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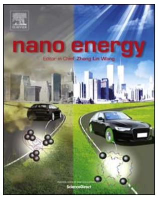

Communication

Optical design and stability study for ultrahigh-performance and long-lived vanadium dioxide-based thermochromic coatings

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ABSTRACT

In this work, thermochromic $Cr_2O_3/VO_2/SiO_2$ (CVS) sandwich structures on glass substrates were designed and fabricated by magnetron sputtering method. Optical design and calculation were employed to optimize the structure using a optimization program. The bottom Cr_2O_3 layer provides a structural template for improving the crystallinity of VO_2 and increasing the luminous transmittance of the structure. Then, the VO_2 layer with a monoclinic (M) phase at low temperature undergoes a reversible phase-transition to rutile (R) phase at high temperature for solar modulation. The top SiO_2 layer not only acts as an antireflection layer but also greatly enhances the environmental stability of the multilayer structures as well as providing a self-cleaning layer for versatility of smart coatings. According to optical measurements, the fabricated CVS multilayer structure exhibits excellent optical performance with ultrahigh solar modulation ability ($\Delta T_{sol} = 16.1\%$) and an improved luminous transmittance ($T_{lum,lt} = 54.0\%$), which is nearly the maximum simulation value for VO_2-based multilayer thin coatings. Meanwhile, stability and deterioration as well as relative mechanisms of the VO_2 coatings were also investigated by monitoring the valence change of the vanadium element. The proposed structure shows remarkable environmental stability due to the dual-protection from the Cr_2O_3 and the SiO_2 layer, which shows negligible deterioration even after accelerated aging of 10^3 h and $4*10^3$ fatigue cycles, while VO_2-single layer samples almost become invalid. Finally, energy-efficient effect was successfully demonstrated using CVS coated glass as the roof of a "winter garden".

1. Introduction

Energy crises and global warming cause numerous problems in human society and drive a focus on energy-saving materials. Due to the excessive use of heating, cooling, lighting, and ventilation, buildings have been estimated to produce about 30% of all anthropogenic greenhouse gas emissions [1] and are responsible for almost 30–40% of the primary energy consumption in the world [2]. The use of chromogenic materials on building fenestration has been demonstrated as an effective way to reduce building energy consumption [3]. Smart coatings based on thermochromic materials are helpful to increase the energy efficiency of buildings and reduce the energy consumption due to their selective modulation of infrared radiation in response to environmental temperature [4]. Vanadium dioxide (VO_2), which is a typical thermochromic material and has been widely investigated due to its unique transition feature [5–8], undergoes a reversible semiconductor-metal transition (SMT) from monoclinic VO_2 (M) to rutile VO_2 (R) at a transition temperature (T_c) of 68 °C [9]. During the phase transition process, VO_2 exhibits a dramatic modulation of optical properties from infrared (IR) transmission to IR shielding in the near-infrared region, which is suitable for energy-efficient coating applications [6,10].

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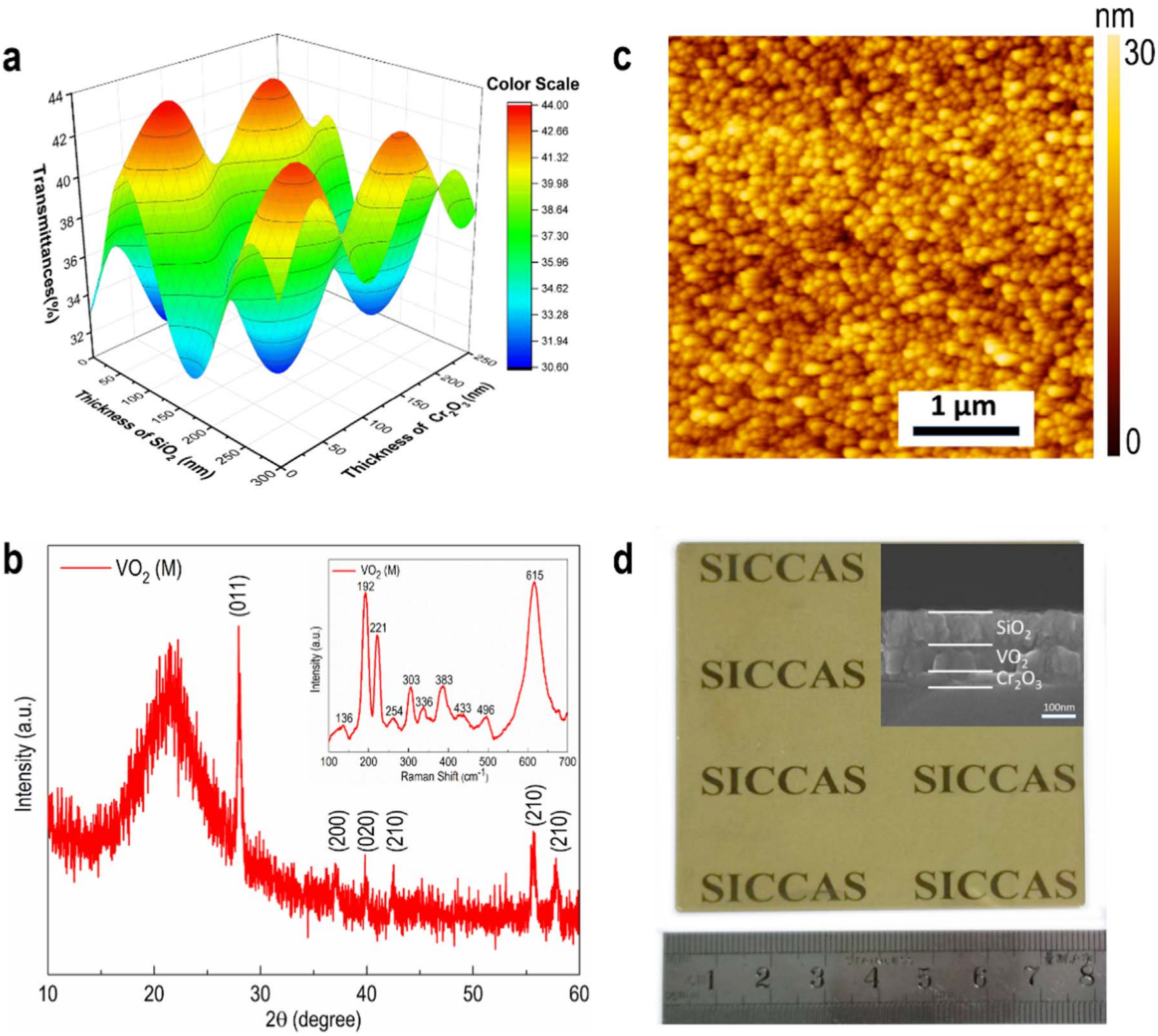

Fig. 1. Simulated Calculations and Schematic Illustration. a) 3D surface image of the luminous transmittance ($T_{lum,lt}$) calculation of the Cr_2O_3/VO_2 (80 nm)/SiO_2 multilayer structure on the thickness design of Cr_2O_3 (bottom layer) and SiO_2 (top layer). b) XRD patterns of the VO_2 film deposited with 40 nm Cr_2O_3 structural template layer at 350 °C (with Raman spectra inset). c) AFM image of the sample in b). d) Digital photo of the large scale CVS thermochromic film on 75 × 75 mm^2 glass substrate.

There are still some obstacles severely limiting the applicability of VO_2 smart coatings to energy-efficient fenestration: (a) the solar modulation ability, denoted as ΔT_{sol}, is usually less than 10%, which is not efficient in practical applications [11]; (b) the small optical band gap of VO_2 causes poor luminous transmittance (T_{lum}) due to absorption in the short-wavelength range [12,13]; (c) oxidation of vanadium element in VO_2 gives rise to environmental instability, which leads to the gradual degradation of thermochromic performance [14]. This is a great challenge for thermochromic VO_2-based coating to reach a satisfactory luminous transmittance accompany with sufficiently solar modulation ability; meanwhile, the coating must be environmentally stable for a long-time use, where efficient thermochromism should be maintained for at least 10 years in practical application.

Optical design of multilayer structures using high-refractive-index dielectric materials has been demonstrated to be an effective way to improve the T_{lum} and/or ΔT_{sol}. In previous work, VO_2-based multilayer structures such as VO_2/ZrO_2 [15], VO_2/TiO_2 [16], $TiO_2/VO_2/TiO_2$ [12], $TiO_2/VO_2/TiO_2/VO_2/TiO_2$ [17], and $SiN_x/NiCrO_x/SiN_x/VO_x/SiN_x/NiCrO_x/SiN_x$ [18] have been proposed. However, improvements made by above structures are not efficient for industrial production, because only unilateral pursuit of distinguished solar modulation ability or luminous transmittances has been achieved in these works. Excellent solar modulation ability (ΔT_{sol}) combining with satisfactory luminous transmittance (T_{lum}) is required, for practical application of VO_2-based coatings as smart windows.

Meanwhile, environmental stability is an important challenge for the practical application of VO_2-based thermochromic smart coatings as desirable thermochromic properties must be maintained over long-time periods. In real environments, VO_2 will gradually transform into the intermediate phases of V_6O_{13} and V_3O_7 and finally into V_2O_5, which is the most thermodynamically stable phase of vanadium oxide but not possess the thermochromic property [19]. In previous works, there are only few researches focus on the thermal stability of VO_2 [18–21]. Thermal treatment of VO_2 films at high temperatures (usually ~300 °C) has been carried out to evaluate relative thermal stability. However, such high temperatures are nonexistent in actual environments. Systematic investigation of the environmental stability for VO_2 films is absent.

In this work, optical design and stability study have been carried out for ultrahigh-performance and long-lived VO_2-based thermochromic coatings and the $Cr_2O_3/VO_2/SiO_2$ structure has been proposed. Cr_2O_3, the most thermodynamic stable phase of chromium oxides [22], has similar lattice parameters to VO_2 (Cr_2O_3, hexagonal, a = 0.496 nm, c = 1.359 nm; VO_2(R), tetragonal, a = 0.455 nm, c = 0.286 nm). Low formation enthalpy ($\Delta H_{Cr_2O_3} = -1129\mathrm{KJ/mol}$) allows for a wide range of Cr_2O_3 fabrication temperature (30–900 °C). These properties make Cr_2O_3 a promising buffer layer material for deposition of thermochromic VO_2 films to lower the deposition temperature as well as