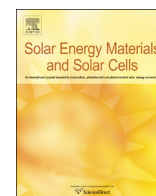




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Multilayer ITO/VO₂/TiO₂ thin films for control of solar and thermal spectra



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ABSTRACT

In this study, a multilayer thin film of ITO/VO₂/TiO₂ was investigated for simultaneous control of the solar and thermal spectra with potential application as an energy-efficient coating for windows in built environments. The functions for these layers were: low emissivity, thermochromism, and anti-reflectance in the visible region. Films were deposited using reactive magnetron sputtering and characterized with scanning electron microscopy, X-ray diffraction, X-ray photoelectron spectroscopy, UV–vis–NIR spectrophotometry, and Fourier transform infrared spectroscopy. The results demonstrate that relatively high luminous transmittance, low emissivity, and favorable thermochromism can be achieved for a film with a transition temperature centered at 52 °C with a hysteresis width of 18 °C. This shows that an advancement of the previous state of the art can be made by restricting the Scherrer grain size of the VO₂ layer to 92 nm.

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1. Introduction

More than 40% of primary energy in the U.S. is used in buildings and this usage is projected to continue for the foreseeable future [1]. Given that windows are a major pathway for energy losses from buildings, one way to improve energy efficiency is through the application of coatings with suitable properties. In temperate climates it is desirable that the optical properties of such window coatings can vary in response to a stimulus (chromogenic thin films). In this way the material can control the propagation of light depending on the conditions of the environment. One class of chromogenic coatings, thermochromic, changes optical properties in response to temperature. These materials could potentially be inexpensive relative to other technologies such as electrochromic coatings, because of their simplicity (i. e. one layer of material without the need for an applied voltage).

Vanadium(IV) oxide is an interesting thermochromic material because its transmittance in the visible region is relatively high and constant with temperature; however, its transmittance in the infrared region decreases significantly when the material is heated above its transition temperature (τ_c). Therefore, a thin layer of VO₂ could be used to control solar irradiance for windows in built environments. The change in VO₂ optical properties is associated with a phase transition from a semiconducting monoclinic to a

metallic rutile structure [2]. A major technical challenge for this material is that τ_c in the bulk monocrystalline form is about 67–68 °C [3,4]. In the polycrystalline thin film form, τ_c appears to be close to 55 °C [5–7] although some researchers have reported values up to 68 °C [8]. Some previous studies have shown that τ_c can be altered by about 5 °C by varying the grain size of VO₂ [9,10]. The advantage of this approach compared to doping the material with a cation such as W⁴⁺ [11] is that it does not reduce the luminous transmittance (T_{lum}) and thermochromism of VO₂ [10]. High T_{lum} is important for transmitting daylight into buildings. T_{lum} can be increased by applying a suitable anti-reflective layer (such as TiO₂) to the VO₂ [5,12–15].

The energy-efficient potential of VO₂ could be further enhanced through the application of a thin coating of low emissive (low-E) material. Low-E coatings act as “hot mirrors,” reflecting mid-IR radiation but transmitting most of the visible light [16]. These optical properties can be used to control the flow of thermal radiation (i.e. 5–10 μm wavelength). One class of high-performing low-E films is transparent conducting oxides (TCOs), which includes F_xSnO_{2–x} and (SnO₂)_x(In₂O₃)_{1–x} [17]. TCOs are favorable for low-E due to their wide optical band gap which enables high luminous transmittance, yet they also have free carriers which can reflect lower-energy photons in the thermal spectrum. By combining thermochromic and low-E materials into a unified multilayer design, both solar and thermal spectra can be controlled simultaneously. One such study was performed through the synthesis and characterization of a multilayer FTO/VO₂/TiO₂ coating [13]. While

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that study demonstrated an innovative multilayer design, it also possessed a relatively high transition temperature centered at 71 °C with a hysteresis width of 17.4 °C [13]. For practical application of VO₂, it is desirable to lower τ_c close to room temperature (less than 25 °C). Furthermore, the luminous transmittance (T_{lum}) in [13] was about 44%, and it is desirable to raise T_{lum} to 55% or more for daylighting purposes in buildings [18]. Thus, there are technical challenges that need to be overcome before these multilayer systems can be utilized for energy efficiency.

In the current study, multilayer ITO/VO₂/TiO₂ samples were synthesized to simultaneously achieve low emissivity, thermochromism, and visible anti-reflectance. The results show that these properties can be combined while still achieving a transition temperature centered at 52 °C with a hysteresis width of 18 °C. Moreover, T_{lum} of 56% is obtained through precise design and synthesis of the multilayer system. This work demonstrates that an advancement in τ_c can be made by restricting the Scherrer grain size of the VO₂ layer to approximately 92 nm.

2. Materials and methods

The goal of this work was to synthesize multilayer films with low emissivity, thermochromism and a relatively low (less than 55 °C) transition temperature. The following steps were performed to achieve this goal. First, approximately 100 nm thick VO₂ films were reactively sputtered on glass substrates using a procedure that has been reported elsewhere [10]. The refractive indices of these VO₂ films as well as a commercially available ITO film were then characterized using a Woollam M-2000 spectroscopic ellipsometer. Both transmittance and reflectance measurements were performed with the ellipsometer and then a basis spline (B-Spline) method was used to determine the optical properties from the measured amplitude and polarization [19]. The B-Spline layer enables a high degree of flexibility in determining the complex index of refraction versus wavelength. This is achieved by specifying the optical constants at a number of control points which are equally spaced in photon energy. The values of the optical constants are then adjusted to reconstruct the measured amplitude and polarization with the B-Spline model. Values of the optical constants between control points are interpolated. Thus, the B-Spline layer is a very flexible approach for modeling the refractive index and it is especially useful for partially absorbing materials such as the VO₂ and ITO films used in this study. Next, the measured refractive indices of the VO₂ and ITO were used as input parameters for the program TFCalc by Software Spectra, Inc. TFCalc is used to simulate the optical performance of thin films and it has functionality for designing and optimizing anti-reflective coatings. Required inputs for the program include refractive index and layer thickness. A three layer structure of ITO/VO₂/TiO₂ was simulated with the program. The refractive index of TiO₂ was taken directly from the library of available materials included with TFCalc [20] and was verified to accurately model the behavior of single-layer TiO₂ on glass. The thickness of the TiO₂ layer in the three-layer structure was numerically optimized to achieve minimum reflectance in the visible region (400–700 nm).

After the multilayer design was optimized, the next step was to synthesize the structure. Commercially-available ITO glass was used as the substrate (VisionTek Systems Ltd.). VO₂ was deposited on the ITO layer using the procedure referenced above [10]. The samples were then annealed in air at 365 °C for 30 min using a Barnstead Thermolyne 47,900 furnace. After the first annealing process was completed, the samples were returned to the sputtering system and a layer of TiO₂ was deposited on the samples.

The procedure for the TiO₂ deposition process can be found in a previous publication [21]. The TiO₂ deposition process in this study had some slight differences from the one cited above, as follows. The sputtering power was 100 W, the deposition time was 7.75 min and the substrate was maintained at room temperature. These parameters were selected to produce a 34 nm thick TiO₂ layer, which was chosen based on the results of the TFCalc simulation. Following the TiO₂ deposition, the samples were annealed for a second time at 365 °C. The second annealing process was conducted for 15, 30, and 45 min, respectively. Therefore, in this study the VO₂ and TiO₂ layers were annealed for different lengths of time. The relationship between the two is: $x_1 = x_2 + 30$ min, where x_1 and x_2 are the VO₂ and TiO₂ annealing times in minutes, respectively. This two-step annealing process was used because it was found to produce a higher level of thermochromism than annealing the multilayer film in a single step.

Naturally-fractured cross sections of the films were characterized with an FEI Sirion scanning electron microscope (SEM). The working distance for SEM was 5 mm, the accelerating voltage was 5 kV, and the scan was performed in ultra-high resolution mode. Next, crystallinity of the samples was characterized with X-ray diffraction (XRD) using a Bruker D8 Discover with GADDS. Cu K α was used as the radiation source for XRD, and data was collected from 2θ of 15–70°. After XRD spectra were obtained, crystalline grain size was estimated using the full-width at half-maximum (FWHM) of the monoclinic (011) peak and the Scherrer equation [22,23]

$$d = \frac{K\lambda}{(\beta - \beta_0) \cos \theta} \quad (1)$$

where d is the grain size, K is a dimensionless shape factor assumed to be 0.9, λ is the wavelength of the radiation source (0.154184 nm), β is the measured FWHM (in radians), β_0 is a correction factor to account for instrumental broadening and θ is the Bragg angle. The value of β_0 was estimated to be 0.00232 rad (0.133°) based on an LaB₆ standard [24]. The FWHM was measured using the built-in functions of the DIFFRAC. EVA 3.0 software.

Chemical compositions of the as-deposited and 45 min annealed TiO₂ layers were characterized with high-resolution X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS Ultra. Monochromatic Al K α was used as the radiation source for XPS, and the data was analyzed with CasaXPS 2.3.15. The spectra were corrected by setting the C 1s binding energy to 284.6 eV, which is common practice for XPS analysis [25].

Transmittance of the films was obtained with UV–vis–NIR spectrophotometry using a Varian Cary 5000. The measurement was performed between wavelengths of 250 and 2500 nm. The following equation was used to integrate the data into three scalar values which can be used to compare different samples in a quantitative and objective way [10]:

$$T_{reg.}(\tau) = \int \varphi_{reg.}(\lambda) T(\lambda, \tau) d\lambda / \int \varphi_{reg.}(\lambda) d\lambda \quad (2)$$

where λ is the wavelength of the incident light, $\varphi_{reg.}$ is a weight function for a region, τ is the sample temperature and T is transmittance. Three regions were used as domains of integration: UV (250 < λ < 400 nm), visible (400 < λ < 700 nm), and NIR (700 < λ < 2500 nm). For the UV and NIR regions, the AM1.5 spectrum was used for φ [26]. For the visible region, the luminous efficiency of the light-adapted eye was used for φ [27]. An additional spectrometry measurement was performed in which the wavelength was fixed at 2500 nm, and the temperature was cycled from 25 to 85 °C in 2 °C increments. The derivative of this measurement was calculated, and the temperature corresponding to the maximum magnitude was defined as the critical transition temperature (τ_c).

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