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A combined experimental and theoretical study into the performance of multilayer vanadium dioxide nanocomposites for energy saving applications

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ABSTRACT

In the built environment there is a increasing issue of heat management, with buildings expending significant energy resources to maintain comfortable living temperatures. In many parts of the world, this entails the use of both heating and cooling during daylight hours depending on ambient temperatures. Due to the variation in the desired temperature control classical solutions can become counter productive in their aim of maintaining comfortable temperatures, therefore it is important to employ adaptive solutions that vary their functionality based on circumstance, such as window films with thermochromic or electrochromic properties. Here, we present a design for a thermochromic smart window film based on a multilayer stack of silica, titania and vanadium dioxide (VO_2). The design makes use of coherent interference within the multi-layered structure to suppress the typically high reflection of visible light and improve the reflective component of solar modulation. This allows us to simultaneously improve the visible transmittance and solar modulation of the film above what would be possible with a single layer of vanadium dioxide film. Guided by simulation, the multilayer structure is fabricated using a scalable sol-gel method and results are compared with simulations and a single layer VO_2 reference sample.

Keywords: smart windows, anti-reflection, vanadium dioxide, multilayer

1. INTRODUCTION

As cities grow and become more densely populated there is a increasing issue of temperature management, with buildings expending significant energy resources to maintain comfortable living temperatures. Windows are often cited as the least energy efficient components of buildings and as a result there are a number of commercial products available to increase the energy efficiency of windows,[1] such as low/high solar gain windows, which minimise/maximise generation of indoor heat from solar irradiance. However, due to seasonal variations in temperature these static solutions often become counter productive in their aim of maintaining comfortable temperatures. As such, windows that can adapt to changes in conditions, by way of thermochromic or electrochromic switching, have become an attractive option for those aiming to improve the energy efficiency of the built environment.

The prime candidate material for thermochromic window films is vanadium dioxide (VO_2),[2] which exhibits a heat-mediated phase transition between a semiconducting and metallic state at a critical temperature that may be tuned via doping.[3] The phase transition of VO_2 significantly modulates its optical properties, with the high temperature metallic state absorbing and reflecting considerably more infrared radiation than the lower temperature monoclinic state due to the presence of free electrons; a window coated with a VO_2 film may

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passively vary its transmission of infrared radiation based on the ambient temperature, in doing so reducing the temperature management energy-load.

One of the major issues with vanadium dioxide as a window coating material is its high visible reflectance. In recent years vanadium dioxide nanoparticle based coatings have been proposed[4] as a method to improve performance however these are limited by their large phase transition hysteresis widths which result from the small domain sizes.[5,6] A number of structured designs have been presented in literature to overcome the high reflectance of vanadium dioxide including the use of multilayer[7,8] and graded index structures[9,10] however none so far have managed to achieve their predicted theoretical performances. Here, we present a design for a thermochromic smart window film based on a multilayer stack of silica, titania and vanadium dioxide (VO_2) fully fabricated from solution based precursors. The design makes use of coherent interference within the multilayered structure to suppress reflection of visible light and improve the reflective component of solar modulation. In doing so, we are able simultaneously improve the visible transmission and solar modulation of the film to surpass what is possible with a single layer film.

2. METHODS & MATERIALS

2.1 Synthesis of vanadium dioxide sol

In a typical reaction, 3.78 g (30 mmol) of oxalic acid dihydrate (98%, Alfa Aesar) was added to a suspension of 1.82 g (10 mmol) V_2O_5 (general purpose grade, Fisher Chemical) in 10 mL anhydrous ethanol (99.8%, denat. 1% MEK + 0.001% denat. benzoate, Acros Organics). The reaction mixture was heated to 80°C for 12 h. The blue solution was filtered and diluted with ethanol to a 0.8 M concentration of vanadium in solution.

2.2 Synthesis of silica sol

A mixture of hydrochloric acid (37%, extra pure, Fisher Chemical), H_2O and half of the prescribed amount of anhydrous ethanol was slowly added at room temperature to a solution of tetraethyl orthosilicate ($[Si(OEt)_4]$, TEOS, 98%, Acros Organics) in the other half of the anhydrous ethanol. The clear solution was stirred for 1 d in a sealed glass vial and was used without further purification. The molar ratios of the reactants were as follows: TEOS:H_2O:HCl:ethanol = 1:4:0.01:20.

2.3 Synthesis of titania sol

A solution of titanium(IV) isopropoxide (TTIP) (Sigma-Aldrich, $>$ 97%), anhydrous isopropanol (IPA) and acetic acid (CH_3COOH) (Sigma-Aldrich, $>$ 99.5%) was kept stirring for 0.5 hours and used soon after. The volume ratios of the reactants were as follows:(TTIP:IPA:CH_3COOH = 1:5:0.4).

2.4 Fabrication of thin films

The spin solutions were uniformly cast onto fused silica substrates by spin-coating at a range of spin speeds for 30 s (SCS G3 Spin Coater). All the spin-cast films were aged in a box furnace at 100°C for 10 min to remove any remaining solvent. The subsequent heat treatments varied for each desired material. Amorphous titania TiO_2(a) and silica SiO_2 were obtained by heating in a box furnace for a further 50 min. whilst monoclinic VO_2 and anatase titania TiO_2(A) were obtained by annealing in a vacuum tube furnace at 550°C for 1 h ($p < 20$ mbar). The tube furnace was ramped up to and down from the set temperature at a ramp rate of 1°C/min. Spin speed curves and optical constants for each material are given in the appendix.

2.5 Optical and thermal characterisations

Optical constants and spin speed thickness curves were obtained for the various materials used using a Semilabs SE-2000 ellipsometer. Spin speed curves and optical constants for each material are given in the appendix. Transmittance and reflectance measurements were performed using a Perkin-Elmer Lambda 950 UV/Vis/NIR spectrophotometer. A heating element was used in conjunction with a k-type thermocouple and Eurotherm 3216 PID controller to control the temperature of the thermochromic films. A second thermocouple was used to monitor the surface temperature of the film at the point of measurement.

3. RESULTS & DISCUSSION

Design and optimisation of the multilayer structure was performed using a transfer matrix method[11] with optical constants measured by ellipsometry taken as inputs (see appendix for plotted optical constants). The specific aims of the optimisation were to minimise luminous reflectance, maximise the solar modulation and maintain a luminous transmittance above 60% (these metrics are defined mathematically in the appendix). To simplify the fabrication, optimisations were limited to four layers. The final design consists of a TiO_2(A) bottom layer and a VO_2 layer followed by a TiO_2(a) and SiO_2 top bilayer. The bottom layer was chosen to be anatase TiO_2 since it must be subjected to high temperatures whilst the VO_2 layer is annealed; by transforming the first layer to anatase before depositing the VO_2 we remove any ambiguity in its composition and optical properties that may arise from the VO_2 annealing step. In fig.1 a schematic of the final design is shown along with a comparison between the simulated reflectance and transmittance of the multilayer structure and a single layer of VO_2 with comparable film thickness.

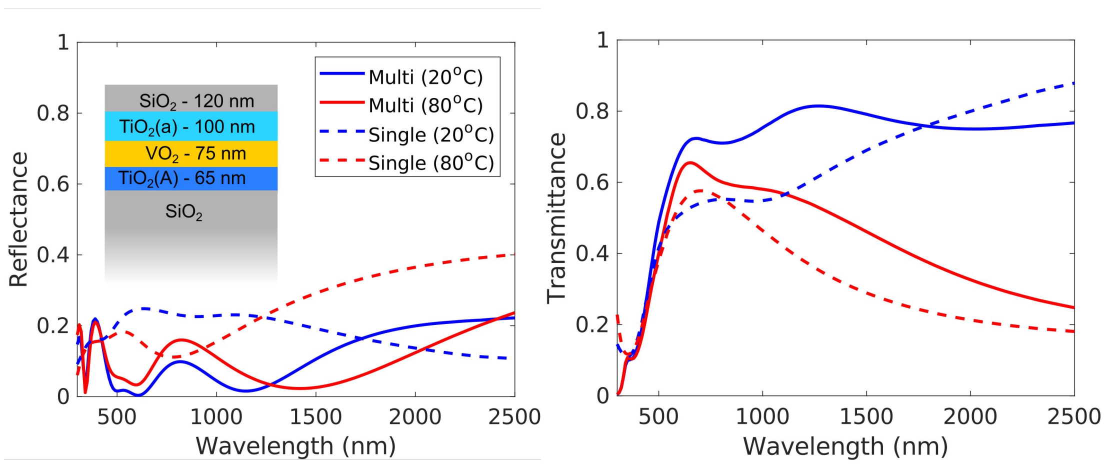

Figure 1. Simulated reflectance and transmittance of optimised multilayer structure compared with a 75 nm thick single layer VO_2 film.

The optimised multilayer design has a solar modulation of 14.0% along with a visible transmittance of 60.3% whilst the single layer film has a solar modulation of 8.78% and a visible transmittance of 47.4%. The key reason for this is the control over visible light reflection. The multilayer structure has a luminous reflectance of only 1.42% whilst the single layer has a much higher luminous reflectance of 23.3%. Differences in the reflectance of the two samples also accounts for the increased solar modulation. The multilayer has a useful solar reflectance modulation of 2.68% whilst the single layer has a detrimental reflectance modulation of -3.97% since it becomes significantly less reflective in its hot state below 1200 nm where solar irradiance is highest.

A comparison between the simulation and experiment is shown in fig.2. The results for the single layer structure match well with the simulation. The single layer film has a solar modulation of 50.15% and a visible transmittance of 8.84% and was found to by fully switched at 80°C. The multilayer film matched its expected visible transmittance well (60.8%), however the solar modulation was found to be significantly less than expected (7.76% vs 14.0%). It is expected that this difference has been caused by diffusion of titanium ions from the bottom layer into the VO_2 layer during the 550°C annealing step. This is evidenced by the fact that the temperature at which the film had fully switched was found to be much higher than for the single layer film (110°C vs 80°C); in previous works titanium doping of VO_2 has been found to significantly increase the transition temperature.[12] Further investigations using x-ray photoelectron spectroscopy (XPS) are needed to confirm that titanium diffusion has occurred and if so to quantify it. One method to reduce the diffusion would be to re-optimise the design to incorporate a silica barrier layer between the VO_2 and TiO_2 layers.[8]

In fig.3 the measured visible reflectance is shown for both the multilayer and single layer films. The single layer film has a luminous reflectance of 26.3% whilst the multilayer film exhibits a significantly suppressed luminous

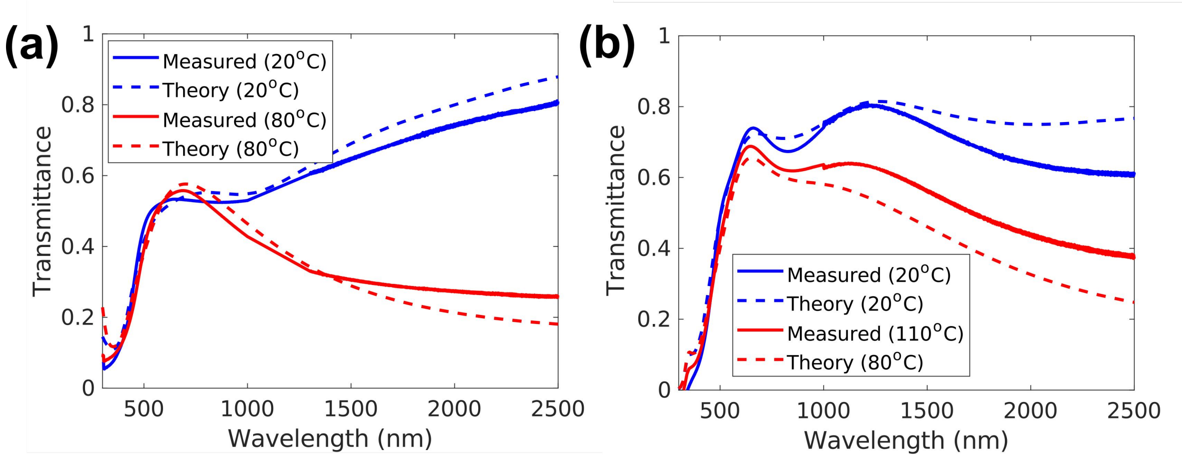

Figure 2. Comparison between simulated and measured transmittance for (a) 75±2 nm thick single layer and (b) multilayer films in both low temperature semiconductor and high temperature metallic states.

reflectance of 10.0%. Considering that $T = 1 - A - R$ and that the measured values for transmission in the visible were comparable to the simulated values, this result also suggests that the VO_2 layer is absorbing significantly less visible light than expected. This may also be caused by titanium ion diffusion though further investigations are required to confirm this.

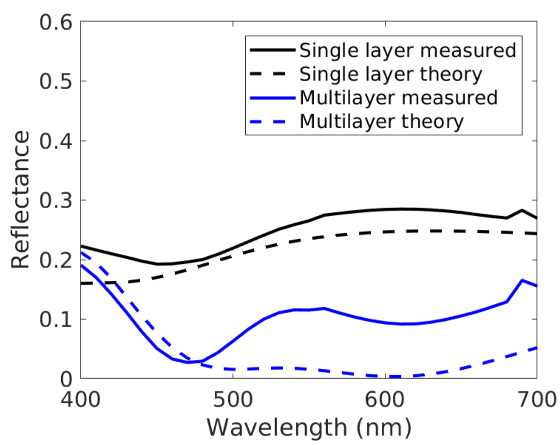

Figure 3. Comparison between simulated and measured visible reflectance for (a) single layer and (b) multilayer films in the low temperature semiconductor state.

4. SUMMARY & CONCLUSIONS

The simulated design presented here significantly improves both visible transmittance and solar modulation above that of a single layer film with comparable thickness. It is able to achieve this through thin film interference effects that both suppress visible reflectance and increase the reflective component of solar modulation. The fabricated structure goes some way to achieve the theoretical predictions however its solar modulation is significantly reduced and its transition temperature is significantly higher than expected. It is expected that these negative effects are the result of diffusion of titanium ions from the TiO_2(A) bottom layer during the VO_2 annealing step. Future work will aim to confirm these expectations with XPS and to re-optimise the design to include a SiO_2 buffer layer between the VO_2 and TiO_2(A) layers to prevent diffusion of titanium.

APPENDICES

Calculation of key metrics for optimisation

The luminous transmittance and reflectance are defined by

$$T_{\text{lum}} = \frac{\int T(\lambda)\varphi_{\text{lum}}(\lambda)d\lambda}{\int \varphi_{\text{lum}}(\lambda)d\lambda}, \tag{1}$$

$$R_{\text{lum}} = \frac{\int R(\lambda)\varphi_{\text{lum}}(\lambda)d\lambda}{\int \varphi_{\text{lum}}(\lambda)d\lambda}, \tag{2}$$

whilst the solar transmittance and reflectance modulation are defined by

$$T_{\text{sol}} = \frac{\int T(\lambda)\varphi_{\text{sol}}(\lambda)d\lambda}{\int \varphi_{\text{sol}}(\lambda)d\lambda}, \tag{3}$$

$$\Delta T_{\text{sol}} = T_{\text{sol,cold}} - T_{\text{sol,hot}} \tag{4}$$

$$R_{\text{sol}} = \frac{\int R(\lambda)\varphi_{\text{sol}}(\lambda)d\lambda}{\int \varphi_{\text{sol}}(\lambda)d\lambda}, \tag{5}$$

$$\Delta R_{\text{sol}} = R_{\text{sol,hot}} - R_{\text{sol,cold}} \tag{6}$$

where $T(\lambda)$ and $R(\lambda)$ denotes the transmittance and reflectance at wavelength λ respectively, φ_{lum} is the spectral sensitivity of the human eye, and φ_{sol} is the solar irradiance spectrum for air mass 1.5.

Dielectric constants derived from ellipsometry

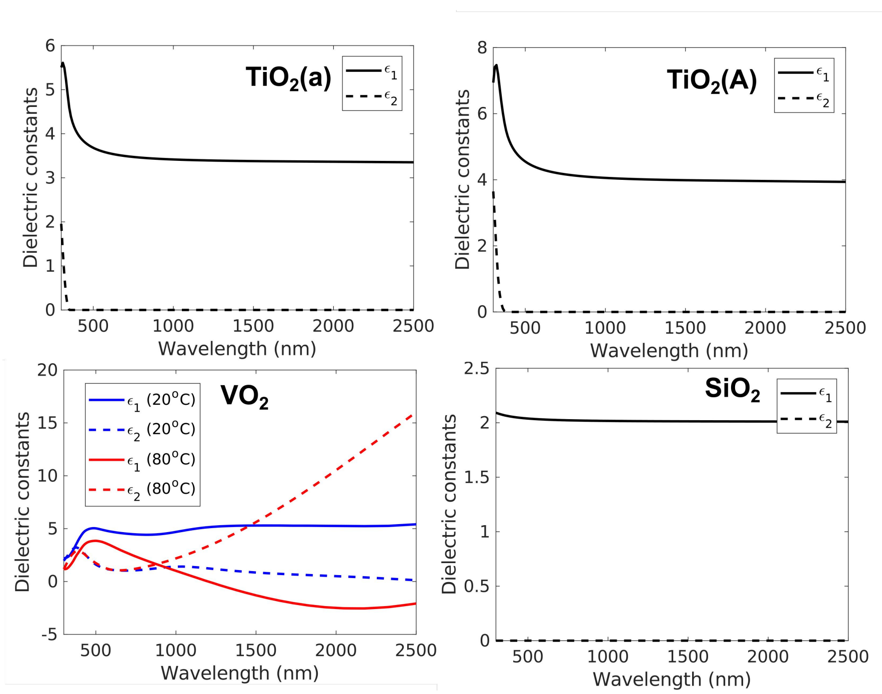

Figure 4. Dielectric constants derived from ellipsometry.

Spin speed thickness curves for sol-gel films

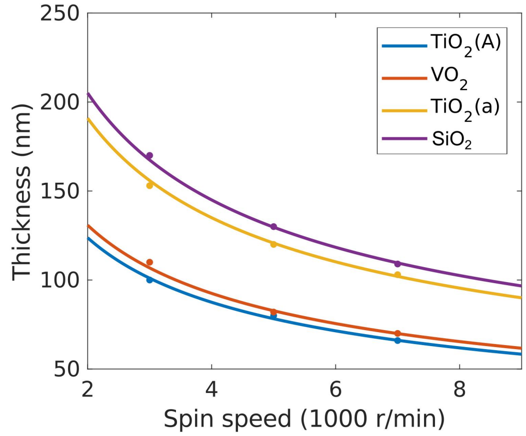

Figure 5. Spin speed thickness curves for sol-gel films.

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