VO$_2$-based double-layered films for smart windows: Optical design, all-solution preparation and improved properties

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ABSTRACT

An all-solution process was developed to prepare VO$_2$-based double-layered films containing SiO$_2$ and TiO$_2$ antireflection layers. These double-layered films were optimized to improve luminous transmittance (T_{lum}) and switching efficiency (ΔT_{sol}). The substrate/VO$_2$/TiO$_2$ double-layered structure showed the largest improvement of 21.2% in T_{lum} (from 40.3% to 61.5%). T_{lum} could be further improved to the maximum of 84.8% by combining film thickness optimization and antireflection layer deposition. ΔT_{sol} (usually below 10% for single VO$_2$ films) could be improved by adjusting the position of antireflection peaks (the highest ΔT_{sol} was 15.1%). A sample with balanced T_{lum} and ΔT_{sol} showed T_{lum} of about 58% (20 °C) and 54% (90 °C), and ΔT_{sol} of 10.9%. This work is an important technical breakthrough toward the practical application of VO$_2$-based smart windows.

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1. Introduction

Energy conservation has directed a global trend toward sustainable development. Due to global warming, air conditioning systems have been widely used in daily life, thus inducing a series of problems [1], including increases in electricity consumption and carbon dioxide emissions along with the formation of other atmospheric pollutants from the electricity-generation process. Air conditioning in China accounts for 40–60% of a building's energy consumption (the exact figure depends on the area of the building) and, overall, uses 28% of the total available primary energy. These figures will grow rapidly with urban development. One effective way to reduce the amount of electricity consumed by cooling is to apply solar-control coatings to glass windows, or so-called "smart windows". Because room lighting demands transparency, most of the smart windows are designed to intelligently control the amount of light and heat (mainly in the near infrared region) passing through in response to an external stimulus such as light (photochromic) [2], heat (thermochromic) [3–5] or electricity (electrochromic) [5–7]. In this regard, the thermochromic smart window, typically based on a vanadium dioxide (VO$_2$) functional layer, has received particular interest due to two aspects. First, it can respond to environmental temperatures, making reversible structural changes from an infrared-transparent semiconductive state to an infrared-blocking metallic state. Second, the visible transparency remains almost unchanged.

However, an expensive fabrication method, low visible transparency and insufficient energy-saving efficiency limit the application of VO$_2$ smart windows in architectures. The main preparation methods for VO$_2$ films are based on gas-phase reactions such as sputtering deposition [3,4], chemical vapor deposition [8,9], pulsed laser deposition [10] and ion implantation [11]. These methods are superior in terms of precise control of process parameters such as oxygen partial pressure (typically in the range of 0.06–0.13 Pa) and film features, including thickness and microstructure [12,13]. They are, however, restricted by expensive equipment. Low visible transmittance (integral transmittance $\leq 40\%$) of VO$_2$ films originates from strong absorption and high reflectance [14,15]. Switching efficiency (ΔT_{sol}) refers to a difference in the solar energy transmittance across metal–insulator phase transition (MIPT) and is used to characterize the thermochromic properties of VO$_2$ films. This value is usually below 10% for a single-layered VO$_2$ film [3,4] .

The current techniques used to improve visible transparency mainly include Mg doping [16], formation of mixtures (VO$_2$/SiO$_2$) [17], regulation of the thickness of VO$_2$ films [18] and deposition of antireflective layers [3,4,19–22]. Among these techniques, VO$_2$-based multi-layered structures containing antireflection layers show better optical performance, especially a balance between luminous transmittance (T_{lum}) and switching efficiency

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(ΔT_{sol}). Moreover, the antireflective layer can protect VO_2 from oxidation and add new functions such as photocatalysis [22,23]. ΔT_{lum} represents the improvement of T_{lum} after antireflecion. An integrated improvement of 23% (from 32% to 55%) in T_{lum} can be achieved for VO_2/ZrO_2 double layers using ZrO_2 as an antireflective layer [24]. A $TiO_2/VO_2/TiO_2$ three-layer film shows ΔT_{sol} =2.9% and ΔT_{lum}=27% (increased from 31 to 58%) [21]. A $TiO_2/VO_2/TiO_2/VO_2/TiO_2$ five-layer film can improve ΔT_{sol} to 12.1% (6.7% for the single VO_2 film) [25]. All of these films were prepared by gas-phase deposition, and it seems difficult to improve ΔT_{lum} and ΔT_{sol} simultaneously at a higher ΔT_{lum} level for VO_2 films. ΔT_{sol} of the $TiO_2/VO_2/TiO_2$ three-layer film decreased from 3.9% to 2.9%, while T_{lum} of the $TiO_2/VO_2/TiO_2/VO_2/TiO_2$ five-layer film just increased by 4% (from 41% to 45%).

The present work was conducted to develop an all-solution preparation process for VO_2-based double-layered films. The study began with the optical optimization of the structure of the double-layered films by combining basic interference principles with spectral simulation, followed by all-solution preparation and investigation of the improvement in T_{lum} and ΔT_{sol} to confirm the computational predictions. By adding a quarter-waved optical thickness TiO_2 film on VO_2, the integrated luminous reflectance (R_{lum}) of VO_2 was reduced dramatically from 31.2% to 3.0%, and T_{lum} is close to that of the $TiO_2/VO_2/TiO_2$ layer films [21]. These results are comparable to the films prepared by gas-phase deposition [4,21], but ΔT_{sol} is slightly higher (6.9% vs. 6.0%). In addition, methods to improve ΔT_{sol} while maintaining a high ΔT_{lum} were explored; the highest ΔT_{sol} was 15.1% for optimized double-layered films, which still showed T_{lum}=49.5% at 20 °C and 44.8% at 90 °C.

2. Experimental

2.1. Film preparation

All the reagents were bought from Sinopharm Chemical Reagent Co. Ltd. and used without further purification. VO_2 thin films were prepared by a polymer-assisted deposition method, which has been reported in our previous works [26]. $VOCl_2$ is unstable, and $VOCl_2$ solutions were prepared in this study to keep fresh. Briefly, concentrated HCl (38%, 6 mL) and a solution of 1 g of $N_2H_4 \cdot HCl$ added to an aqueous suspension (50 mL) containing 3.5 g of vanadium pentoxide (V_2O_5) were prepared. After being treated in a water bath with stirring, a blue solution was obtained. Then an additional small amount of V_2O_5 or $N_2H_4 \cdot HCl$ was added to this solution until it contained no VO_2^+ or V^{3+}. Then the suspension was filtered and a clear $VOCl_2$ solution (pH ≈ 1) was obtained. The final concentration of the $VOCl_2$ solution was adjusted to 0.1 mol L^{-1}. 6 wt% of polyvinylpyrrolidone (PVP) was added to the solution as a film-forming promoter. Films

were coated on clean fused-silica substrates by spin-coating of 180 μL of solution twice at 400 rpm for 6 s and at a high speed ranging from 3000 to 6000 rpm for 30 s to control the thickness. After drying at 60 °C for 10 min, films were annealed at 550 °C for 10 min in a nitrogen atmosphere. The acquired samples were ultrasonically cleaned by acetone and alcohol before preparing other layers on them.

SiO_2 sol was prepared by mixing tetraethoxysilane (TEOS), absolute ethanol and deionised water (the pH was adjusted to 1.25 by hydrochloride) at a volume ratio of 1:30:0.42 [27]. TiO_2 sol was prepared using tetraisopropoxide (TIPT), deionized water (the pH was adjusted to 1.10 by hydrochloride) and absolute ethanol at the volume ratio of 1:12:0.063 [28]. The concentrations of Si^{4+} and Ti^{4+} were about 0.4 mol L^{-1}. Both sols were kept in closed glass containers at 60 °C for two days. SiO_2 and TiO_2 films were prepared both on VO_2 layers for antireflection and on Si substrates for determining thickness and refractive index (RI). The spin parameters were similar to those used for preparing VO_2 films, except that the speed varied from 1000 to 5000 rpm. To get high refractive index films at low temperature, the obtained samples were dried at 40 °C and relative humidity of 40% for about 15 min before being heated at 110 °C for a minimum of 2 h [28].

2.2. Characterization

The transmittance spectra at normal incidence and reflectance spectra at a 5° incidence angle from 240 to 2600 nm were measured using a Hitachi U-4100 spectrometer. Integrated luminous (T_{lum}, 380–780 nm) and solar transmittance (T_{sol}, 240–2600 nm) values were obtained from the following equation:

$$T_i = \int \varphi_i(\lambda)T(\lambda)d\lambda / \int \varphi_i(\lambda)d\lambda \qquad (1)$$

where $T(\lambda)$ denotes transmittance at wavelength λ, i denotes lum or sol, φ_{lum} is the standard luminous efficiency function for the photopic vision, and φ_{sol} is the solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon) [29].

Hysteresis loops were measured by collecting the transmittance of films at a fixed wavelength (2000 nm) at an approximate interval of 2.0 °C. Refractive index (RI) and thicknesses of SiO_2 and TiO_2 films on Si substrate were precisely determined with a spectroscopic reflectometer (Filmetrics F20). The reflectance spectrum was measured, and the film thickness and optical constants were obtained by analyzing the reflectance spectra with software (Filmetrics F20). The thicknesses of VO_2 films were also measured by F20. The surface morphologies of the films were determined by field emission scanning electron microscopy (FE-SEM, JSM 6700F, JEOL, Tokyo, Japan) and atomic force microscopy (AFM, Nanocute SII, Seiko, Japan). The room-temperature
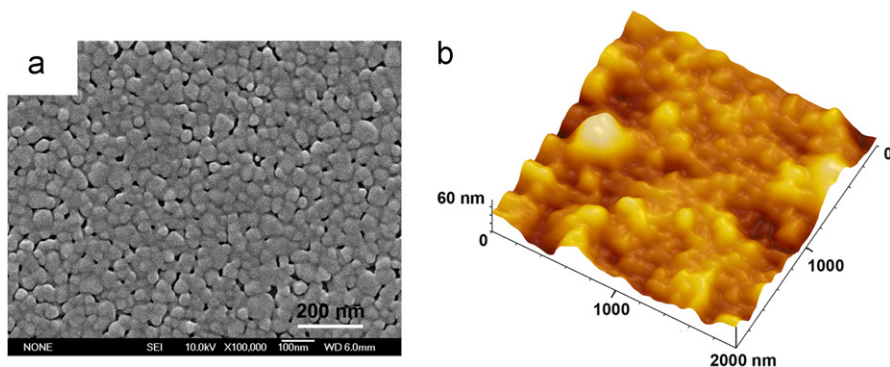

Fig. 1. Scanning electron microscopy photograph (a) and atomic force microscopy image (b) of single VO_2 film.