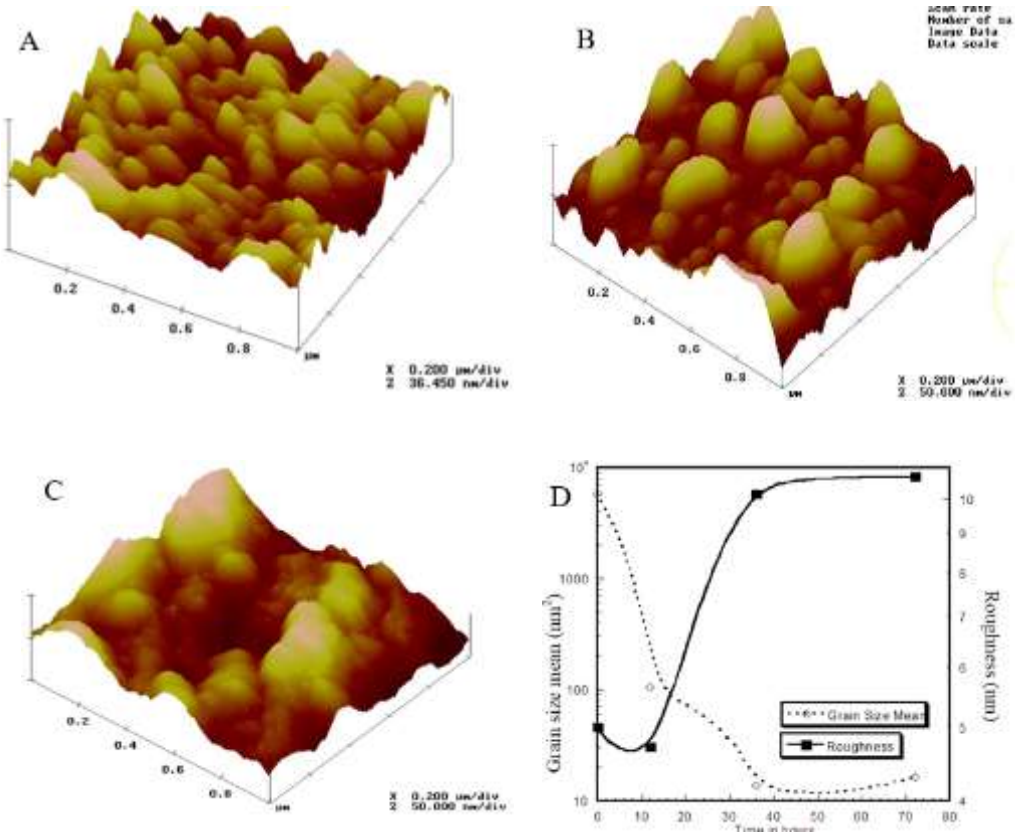

Figure 2: AFM images of fresh VO_2 samples (A) and those exposed to a temperature of 100 °C in ambient air for 36 (B) and 72 hours (C). (D) Variation of grain size mean and surface roughness (Ra) of the samples exposed for different time periods.

Figure 3 (A) shows spectral transmittance of fresh VO_2 films and that of the films exposed to ambient air at 100 ˚C for time durations of 12, 36 and 72 hours. Clear thermochromism is observed for fresh VO_2 films with significant switching in the transmittance, from being transparent in the semiconducting phase at room temperature ($\tau < \tau_c$) to relatively opaque in the metallic phase at a temperature above τ_c. The switching is particularly pronounced in the near-infrared part of the solar spectrum at wavelengths, $\lambda \geq 1000$ nm. During the first heating cycle, a significant deterioration in transmittance is observed particularly in the low-temperature phase (LTP). This resulted in a significant drop in the transmittance switching between the two phases in the near-infrared spectral region, $\Delta T_{\lambda=2000\ nm}$ from ~ 45% for fresh samples to ~ 30% for exposed samples. In the subsequent heating cycles, however, the transmittance of the films was observed to be relatively stable. VO_2 is not thermodynamically stable, compared to, say, the more stable V_2O_5 and hence oxidation to more stable oxides is the likely mechanism for the observed degradation. Mixed VO_2 phases could also occur on the top layer of the film due to uncontrolled exposure to oxygen as opposed to highly controlled oxygen flow during film deposition as has been observed in our previous work (Mlyuka 2010). Samples exposed in air at a temperature of 400 ˚C for about two hours completely lost thermochromism as they did not switch at all (Figure 3(B)), further supporting oxidation to the more stable V_2O_5 as the main reason for the observed degradation in thermochromism.

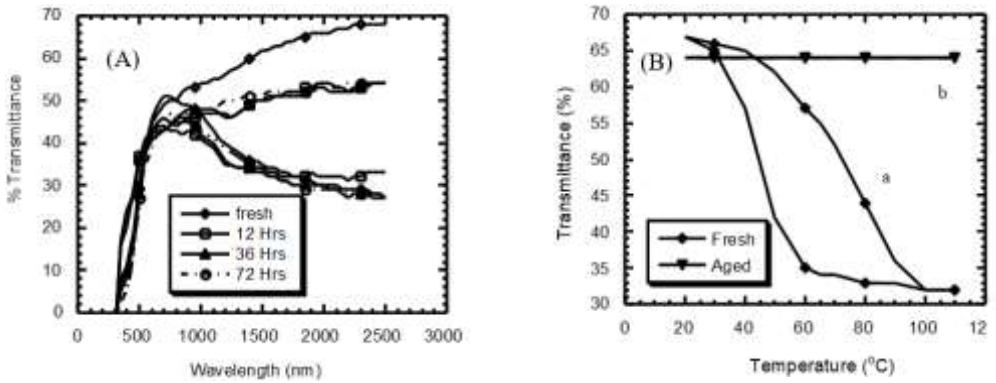

Figure 3: (A) Spectral transmittance at room temperature, ~ 28 ˚C $(\tau < \tau_c)$ and at 100 ˚C $(\tau > \tau_c)$ for VO_2 films heated at 100 ˚C for 12, 36 and 72 hours. (B) Temperature dependence of transmittance at $\lambda = 2000$ nm for fresh VO_2 films and those exposed to a temperature of 400 °C for two hours.

Stability of VO_2 films at Extreme Humidity

There was a notable change in the physical appearence of the films for all the durations in which sample films were subjected to elevated humidity conditions. The films appeared pale in colour, the effect weakening from the middle towards the edge of the substrate. Figure 4 shows spectral transmittance of vanadium dioxide films subjected to extreme value of ~ 89% RH humidity for different time durations. A significant change in optical transmittance of the films especially in the metallic phase was observed, changing from 19% transmittance for fresh samples to 38% transmittance for samples subjected to 89% RH for 3 weeks. In semiconductor phase on the other hand, there was only an insignificant change; from 69% transmittance for fresh samples to 67% transmittance for the exposed samples, all evaluated at a wavelength, $\lambda = 2000$ nm. The corresponding difference in transmittance at this wavelength, $\Delta T_{\lambda=2000\,nm}$, between the semiconducting and metallic phases was 40% and 29%, for fresh and exposed films, respectively. This difference is significant enough to suggest that severe humidity does indeed affect the optical switching behaviour of VO_2 films.

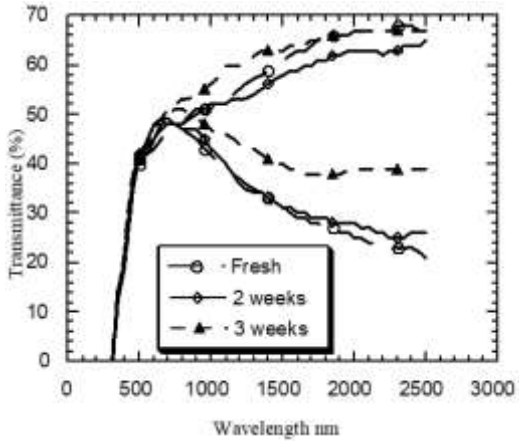

Figure 4: The effect of exposure to extreme humidity over different time durations on the spectral transmittance of VO_2 thin films.

Electron micrographs of vanadium dioxide films subjected to extreme RH humidity of ~ 89% show notable change in the structure of the films (Figure 5 left panel). The exposed films appear to have formed some wide continuous clusters, while at the same time, regions with increased porosity were observed. The cluster formation could be attributed to chemisorption of water molecules on the films surface. This type of adsorption is irreversible probably due to formation of other different oxide states (Goodacre et al. 2020).

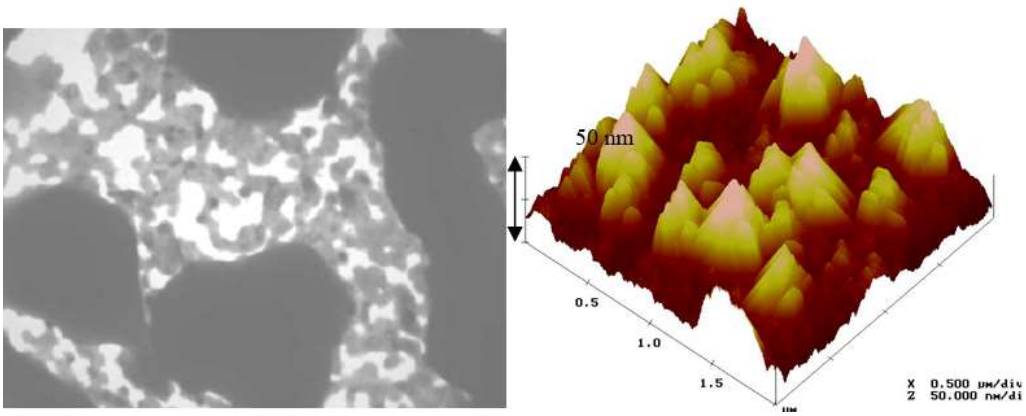

Figure 5: TEM micrograph (left panel) and 3D AFM image (right panel) of VO_2 film exposed to ~ 86% RH for three weeks.

Figures 5 (right panel) shows the atomic force micrograph of vanadium dioxide films exposed to ~86% RH for two weeks. There is a marked difference between this AFM micrograph of the exposed film and that of the fresh film (Figure 2 (A)). The exposed films seem to have larger voids with fewer but larger grains. The observation correlates well with that from the TEM micrograph and might both explain the observed changes in transmittance particularly in the metallic phase of the VO_2 films and the associated deterioration in optical switching after exposure to extreme relative humidity. Extreme relative humidity may cause chemisorption and/or condensation of water molecules onto the inner walls of the films' voids which will change the effective dielectric function of the films and hence the observed deterioration of the optical properties (Chang et al. 2019).

Conclusions

Stability of thermochromic VO_2 thin films agaist harsh conditions of temerature and relative humidity was investigated. Optical transmittance switching, $\Delta T_{\lambda=2000\ nm}$, of the films displayed significant degradation from ~ 45% and ~ 40% for fresh samples to ~ 30% and ~ 29% for the samples exposed to higher temperature at 100 ˚C in ambient air and high relative humidity at 89%, respectively. The films however retained significant thermochromisn even after beeing exposed to extreme values of ambient air temperature and relative humidity for 72 hrs and 3 weeks, respectively. Exposure of the films at 400 ˚C led to complete loss of thermochromism, even when exposed only for a short time. The AFM and bright field TEM images revealed increased roughness and voids, respectively, for the exposed films, at least partially explaining the observed changes in opticla switching. Oxidation to higher vanadium oxides such as V_2O_5 after high temperature exposure of the films likely have the highst contribution to the observed deterioration in optical whitching of the films. It is clear from these results that, the films, though still display thermochromism after exposure, need

a mechanism to protect against harsh environment if the films are to be used in practical smart window coatings. It coul be of interest if chemical analysis was done to elucidate changes in the oxidation states of the films with exposure to extreme temperature and humidity as well as the effect of other conditions not studied in this work including salinity, strain, acidic rainfall, and scratches.

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