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Multifunctional overcoats on vanadium dioxide thermochromic thin films with enhanced luminous transmission and solar modulation, hydrophobicity and anti-oxidation

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Vanadium dioxide (VO_2) has a great potential to be utilized as solar energy switching glazing, even though there exist some intrinsic problems of low luminous transmittance (T_{lum}) and poor oxidation resistance. Si–Al based anti-reflection (AR) sol–gel coatings processed at low temperature have been developed to tackle these issues assisted by adjusting ramping rate and annealing temperature. Si–Al based AR coating gives large relative enhancement on the transmittance (22% for T_{lum}, 14% for the whole solar spectrum T_{sol},) and successfully maintains IR contrast at 2500 nm wavelength with 18% relative increase in solar modulation (ΔT_{sol}). The optimized Si–Al based AR coating annealing conditions are recorded at 3 °C/min ramping rate and 100 °C annealing temperature. Fluorinated-Si based gel offers a new direction of multifunctional overcoat on thermochromic smart windows with hydrophobicity (contact angle 111°), averaged 14% relatively increased luminous transmittance and enhanced oxidation resistance.

1. Introduction

Solar energy modulating vanadium dioxide (VO_2) has been a leading thermochromic material as it exhibits an excellent temperature-responsive behavior at a critical transition temperature (τ_c) of 341 K (68 °C) near room temperature, which makes it the excellent candidate as smart architectural glazing [1]. VO_2 is able to adjust the inflow of solar heat by switching the transmittance in the infrared (IR) region (780–2500 nm), while maintaining the visible transmittance. However the main obstacles of VO_2 to commercialization in large scale are low luminous transmittance (T_{lum}) while maintaining high solar modulation (ΔT_{sol}) due to strong light absorption in the visible wavelength [2,3] and long term stability as VO_2 thermochromic phase is thermodynamically unstable when it is exposed to the air for a long period [4] or abused at high temperature (above 300 °C) [5]. The issue of low T_{lum} has been tackled either by modification of films' compositions and structures or by applications of single/multi-layer anti-reflection (AR) coatings. T_{lum} values could be increased from 34.8% to 38.6% by F-doping [6] and from 41% to 51% by Mg-doping [7] at the cost of jeopardized IR switching ability. Nanoporous thermochromic VO_2 could reduce optical constants therefore to enhance the T_{lum} [8,9]. Three-layer coating of $TiO_2/VO_2/TiO_2$ and five-layer coating $TiO_2/VO_2/TiO_2/VO_2/TiO_2$ have been investigated by Jin et al. [10] and Mlyuka et al. [3], respectively. Three-layer structure displays the greatest percentage of relative T_{lum} enhancement by 86%, while five-layer structure could achieve ~12% ΔT_{sol}. ZrO_2, TiO_2 and SiO_2 have been used to study the AR effects [11–14]. They have proposed to use ZrO_2 as an AR material to enhance T_{lum} from 32% to 55% for 50 nm VO_2 films. Nonetheless, the IR switching ability is decreased by the presence of ZrO_2. Most of the reported AR coatings have been produced by physical vapor deposition which needs high vacuum and expensive experimental set up. Hereby, a simple solution of Si–Al based sol–gel overcoat is fabricated at lower temperature (<250 °C) which can enhance both T_{lum} and ΔT_{sol}. Furthermore, fluorinated-Si based overcoat has a very low surface energy [15] and provides high temperature stability [16]. Fluorinated-Si based gel opens up a new route of multifunctional overcoat on VO_2 thermochromic thin films with improved T_{lum}, together with hydrophobicity and anti-oxidation effects.

2. Experimental

2.1. Preparations of AR sol–gel solutions

All chemicals were purchased from Alfa Aesar without further purification. Two different AR solutions, Si–Al based and

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fluorinated-Si based solutions were prepared via sol–gel method. Si–Al based gel was synthesized as below: aluminum tri(sec-butoxide) (ASB) was dissolved in 90 mL H_2O at 80 °C with stirring vigorously for 4 min. HNO_3 was added to adjust pH = 3–4 followed by continuously stirring for 2 h. Subsequently, 10 g polyvinylpyrrolidone (PVP) was mixed with the solution and cooled down to the room temperature with stirring for 30 min. Furthermore, the mixture was merged with 65 mL trimethoxysilane (MTMS) and 130 mL methanol slowly, and finally agitated ultrasonically for one more hour.

For preparing a fluorinated-Si based sol–gel solution, a tetraethyl orthosilicate (TEOS) precursor was diluted according to the molar ratio as TEOS:ethanol (95%):H_2O = 1:8.14:2. Hydrochloric acid (HCl, 37%) was dropped into the mixture until pH < 2. The solution was stirred for about 2 h followed by aging for at least one day before merging with 1H, 1H, 2H, 2H-fluorooctyl triethoxysilane (FOS)/methanol/H_2O system to form the mixture with the FOS ratio of 0.5 vol.%, 1 vol.% and 5 vol.%. The volume ratio of methanol to deionized (DI) water was remained at 10:1 for all mixtures. All formulated solutions were magnetic stirred for at least 6 h to ensure homogeneous suspensions.

Vanadium dioxide with approximately 100–200 nm thickness was deposited on ITO (Sn-doped In_2O_3)-glass substrates [17]. AR coatings were dip coated at a withdraw speed of 10 mm/min, followed by annealing in air at various ramping rates and temperatures in order to optimize AR effects.

2.2. Characterization

The goniometer, First Ten Angstroms 32 (FTA32) is employed to test the contact angle. The surface morphologies of the films were determined by the atomic force microscopy (AFM, DI-3100, Bruker, Germany) using tapping mode. X-ray diffraction was performed on a Shimadzu XRD-6000 X-ray diffractometer (Cu Kα, λ = 0.15406 nm) with 40 kV voltage and 30 mA current. The thickness of the VO_2 film was measured by Alpha-Step IQ Surface Profiler. The transmittance in the range of 250–2500 nm and the hysteresis loops (20–100 °C) at the wavelength of 2500 nm were measured with a UV–vis–NIR spectrophotometer (Cary 5000, Agilent Ltd.) equipped with a Linkam PE120 system peltier simple heating and cooling stage.

The integral luminous transmittance (T_{lum}, 380–780 nm) and solar transmittance (T_{sol}, 280–2500 nm) were calculated based on the recorded spectra using the following expression:

$$T_{lum/sol} = \frac{\int \varphi_{lum/sol}(\lambda)T(\lambda)\,d\lambda}{\int \varphi_{lum/sol}(\lambda)\,d\lambda}$$

where $T(\lambda)$ is the recorded film transmittance, φ_{lum} is the standard luminous efficiency function for the photopic vision of human eyes [18], and φ_{sol} is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon) [19]. ΔT_{sol} is attained from $\Delta T_{sol} = T_{sol(20\,°C)} - T_{sol(90\,°C)}$.

3. Results and discussion

3.1. Si–Al based sol–gel AR coating

3.1.1. The effect of ramping rate

Si–Al AR coatings with different ramping rates have been annealed at 100 °C. The data are tabulated in Table 1 and with AR coatings, both T_{lum} and T_{sol} have been increased which suggests that the Si–Al coatings are able to provide AR effect in the solar spectrum (250–2500 nm). Moreover, the ΔT_{sol} could be enhanced which is due to the fact that AR effects are more noticeable for low temperature compared with high temperature. For example, for 3 °C/min sample, the change of T_{sol} at 20 °C between with (59.4%) and without (52.0%) AR coating is 7.4%, while the difference at 90 °C is 6.8%. The enhancement difference between low and high temperature results in 0.6% increase of ΔT_{sol} from 3.4 to 4.0%.

Table 1
Summary of thermochromic properties versus ramping rate (annealing temperature 100 °C).

Ramping rate (°C/min)	T_{lum} (20 °C) (%) (without/with AR coating)	T_{lum} (90 °C) (%) (without/with AR coating)	T_{sol} (20 °C) (%) (without/with AR coating)	T_{sol} (90 °C) (%) (without/with AR coating)	ΔT_{sol} (%) (without/with AR coating)
3	51.0/62.3	54.4/65.0	52.0/59.4	48.6/55.4	3.4/4.0
5	48.5/58.6	53.9/62.7	53.3/58.7	51.1/55.6	2.2/3.1
10	49.9/55.0	54.8/59.1	52.5/53.6	52.5/52.1	0.0/1.5

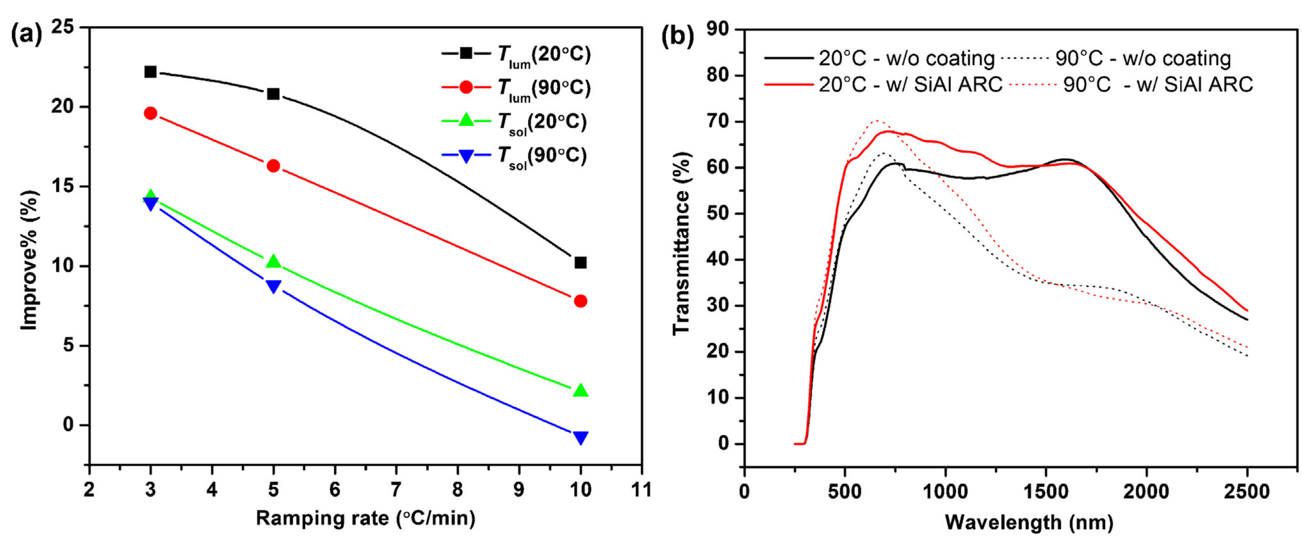

Fig. 1. (a) Plots of improve% versus ramping rate for VO_2 thin film with Si–Al sol–gel overcoat (annealing temperature 100 °C); (b) the UV–vis–NIR spectra of VO_2 thin film with and without Si–Al overcoat annealed at 100 °C with 3 °C/min ramping rate.