Effects of substrate materials on the structure and electrical property of thermochromic VO_2 film

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VO_2 films were prepared on silicate glass, mica and quartz substrates respectively with the sol-gel method and subsequent spin coating technique. It was found that the substrates could significantly affect the film's structure and property. The film on quartz substrate had the highest purity and the best crystallinity, and that on glass substrate followed. For all prepared films, the resistivity was temperature dependent, and the heating and cooling curves formed a hysteresis loop. The resistivity of quartz film at the room temperature was about 7 times that of mica film, and about 14 times that of glass film. During the heating process, the phase transition points of the films on silicate glass, mica and quartz substrates were 67℃, 68℃ and 64℃, and their resistivity mutations were about 2.1, 3.0 and 2.5 orders of the magnitude respectively.

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1. Introduction

Vanadium oxides usually form a complicated phase diagram because of the multivalent vanadium ion (such as V^{2+},V^{3+},V^{4+} and V^{5+}) and a wide range of ordered point defects, which can produce Magnaé Li phases such as V_nO_{2n-1} ($3 \leqslant n \leqslant 9$) [1-3]. Compared with other metallic compounds with phase transition, the phase transition of vanadium dioxide (VO_2) occurs at 68℃, which is the nearest to room temperature [4]. The nature of this transition is related to the crystal structure transformation from monoclinic to tetragonal system. During the thermochromic phase transition, VO_2 exhibits large changes in the infrared transmittance and the electromagnetic property [5]. Normally, VO_2 film is optically transparent below the transition temperature and is reflective at higher temperatures. In particular, the transmission for wavelengths up to several micrometers can range from more than 70% in the insulator state to less than 1% in the metallic phase. Besides, such a phase transition is also accompanied with a jump of electrical conductivity. Due to these unique optical and electrical properties, VO_2 film has a wide variety of potential applications such as thermal switches, thermal resistors, electrical and optical switches [6-8], and energy-efficient smart windows for buildings [9].

A great number of methods have been applied to prepare VO_2 film, such as RF magnetron sputtering [10, 11], pulsed laser deposition (PLD), sol-gel method [12], and chemical vapor deposition (CVD) [13]. The sol–gel method is a very nice and promising choice for industry production because of its obvious advantages including short reactive time, low annealing temperature, and low cost. In the sol-gel method, the selection of precursor is so crucial for film growth that the stability and low toxicity of precursor should be carefully considered [14].

In order to improve the electrical property of VO_2 film, the effects of substrate materials, such as silicate glass, mica and quartz glass, on the film's structure and property are investigated in this paper, and the film will be prepared with the sol-gel method and subsequent spin coating technique.

2. Experiment procedure

2.1. Preparation of VO_2 film

Firstly, analytically pure (AR) vanadium (IV) - oxy acetylacetonate was dissolved into excessive methanol. Then, the mixture was agitated continuously with a magnetic stirrer to obtain a uniform solution. Thirdly, the solution was filtered with 0.2 μm injection filter to remove tiny insoluble particles that might cause pollution. Afterwards, the concentration of vanadium was adjusted to 0.2 mol/L by volatilizing methanol. The precursor solution was aged for a week at room temperature before the spin coating.

The silicate glass, mica and quartz glass were chosen as substrates. All the substrates were ultrasonically cleaned with detergent and ethanol in an ultrasonic bath for 20 min. After the two-step cleaning, the substrates were dried in oven, and VO_2 film was prepared on the substrates by the spin coating technique. After coating, the film was dried at 80℃ for 25 min. This spin coating process was repeated five times to increase the film thickness. Afterwards, the film was annealed at 550℃ in a nitrogen atmosphere (the purity > 99.99%) for 60 min.

2.2. Characterization

The crystal structure was characterized by X-ray diffraction (XRD) on a Rigaku D/MAX-2500 diffractometer in the reflection mode with Cu Kα (λ = 0.154 nm) radiation. The surface morphology of the film was observed by a Hitachi S-4800 field emission scanning electron microscope (FE-SEM). The electrical property of the film was tested with the standard four point probe technique.

3. Results and discussion

3.1. Structural characterization

Fig. 1 shows the XRD patterns of the films on different substrates. For convenience, the film on silicate glass is named as "the glass film", the one on mica as "the mica film", and the one on quartz glass as "the quartz film". From Fig. 1, there are two strong peaks at 27.88 º and at 57.62 º in the XRD pattern of the quartz film, which correspond to (011) and (022) crystal planes of VO_2 monoclinic phase respectively. The large broad peak in the quartz film curve indicates that SiO_2 is in an amorphous state. However, in the XRD pattern of the mica film, there are three strong peaks at 17.87 °, 26.86 ° and 45.65 °, which can be indexed to (011) plane of the transparent mica, and a small peak at 27.88 º, which can be indexed to (011) plane of VO_2 monoclinic phase. It is noticed that the mica is in a crystalline state itself, so that the peak of VO_2 (M) is not so strong. For the glass film, there is one strong peak at 27.88 º and three weak peaks at 36.96 °, 42.08 ° and 55.48 ° in the XRD pattern, which can be indexed to (011), (21-1), (21-2) and (220) planes of VO_2 monoclinic phase respectively. Another tiny peak at 57.56 ° may correspond to the formation of a little NaV_6O_{11} phase. This may result from the entry of a few number of sodium ions into the VO_2 crystal lattice.

To sum up, VO_2 (M) film of high purity can be prepared on all the three substrates. Specially, the quartz film has the highest purity and the best crystallinity, and the glass film is at the second place.

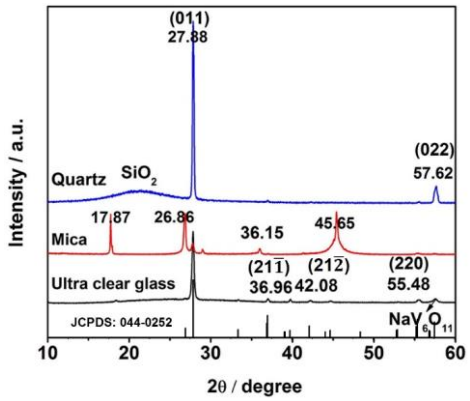

Fig. 1. XRD patterns of the films on different substrate materials

3.2. Surface morphology

Fig. 2 presents the surface morphologies of the films. It can be seen that all the films consisted of round particles. In Fig. 2(a), the size of the particles is rather large (about 100~300 nm) and well-distributed, but there are a lot of voids on the film. In contrast, the particles in the quartz film are very fine (about 50~100 nm), and they are piled up compactly. For the mica film, its particle size is rather uneven from 50 to 200 nm, and there are also a lot of voids.

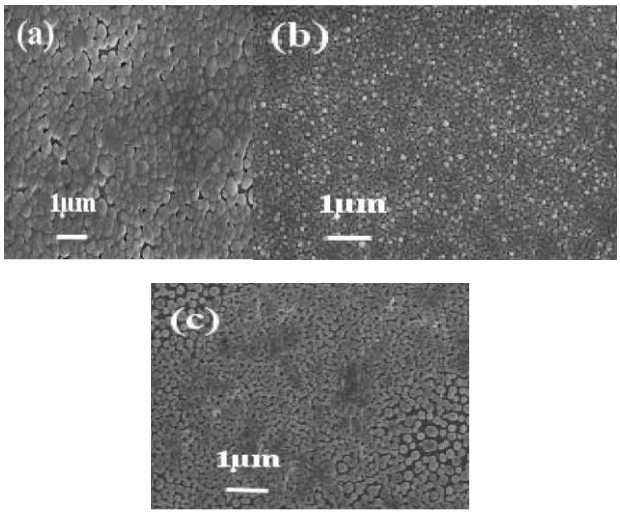

Fig. 2. Surface morphologies of the films on different substrate materials: (a) the glass film; (b) the quartz film; (c) the mica film

3.3. Electrical property

Fig. 3 shows the dependence of electrical resistivity on temperature for the glass film. From room temperature to 67℃, the resistivity of the film decreases slowly, with a slope of about 0.77 KΩ/℃. Once the temperature exceeds 67℃, the slope turns to be about 8.93 KΩ/℃. Therefore, it can be determined that the phase transition point is 67℃ in the heating process. However, when the temperature is over 70℃, the electrical resistivity keeps almost a constant of about 0.2 KΩ. On the other hand, in the cooling process, till the temperature decreases to 60℃, the electrical resistivity begins to rise acutely at a slope of about 5.9 KΩ/℃, and then it increases with a slope of about 0.93 KΩ/℃. Therefore, it is determined that the phase transition point is 60℃ in the cooling process.

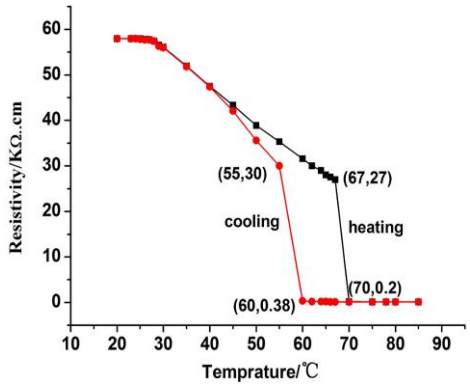

Fig. 3. Resistivity-temperature relationship of VO_2 (M) film prepared on the silicate glass

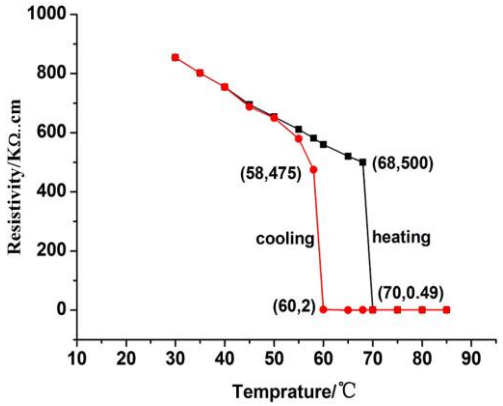

Fig. 4. Resistivity-temperature relationship of VO_2 (M) film prepared on the quartz substrate

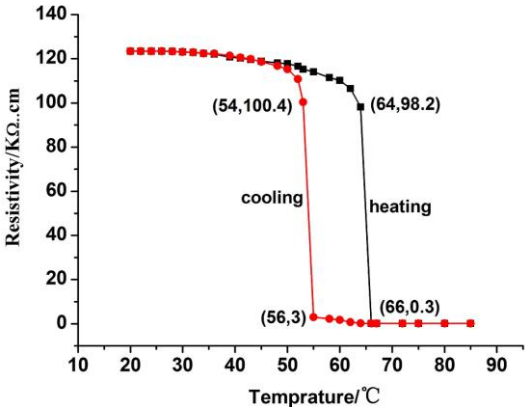

Fig. 5. Resistivity-temperature relationship of VO_2 (M) film prepared on the mica substrate

It is noticed that the heating curve and the cooling curve form a thermally induced hysteresis loop. The difference between the heating transition point and the cooling transition point, named as the hysteresis width, is 7℃, and the mutation is about 2.1 orders of magnitude.

Fig. 4 shows the temperature dependence of the resistivity for the quartz film. Similarly, the resistivity falls slowly before 68℃, with a slope of 9.3 KΩ/℃; when the temperature is over 68℃, the slope increases to 249.7 KΩ/℃. However, as the temperature further increases, the electrical resistance keeps almost a constant of 0.49 KΩ. Therefore, it is determined that the phase transition point is 68℃ in the heating process. On the other hand, in the cooling process, before the temperature falls to 60℃, the electrical resistivity rises *very slowly with a slope of 0.151 KΩ/℃; after that, the electrical resistivity rises* rapidly with a slope of about 236.5 KΩ/℃, and then it increases with a slope of about 12.7 KΩ/℃. Therefore, it is determined that the phase transition point is 60℃ in the cooling process. The heating curve and the cooling curve also form a thermally induced hysteresis loop. The hysteresis width is 8℃, and the mutation is about 3.0 orders of magnitude.

The temperature dependence of the resistivity for the mica film is also similar to that for the glass film. As Fig. 5 shows, the resistivity of the mica film decreases slowly with the increase of temperature from room temperature to 64℃, and then decreases rapidly with a slope of 48.95 KΩ/℃. Once the temperature exceeds 66℃, it almost keeps a constant of about 0.3 KΩ. Therefore, it is determined that the phase transition point is 66℃ in the heating process. Conversely, when the temperature decreases to 56℃, the film resistivity begins to increase acutely with a slope of about 32.5 KΩ/℃. Thus, it can be determined that the phase transition point is 56℃ in the cooling process. The hysteresis width is 10℃, and the mutation is about 2.5 orders of magnitude.

Although the above three loops are similar, there are also obvious differences among them. Firstly, the resistivity of the quartz film at room temperature is about 7 times that of the mica film, and about 14 times that of the glass film. Secondly, for the heating process curves, the phase transition points of the films prepared on silicate glass, quartz and mica are 67℃, 68℃ and 64℃ respectively, and their maximum slopes are 8.93 KΩ/℃, 249.7 KΩ/℃and 48.95 KΩ/℃ respectively. Thirdly, their mutations are about 2.1, 3.0 and 2.5 orders of magnitude, and their hysteresis widths are 7℃, 8℃ and 10℃, respectively.

It is worth noting that the resistivity of the glass film at room temperature is only about one seventh that of the mica film, and one fourteenth that of the quartz film. As Fig. 1 shows, there is a little NaV_6O_{11} phase in the glass film, demonstrating that a few number of sodium ions of the ultra-glass enter into the VO_2 crystal lattice. Sodium ions have very small radius, and are prone to playing the role of carriers. Therefore, the carrier concentration in the VO_2 film can be increased a great deal, which leads to the decrease of the glass film resistivity. On the other hand, Fig. 2 shows that the particles in the quartz film are very

fine, about 50~100 nm, which is far below that of the other two. Since the VO_2 film is a polycrystalline film composed of many grains, the grain boundary scattering is one of the key factors influencing the resistivity. The finer the grains are, the more the grain boundaries, and the stronger the scattering, thereby leading to the higher resistivity of the film. Moreover, if the average size of the grains, *d*, is close to the mean path of the carriers, λ, then λ is subjected to *d*; small λ can result in the increase of the film resistivity.

Finally, although there is a great difference among the resistivity of the three films at room temperature, this difference almost disappears when the temperature exceeds their phase transition point. This phenomenon results in the large difference of their mutations. Among the three films, the phase transition point of the mica film is 64℃, below that of the others. This may be due to that the mica is in a polycrystalline state itself, and can contribute to the nucleation of VO_2 film.

4. Conclusions

In summary, VO_2 film was prepared with the sol-gel method and subsequent spin coating technique, and the effects of substrate materials on its structure, morphology and electrical property were investigated. Some conclusions can be drawn as follows:

(1) VO_2 (M) film of high purity can be prepared on the silicate glass, the quartz glass and the mica. Among these films, the quartz film has the highest purity and the best crystallinity, and the glass film is at the second place.

(2) The films on different substrates consisted of round particles. The particles in the quartz film have a diameter of about 50~100 nm, and are piled up compactly.

(3) The resistivity of all the three films is temperature dependent, and the heating and cooling curves can form a thermally induced hysteresis loop. However, the substrate can affect the film resistivity at room temperature, the resistivity mutation, the phase transition point both in the heating process and the cooling one, as well as the hysteresis width. The resistivity of the quartz film at room temperature is about 7 times that of the mica film, and about 14 times that of the glass film. For the heating process curves, the phase transition points of the films prepared on silicate glass, quartz and mica are 67℃, 68℃ and 64℃ respectively. Their mutations are about 2.1, 3.0 and 2.5 orders of magnitude, and their hysteresis widths are 7℃, 8℃ and 10℃ respectively.

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