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Optical properties of vanadium dioxide thin film in nanoparticle structure

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ABSTRACT

The thermo-optic effect and infrared optical properties of VO_2 nanoparticles were studied to obtain an optical material with special property that can be used in smart windows. The reflectance and transmittance spectra of the VO_2 nanoparticles with different duty cycles at different temperatures were simulated with a specific dispersion relation. Vanadium metal nanoparticles were deposited on glass substrate by magnetic reactive sputtering with porous alumina template (AAO) mask, and the VO_2 nanoparticles were prepared by thermal oxidation. The nanostructure and optical properties of the VO_2 nanoparticles were characterized by atomic force microscopy, X-ray photoelectron spectroscopy, X-ray diffraction, and spectrophotometry. The method of preparation of the sample is economical and the phase transition temperature is observed to drop to 43 °C. The transmission at 1700 nm exhibits a variation of 29% between the metallic and semiconducting states. The VO_2 nanoparticles exhibit a significant thermochromic property. The transmittance of the VO_2 nanoparticles is improved compared with the VO_2 film. The decrease in phase transition temperature and the enhancement of optical properties demonstrate that VO_2 film in nanoparticle structure is a viable candidate material for smart windows.

1. Introduction

Smart windows can adjust optical transmittance automatically to balance room temperature and to save solar energy. For the development of smart windows, vanadium dioxide (VO_2) thin film is a potential material for solar energy conservation because of its unique thermo-optic effect. At temperatures near 68 °C, VO_2 thin films undergo reversible semiconductor–metal phase transition (SMPT) [1–3]. Low-temperature monoclinic structure semiconductor state is converted to high-temperature rutile structure metallic state. Accordingly, the optical properties of VO_2 thin films are modified dramatically in the infrared band but weakly in the visible band. Thus, VO_2 thin films can be used as an energy-saving material in buildings, vehicles, and aircrafts by adjusting infrared light [4,5].

VO_2 thin films could be a good candidate material for smart window fields if it had the following features: high optical transmittance in the visible band to ensure enough room light, high optical transmittance ratio before and after phase transition in infrared band, and low phase transition temperature close to room temperature. However, its application is limited by its high phase transition temperature (68 °C) [6]. In 1998, Ebbesen et al. [7] observed extraordinary optical transmission through sub-wavelength hole arrays. Since then, many researchers have focused on the optical properties of sub-wavelength metal structure, the application of which is extended to nanolithography, optical storage, biochemical sensing, sub-wavelength imaging, and semiconductor light-emission. Moreover, several studies found that the phase transition temperature of VO_2 films can be decreased effectively by regulating film grain size [8,9]. In view of reversible SMPT, VO_2 films can be applied to smart windows by adopting a nanoparticle structure.

In order to solve the problems of VO_2 thin films including high phase transition temperature, broad width of thermal hysteresis loop and lower infrared transmittance, in this study, a mathematical model of the reflectance and transmittance of VO_2 nanoparticles was established to analyze the optical properties of VO_2 nanoparticles as an energy-efficient and practical material for smart windows. The influence of nanoparticle duty cycle on infrared optical properties was discussed. Based on porous alumina

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template (AAO), vanadium metal nanoparticles with 0.8 duty cycle were sputtered, and VO_2 nanoparticles were prepared by thermal oxidation. The composition and surface morphology as well as the optical properties of the prepared VO_2 nanoparticles were measured and analyzed.

2. Theory

The mechanism of VO_2 phase transition is complex. Its optical parameters change with temperature and wavelength. In addition, the nanomaterial has some unique characteristics, such as plasmon resonance optical absorption and size effect. Phase transition becomes more complex with the introduction of a nanoparticle structure. Thus, a numerical model for the reflectance and transmittance of VO_2 nanoparticles should be established to analyze its optical property.

For a monolayer film, refractive index is the core factor accounting for the changes in optical property. The Sellmeier function in its standard form is not enough to present the changes in refractive index with temperature and wavelength. Based on the thermal effect of VO_2, a specific dispersion relation is proposed and verified. The specific dispersion relation is as follows [10]:

$$n(t,\lambda) = a_1 + a_2 * \lambda + \frac{a_3}{\lambda} + \frac{a_4}{\lambda^2} + a_5(t - t_0) + a_6(t - t_0)^2 + a_7(t - t_0)^3 + \frac{[a_8(t - t_0) + a_9(t - t_0)^2]}{\lambda^2} \quad (1)$$

where λ is the wavelength at the range from 700 nm to 1700 nm, t is the operating temperature, t_0 is the ambient temperature, and the parameters $a_1 - a_9$ are coefficients of determination as shown in Table 1.

Given the uniqueness of the VO_2 nanoparticles, the VO_2 film in nanoparticle structure can be equivalent to a monolayer film. Its equivalent refractive index is described by [11]

$$n_1 = \left| \frac{(1 - F + Fn^2)(F + (1 - F)n^2) + n^2}{2(F + (1 - F)n^2)} \right|^{1/2} \quad (2)$$

where $F = f^2$ is the duty cycle of the nanoparticle, and f is the ratio of the nanoparticle size to the center-to-center spacing of the nanoparticles.

Under normal incidence conditions, the reflectance and the transmittance of the equivalent monolayer film are described as follows:

$$R = \frac{(n_0 - n_g)^2 \cos^2\delta + \left[\frac{n_0 n_g}{n_1} - n_1\right]^2 \sin^2\delta}{(n_0 + n_g)^2 \cos^2\delta + \left(\frac{n_0 n_g}{n_1} + n_1\right)^2 \sin^2\delta} \quad (3)$$

$$T = \frac{4n_g}{(n_0 + n_g)^2 \cos^2\delta + \left(\frac{n_0 n_g}{n_1} + n_1\right)^2 \sin^2\delta} \quad (4)$$

Table 1
Parameters of fitting.

Parameter	Value
a_1	3.7792
a_2	4.7000×10^{-4}
a_3	-2.8395×10^{3}
a_4	1.4403×10^{6}
a_5	2.0780×10^{-2}
a_6	-6.5000×10^{-4}
a_7	3.2602×10^{-6}
a_8	-9.3733×10^{3}
a_9	1.1154×10^{2}

where n_0 is the refractive index of air, n_g is the refractive index of glass, $\delta = 2\pi n_1 H/\lambda$, δ is the phase difference of light from the upper surface to the lower surface, and H is the film thickness. The thickness of VO_2 film is 300 nm both for theoretical and experimental considerations.

The simulated reflectance spectra of the VO_2 nanoparticles with different duty cycles at low and high temperatures are plotted in Fig. 1. T_C is the phase transition temperature. The curve of $F = 1.0$ shows that the characteristics of VO_2 film. A main peak is observed at $\lambda = 770$ nm, and its reflectance is about 17%. The peaks shift and weaken along the short wavelength when the duty cycle decreases. At $\lambda \approx 1100$ nm, the reflectance is minimum at low and high temperatures, and the value does not shift with the change in duty cycle. At $\lambda > 1700$ nm, the reflectance change before and after phase transition is more obvious with increasing wavelength. The variation amount of the reflectance before and after phase transition is about 11% at $\lambda \approx 1700$ nm for $F = 1.0$. The variation becomes smaller as the duty cycle decreases. Variation is only about 0.8% for $F \approx 0.6$.

The simulated transmittance spectra of the VO_2 nanoparticles with different duty cycles at low and high temperatures are plotted in Fig. 2. The figure shows that the variation of transmittance is obvious before and after phase transition as the duty cycle decreases. The variation of the VO_2 film is significantly less than that of $F \approx 0.6$. The reason might be that the decrease of duty cycle weakens the modulation of the optical properties in phase transition.

In addition, the transmittance of the VO_2 nanoparticles at low and high temperatures increases as F decreases. The transmittance for $F \approx 0.6$ is significantly higher than that for $F = 1.0$ because the substrate exposed area increases when the fill factor decreases. The light transmission of glass substrate is significantly higher than that of the VO_2 thin film. The VO_2 nanoparticles for $F \approx 0.8$ not only exhibit remarkable phase transition but also enhance the transmittance significantly before and after phase transition.

The nanoparticles exhibit high transmittance and reflectance at low temperatures and low transmittance and reflectance at high temperatures. Studies showed that the modulation of VO_2 nanoparticles absorption cross section is the main reason causing dielectric optical response, which is due to plasmon resonance before and after phase transition when the level reaches nano-scale [12].

3. Sample preparation and experiment

Vanadium metal nanoparticles were sputtered with a porous alumina template (AAO) mask using a JC500-3/D magnetron sputtering coater (Chengdu Vacuum Machinery Plant, China), and VO_2

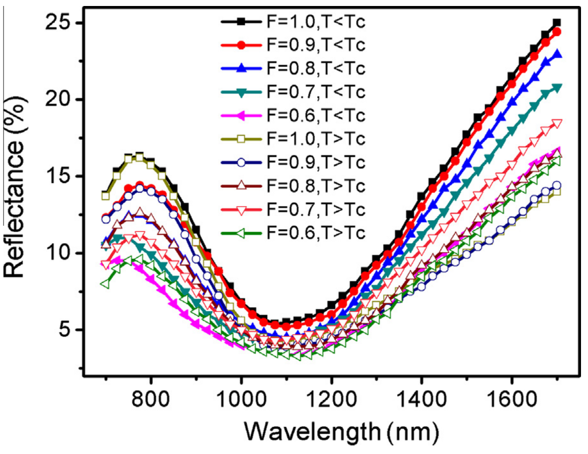

Fig. 1. Simulated reflectance of the VO_2 nanoparticles with different duty cycles.