Infrared Thermochromic Properties of VO₂ Thin Films Prepared through Aqueous Sol-gel Process

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Abstract: The stoichiometric vanadium(IV) oxide thin films were obtained by controlling the temperature, time and pressure of annealing. The thermochromic phase transition and the IR thermochromic property of 400 nm and 900 nm VO₂ thin films in the 7.5 μm-14 μm region were discussed. The derived VO₂ thin film samples were characterized by Raman, XRD, XPS, AFM, SEM, and DSC. The resistance and infrared emissivity of VO₂ thin films under different temperature were measured, and the thermal images of films were obtained using infrared imager. The results show that the VO₂ thin film annealed at 550 °C for 10 hours through aqueous sol-gel process is pure and uniform. The 900 nm VO₂ thin film exhibits better IR thermochromic property than the 400 nm VO₂ thin film. The resistance of 900 nm VO₂ film can change by 4 orders of magnitude and the emissivity can change by 0.6 during the phase transition, suggesting the outstanding IR thermochromic property. The derived VO₂ thin film can control its infrared radiation intensity and lower its apparent temperature actively when the real temperature increases, which may be applied in the field of energy saving, thermal control and camouflage.

Key words: vanadium dioxide; thermochromism; infrared emissivity; sol-gel; thin film

1 Introduction

Thermochromic materials, the optical properties of which can vary with the temperature[1], have received increased interest for applications not only in the visible domain but also in the infrared (IR) region. Focusing on the latter, and more particularly, on the middle infrared (MIR, 3-5 μm) and the long infrared (LIR, 8-14 μm) regions corresponding to the atmospheric transmission windows, three specific applications are mainly addressed on energy-saving building, spacecraft thermal control and military camouflage against IR sensors[2]. Vanadium dioxide (VO₂) is one representative IR thermochromic material, and it can change its optical properties reversibly, especially in the IR region, depending on environmental temperature. The VO₂ thin film undergoes a first order phase transition at about 68 °C, accompanied by a crystallographic transformation from monoclinic structure VO₂(M) to the tetragonal rutile structure VO₂(R)[3]. The optical properties of VO₂ thin films dramatically vary at the transition temperature. At room temperature, the VO₂ thin film is semiconductive with high IR emissivity; above 68 °C, it is metallic with low IR emissivity.

VO₂ thin films have been synthesized by RF sputtering[4], chemical vapor deposition[5], evaporation[6], pulsed laser deposition[7], as well as sol-gel process[8] on various substrates. Many studies have been also done to investigate the thermochromic property of VO₂ thin films in the near infrared (NIR, 0.8-2.5 μm) and MIR regions[9,10], but little attention has been focused on the thermochromic property of VO₂ films in the LIR region. F Guinneton et al[11,12] has studied the IR thermochromic property of VO₂ thin films deposited on silica substrates in the long wavelength region by RF sputtering using V or V₂O₅ targets. However, the investigation of IR thermochromic property of VO₂ thin films prepared by potentially most practical sol-gel process has been little reported, especially the aqueous sol-gel method. This paper aims to report the IR thermochromic properties, especially in the 7.5-14 μm region, of VO₂ thin films derived through a relatively simple aqueous sol-gel process.

2 Experimental

2.1 Samples preparation
The VO₂ thin films were prepared through aqueous sol-gel process followed by vacuum annealing, using V₂O₅ powder as precursor. 10 g V₂O₅ powder was put into a ceramic crucible and heated to 850 °C for 20 minutes in an electric furnace, and then the molten liquid was quickly poured into 250 mL stirred distilled water at room temperature. After vigorous stirring for 2 hours the brownish sol was filtered. The quartz glass substrates cleaned in ethanol and acetone by ultrasonic were dipped into the sol and then pulled out with the rate of 6 mm/s. The films were dried at ambient temperature for about 1 hour, and thicker films can be obtained by repeating this process. The orange red precursor films then formed after the heat treatment conducted in air at 350 °C for 2 hours with the rate of 0.5 °C/min. The black blue VO₂ film samples were gained through the annealing of orange red films under 0.05 Pa vacuum at 550 °C for 10 hours with the rate of 10 °C /min.

2.2 Characterization methods

The Raman spectra of the VO₂ film sample were obtained using a Bruker Senterra Raman spectrometer with the laser wavelength 532 nm. The structure of the VO₂ film sample was determined by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer equipped with Cu Kα (λ=0.154 06 nm) radiation, working in a classical coupled θ-2θ mode. The valence state of vanadium was studied by X-ray photoelectron spectroscopy(XPS) performed on a VG MKII X-ray photoelectron spectrometer using Al Kα (hν=1 486.6 eV) as the exciting source. Scanning electron microscopy(SEM) and atomic force microscopy(AFM) were taken on Hitachi S4800 instrument and NT-MDT Solver & SNOM instrument, respectively.

2.3 Thermochromic property experiments

The differential scanning calorimetry(DSC) measurement of the VO₂ thin film is difficult because of its thinness, so we prepared the VO₂ film on the thin muscovite substrate under the same conditions as above. The film and the muscovite substrate were cut into small pieces together used as the test sample, and the DSC experiment was performed using a CDR-34P differential thermal analyser during 20-120 ℃. Because of the thermal stability of muscovite substrate during 20-120 ℃, the gained DSC curve reflects the property of VO₂ thin film itself. Resistance was measured by pressing two parallel Ag sticks against the film closely. The film sample rested on a heated table controlled by a temperature programmer with platinum resistance sensor, and two Pt100 thermocouples were placed on the film surface measuring the film temperature. The thermal image and IR emissivity test were based on German InfraTec VarioCAM thermal imager working in the waveband 7.5-14 μm.

3 Results and discussion

3.1 Film preparation and characterization

![Fig.1 Raman spectra of (a) the precursor film derived by sol-gel process and (b) the film after annealing under 0.05 Pa vacuum at 550 °C for 10 hours](image)

The stoichiometric VO₂ thin film is difficult to synthesize because of its many different valences, so controlling valence is the key issue to prepare thermochromic VO₂ thin film. We obtained vanadium(IV) oxide thin films through controlling temperature, time and pressure of the annealing. The detailed thermodynamic calculation has been done in the previous work[13] and results show that V₂O₅ will decompose to VO₂ when the annealing temperature reaches 550 °C at the atmospheric pressure of less than 0.06 Pa. In this paper, the orange red high valence precursor film was initially synthesized by aqueous sol-gel process, and then under 0.05 Pa vacuum at 550 °C for 10 hours the precursor film was reduced to black blue vanadium(IV) oxide film. The Raman spectra of the precursor film and the film after annealing are shown in Fig.1. The Raman spectra of the precursor film (Fig.1(a)) shows bands at 992.2, 698.6, 523.2, 478.1, 401.6, 300.3, 280.2 and 140.3 cm⁻¹, which correspond to the bands of V₂O₅ thin film reported by T D Manning et al[14]. The Raman spectra of the annealed film (Fig.1(b)) shows bands at 612.8, 381.3, 342.3, 301.9, 218.6 and 188.8 cm⁻¹, which correspond