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Application-oriented VO_2 thermochromic coatings with composite structures: Optimized optical performance and robust fatigue properties

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ABSTRACT

For decades, VO_2-based smart windows have aroused much interest in energy efficient materials. To meet the practical requirements, VO_2-based thin films should exhibit a high quality performance in equilibrating the solar modulation ability (ΔT_{sol}) and the luminous transmittance (T_{lum}) simultaneously. More importantly, durability and fatigue performance, which determine the life-time in actual use, have rarely been properly explored and obviously cannot be neglected. Herein, SiN_x/VO_2, VO_2/SiN_x and $SiN_x/VO_2/SiN_x$ multilayer structures were proposed and prepared by reactive magnetron sputtering in this work. The amorphous SiN_x not only acts as the antireflection layer for promoting optical performance, but also serves as the ions diffusion barriers or passivation layers on the bottom and/or top of VO_2. As expected, the optimized composite structures successfully enhanced the solar modulation ability (from 10.8% to 14.5%, 34% maximum increase rate of ΔT_{sol}) and luminous transmittance (from 36.1% to 40.4%, 12%maximum increase rate $T_{lum\text{-}L}$) compared with single-layer VO_2, in accordance with our optical modeling. More significantly, fatigue property had been unprecedentedly proposed and measured in about 2 years, demonstrating an ultra-long heating-cooling cycling times (10^4 cycles) in ambient atmosphere for $SiN_x/VO_2/SiN_x$ structure, exhibiting a dramatic life-time of 27 years, while the single layer VO_2 could only provide the life-time of 4 years (1.6×10^3 cycles). Moreover, $SiN_x/VO_2/SiN_x$ structure also presented excellent durability on hot and wet condition, which is three times as the VO_2 film without SiN_x. Complementally, the improvement of the hydrophobicity with SiN_x surface was found by contact angle test, which would make it possible to form an unobstructed view on rainy day. In conclusion, our works can provide facile structures and novel assessment method on fatigue performance for VO_2-based films, and promote the industrial application for smart windows.

1. Introduction

Vanadium dioxide (VO_2), as a classical metal-insulator transition (MIT) material, has gained more concerns due to the controllable first-order phase transition [1]. During the transition process, corresponding near-infrared light reflection properties can be switched reversibly between transparent monoclinic VO_2 (M) and highly reflective rutile VO_2 (R) below/above the critical MIT temperature ($T_c \approx 68\,^{\circ}C$) [1–5]. Therefore, VO_2 can serve as the promising solar modulating coating for smart windows [6–8], which is able to impede heat at high ambient temperature automatically without attenuation of the luminous transmittance, achieving the goal of high efficiency in building temperature management and energy saving [9,10].

For practical utilization of VO_2-based smart windows, the poor performance of unsatisfactory solar modulation ability (ΔT_{sol}) and unbefitting luminous transmittance (T_{lum}) are the two main impediments

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[11], while the improperly high critical transition temperature (T_c) also obstruct the large-scale application [12]. Up to now, lots of efforts were attempted to solve these problems, especially doping, which was regarded as an efficient way. Dopants include W [12–14], Mo [15], Mg [16], Nb [17], Zr [18], F [19,20], *etc.*, had been adequately studied in previous works. Some of them could reduce T_c observably while others could modify ΔT_{sol} and T_{lum} effectively, and even co-doping was used to optimize the mentioned three barriers. However, the confirmable deterioration of switching behavior and ambient stability caused by doping cannot be neglected.

In addition, another significant challenge for VO_2-based films is the environmental instability [21]. Indeed, VO_2 is a thermodynamically metastable oxide in vanadium oxides [22], and could be oxidized to V_2O_5 rapidly in extreme annealing condition at 300 °C or humid water-containing environments [23,24]. To solve this problem, one feasible method is to introduce overlying diffusion barrier such as AlO_x [24,25], SiO_2 [26], ZnO [27], *etc.*, to protect VO_2 from water and oxygen, and extend the life-time. Furthermore, for VO_2-based films, some kind of diffusion barriers can also work as the antireflection (AR) layer when their refractive index (n) are near the range of 2.0-2.4 (at the wavelength of λ= 550 nm) including ZrO_2, TiO_2, ZnO, etc [28]. That is, bringing in appropriate AR layer can availably optimize T_{lum} and ambient stability at the same time, while AR layer may provide additional functions. Previous works had already confirmed that SiO_2 [29], TiO_2 [30,31], WO_3 [32], ZnO [33,34], and Cr_2O_3 [35] worked well with VO_2 films and bring about adjunct protection, photo-catalysis, photo-hydrophilicity, reduction of deposited temperature, anti-fogging and *etc.*, from where we confirm that structure design with unique coating for VO_2 is a feasible route to ameliorate the drawbacks.

SiN_x is a promising covering layer or passivation layer in electronic industry because of its high etch rate in production lines, transparent properties, thermal stability and high humidity stability, good insulation and *etc* [36–39]. The refractive index (n) of SiN_x is nearly 2.0 in visible range, which is in agreement with the requirement of AR layer for VO_2 films [28]. Koo et al. used SiN_x as buffer layer between VO_2 and soda lime glass, found that SiN_x successfully prevented sodium ion diffusion in VO_2 thin films and improved the thermochromic properties [40]. Recently, Zhan et al. designed the $SiN_x/VO_2/SiN_x$ sandwich-structure to increase ΔT_{sol} and T_{lum} of VO_2, and strengthened thermal stability of VO_x-based films [41]. Their works offer an efficient solution in visible transmittance enhancement, not only need to make the structural design in multilayer, but also should optimize the optical performance of films based on computational simulation first. More significantly, for practical application, life-time of smart window determines its potential use in near future. Thus, it is necessary to realize the durability in hot and humid atmosphere and long-time ambient switching fatigue properties of VO_2-based films. Nevertheless, the MIT switching fatigue cycles for life-time of VO_2-based films had not yet received much attention in previous works, while there were no assessment paradigm to follow in switching test.

In this study, SiN_x has been selected as buffer layer, overlying diffusion barrier layer, and AR layer simultaneously, and the corresponding structure of SiN_x/VO_2, VO_2/SiN_x and $SiN_x/VO_2/SiN_x$ (labeled as SV, VS, and SVS respectively) have been designed and fabricated 2 years ago. Variable thickness of SiN_x have been deposited to optimize thermochromic properties of VO_2. Indeed, the proposed VS and SVS structure exhibits excellent energy-saving performance with enhancement of ΔT_{sol} as well as T_{lum}, in good agreement with the optical modeling. As for life-time evaluation on composite structures, SVS exhibits a superior fatigue property in 2-year ultra-long MIT switching cycles as well as the prominent durability on extreme hot and wet condition compared with single VO_2 (labeled as V) layer. In addition, realistic house model simulation demonstrates that proposed structures exhibit a visual energy-saving efficiency. These kinds of VS and SVS structures are able to provide guarantees and promotion in practical utility for smart windows.

2. Experimental section

2.1. Film fabrication

V, SV, VS and SVS structures were prepared on $10 \times 10\,mm^2$ quartz and $75 \times 75\,mm^2$ glass substrates *via* reactive magnetron sputtering system. Deposition conditions for SiN_x and VO_2 were optimized to maximize the thermochromic properties. V_2O_3 (99.95%) and Si (99.99%) targets (diameter of 4 in.) were used for VO_2 and SiN_x layer respectively while deposition course was carried out using integrated lock-load system. An initial pump-down process was executed to reach the original pressure of 5.0×10^{-4} Pa for deposition chamber. Then, when deposited VO_2 films, Ar (99.99% pure) gas as well as the Ar (97%) and O_2 (3%) mixed gases (99.99% pure) with various Ar/(Ar + O_2) proportions were introduced to the atmosphere. Sputtering then took place at a power of 200 W onto substrates of quartz glasses. The Ar/(Ar + O_2) ratio was kept at 0.25 (O_2 ~ 2.4%) and the pressure of chamber was kept at 6 mTorr when the total gas flow is 50 sccm. Temperature of the deposition process was maintained at 430 °C in entire deposition process for VO_2. The SiN_x films were deposited at room temperature at a pressure of 6 mTorr with a gas flow of 50 sccm, and the gas was a mixture of 99.99% purity Ar and N_2 (Ar/N_2 = 4).

2.2. Film characterization

In order to confirm the crystalline structure of thin films, X-ray diffraction (XRD) measurements were conducted on a Rigaku Ultima IV diffractometer with 2θ grazing angle mode using Cu Kα radiation (λ = 0.15418 nm). Films' surface topography and root-mean-square (RMS) roughness were measured by atomic force microscopy (AFM, SII Nano Technology Ltd, Nanonavi Π) apparatus in tapping mode. To confirm the thickness and determine the microstructure of the films, cross-section images and surface morphology were observed using field-emission scanning electron microscopy (SEM, Hitachi SU8220). Transmittances spectra of the as-deposited films in the wavelength range of 350–2600 nm (T) were obtained using a UV–vis–NIR spectrophotometer (Hitachi Corp., model UV-4100) equipped with an accessory heater. The temperature was measured precisely with a temperature sensor in contact with the surface of films, commanded by a temperature controlling unit.

2.3. Service performance and energy-saving efficiency

To fit for the demand of practical application, the service performance was involved, divided into two different parts in evaluation.

Firstly, the fatigue properties of SVS and V films were evaluated by self-made periodic test system, as illustrated in Scheme S1 (Supporting information). This kind of equipment contains two correlative parts, control-system and test-system. To obtain semiconducting/metal states, temperature is deliberately set as 25 °C and 90 °C on heating and cooling route respectively. In addition, the fatigue testing apparatus is set on condition of 25 °C and 60% relative humidity, which is served as ambient atmosphere. Then, heating-cooling process is carried out automatically per 30 min to guarantee the temperature stability and providing adequate time for detecting, and the detector records the transmittance of the beam at different states of the sample. Finally, the recorded transmittance data is transformed into computer and memorized. Moreover, the cycling number is 48 times per 24 h, and the total number is executed over 35,000 times, indicating that our fatigue test undergoes more than 2 years.

Next, accelerated aging test was executed to estimate the environmental durability of films. Samples were put in a constant temperature humidity chamber with the setting conditions of T_h = 60 °C and 90% relative humidity while the optical spectra of films were measured per 24 h. To confirm the failure mechanism of single layer VO_2 after fatigue cycling, X-ray photoelectron spectroscopy (XPS, Thermo Fisher