Structure and optical properties of VO$_2$ film derived from a low temperature sol-gel and facile thermal process

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A novel process was developed for preparing thermochromic VO$_2$ film on commercial float glass by a low temperature V$_2$O$_5$ sol-gel method combined with a facile thermal reduction technique. The structure and optical properties of the films were determined by X-ray diffraction (XRD), Scanning Probe Microscopy (SPM), ultraviolet-visible (UV-Vis) spectroscopy and infrared (IR) spectroscopy. The as-prepared coating glass has larger transmittances at 343K than 293K from 717nm to 900nm, smaller transmittances at 343K than 293K from 2500nm to 4450nm. Through the thermochromic VO$_2$ film the maximum transmittance difference between 343K and 293K is up to 50% in infrared wavelength.

1. Introduction

Vanadium dioxide undergoes a reversible semiconductor-to-metal (S–M) transition at approximately 341K [1]. Substantial changes in optical transmittance and electrical conductivity are observed as the changes from semiconductor to metal. Practical applications include energy-efficient windows [2-5] and optical or electrical switching elements [6-8]. Deposition techniques for VO$_2$ films include sputtering [9-12], evaporation [13,14], pulsed laser deposition [15], Chemical vapor deposition [16,17], liquid-phase deposition [18], and sol–gel techniques [19-27]. The sol can be prepared by an alkoxide [19-21], an oxyacetylacetone [22] and an aqueous precursor [23-27]. The sol–gel technique is potentially the most practical for coating large area substrates. The inorganic aqueous sol–gel method was found to produce films of comparable quality to the alkoxide method without using an expensive precursor and a dry atmosphere during coating. The previous researches on inorganic aqueous sol for VO$_2$ films were mostly by melting V$_2$O$_5$ and quenching it in distilled water, the substrate sides involved were specific ones for filming, and the subsequent thermal processing needed a long period of time. In this paper a facile method to prepare inorganic aqueous sol and VO$_2$ crystallite film on commercial float glass was developed, and the optical transmittance of the coating glass at above and below VO$_2$ phase transition temperature were determined. This work contributed a simple method and basic parameters to the practical application of VO$_2$ material in smart and energy-efficient window.

2. Experimental

The inorganic aqueous sol was prepared by mixing vanadium pentoxide (V$_2$O$_5$, 99.5%) and Hydrogen peroxide solution (H$_2$O$_2$, 30%) with a ratio of 1g to 50ml at 273.15K under magnetic stirring. The deposition was carried out by dip coating on a commercial float glass substrate (50×20×2mm). The deposited glass was placed into a tube furnace, after the temperature reached 800K, a mixture flow of NH$_3$ (5 ml/min) and N$_2$ (110 ml/min) was passed through the furnace for 2 h[28], then the furnace was naturally cooled to 500 K and the VO$_2$ crystallite film was formed on the glass surface.

The structure of the film was determined by using a D/max-2400 X-ray diffractometer (Rigaku, Japan) in a reflection mode with Cu Ka (l = 0.154 nm) radiation and a graphite monochromator. The 2θ scanning rate was 4°/min. The surface and grain size of the films were inspected by a Scanning Probe Microscope (CSPM5000 of Being Nano-Instruments Ltd, China) at the mode of AFM. In-situ UV-visible spectra were recorded on a spectrophotometer (UV-2450, Shimadzu, Japan) connected to a temperature-control apparatus. In-situ IR spectra were measured by a spectrometer (AVATAR370, Thermo Nicolet, America) equipped with a temperature-control apparatus.

3. Results and discussion

The glass surface was yellow after dip coating and became blue after thermal reduction. The XRD patterns of the coating glass were shown in Fig.1. The XRD pattern A has no notable peaks and it means that the film is amorphous structure before thermal reduction. The XRD pattern B has two diffraction peaks and it indicates that the crystal species appear in the film after thermal reduction. By comparing with standard JCPDS card of XRD data documents, The peak at 28° matches up to the crystal planes (011) of monoclinic VO$_2$ (PDF ID number

43-1051). It indicates that the (011) peak is the preferred orientations of VO_2 crystallites in the film. The peak at 40-44° is perhaps from VO (PDF ID number 75-0048) which gives strong diffraction peak (200) within 40-44°[29]. Fig. 1 showed that the peaks are relatively broad. It could be due to the presence of nanostructural defects and impurities. The AFM image of the film was shown in Fig.2. The grain analysis results reported that the average radius of grains is 154nm and the average height is 14nm.
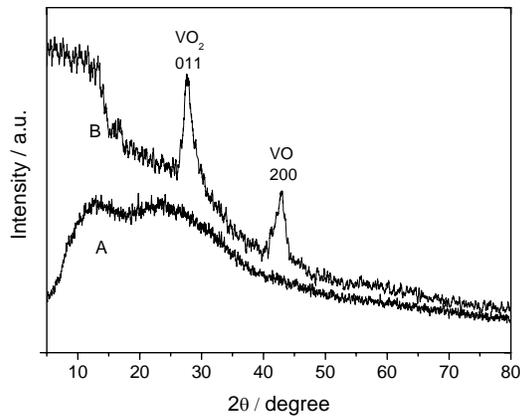
Fig.1. XRD diffraction patterns of the coating glass. A) before thermal reduction; B) after thermal reduction.
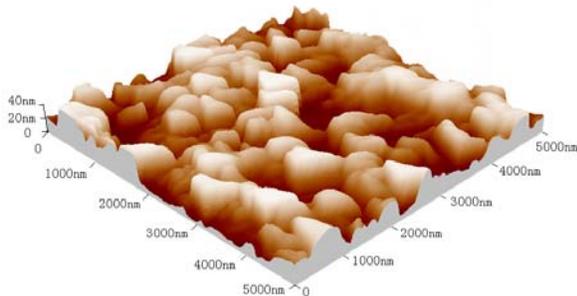
Fig. 2. AFM image of the VO_2 crystallite film.

UV-visible spectra of the raw and coating glasses were shown in Fig.3. It is indicated that the coating glass has larger transmittances at 343K than 293K between 310nm and 717nm, and smaller transmittances at 343K than 293K between 717nm and 900nm. Recently the above change between visible and near infrared light was also described by Dejene at al [30]. Moreover, the film substantially lowered the transmittances of the glass from more than 83% to smaller than 51% in visible wavelength. IR spectra of the raw and coating glasses were shown in Fig.4. In IR spectra the coating glass has smaller transmittances at 343K than 293K between wave number $2200cm^{-1}$ and $4000cm^{-1}$(4450nm and 2500nm), and from wave number $3700cm^{-1}$ to $4000cm^{-1}$(2700nm to 2500nm) the transmittance difference between 343K and 293K is about 20%. This result indicates that the thermochromic VO_2 film was successfully prepared on the commercial float glass. It should be noted that the raw (uncoating)

glass has the transmittance smaller than 40% in infrared wavelength, and the transmittance of the coating glass was the product of the transmittance percentage of the raw glass and that of the film. Therefore, the function of the as-prepared VO_2 crystallite film on controlling infrared light transmittance is more remarkable than that shown in Fig.4. The maximum transmittance difference of the film at 343K and 293K could be deduced and it reached up to 50% from 2500nm to 2700nm. The calculated transmittances T(%) were shown in Table 1.

Table 1. Maximum transmittance differences of the coating glass and film.

Glass T_G(%)	Film T_F(%)	The Coating Glass T_{CG}(%)= T_G(%)×T_F(%)
40	62.5	25
40	12.5	5
Differences	50%	20%
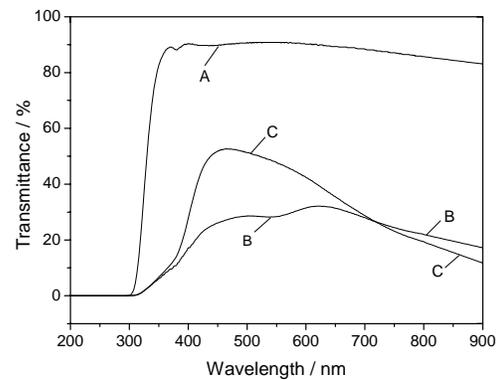
Fig. 3. UV-visible spectra. A) the raw glass at both 293K and 343K; B) the glass with VO_2 crystallite film at 293K; C) the glass with VO_2 crystallite film at 343K.
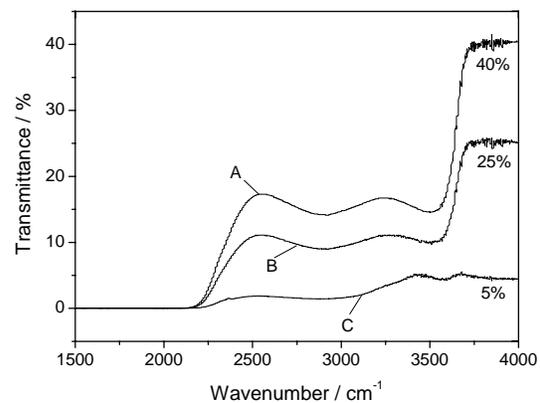
Fig. 4. IR spectra. (a) the raw glass at both 293K and 343K; (b) the glass with VO_2 crystallite film at 293K; (c) the glass with VO_2 crystallite film at 343K.

The repeated determinations proved that the thermochromic properties of as-prepared VO_2 films are reversible. As described the process of preparing thermochromic VO_2 film is easy, with short period and low cost. Therefore the VO_2 films derived from the low temperature sol-gel and facile thermal process have a great potential to be applied in smart and energy-efficient window.

4. Conclusions

A facile method was developed for preparing thermochromic VO_2 film on commercial glass by a low temperature inorganic sol-gel and thermal reduction process. The experimental results indicated that the present process is a convenient and efficient approach to synthesize VO_2 crystallite film on glass. The product glass with VO_2 film has been found with larger transmittances at 343K than 293K in the visible wavelength from 717nm to 900nm, smaller transmittances at 343K than 293K in the infrared wavelength from 2500nm to 4450nm. The transmittance difference of the coating glass between 343K and 293K is about 20% in infrared wavelength from 2500nm to 2700nm, and that of the thermochromic VO_2 film reaches up to 50%. In addition the transmittances of the coating glass are lower than 51% in visible wavelength and need to be improved for the practical application in energy-efficient window. The phase transition temperature of VO_2 film and the film surface roughness need to be investigated and adjusted further according to the practical application requirements.

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