

Effects of TiO₂ Interlayers on the Optical Switching of VO₂ Thin Films Grown by Sol-Gel Process

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Abstract: Thermochromic VO₂ and V_xW_{1-x}O₂ films were deposited on TiO₂/mica substrates. The TiO₂/mica substrates were fabricated *via* Sol-Gel process, and the hydrophilicity of the TiO₂/mica substrate was improved under UV light irradiated. The V₂O₅ sol was deposited on the TiO₂/mica substrate by the spin coating method, and then it was annealed. SEM and XRD analysis were applied to analyze the morphology, phases and microstructure of the films. FTIR was used to study the thermochromic properties. The results suggest that VO₂/TiO₂ grow preferentially along single orientation. V_xW_{1-x}O₂/TiO₂ composite film is impossible to fabricate single orientation films. TiO₂ interlayers are favorable to compact the VO₂ thin films and reduce the transition temperature. It will make the hysteresis width of V_xW_{1-x}O₂/TiO₂ composite film reduce to about 4°C particularly.

Key words: vanadium dioxide film; composite film; Sol-Gel method; photo-hydrophilicity; thermochromism

Many vanadium oxides compounds (such as V₂O₃, V₂O₅, VO, VO₂, V₆O₁₃) undergo insulator to metal-phase transitions^[1-2]. Among these, VO₂ is one of the most attractive oxides due to its first-order metal-insulator transition at 68°C closing to the room temperature and its sharp insulator to metal transition. Below 68°C, VO₂ has a monoclinic structure with the P21/c space group. And above the phase transition temperature, it is turn to a tetragonal lattice with the P42/mnm rutile space group. Various deposition techniques have been used to fabricate VO₂ film such as magnetron sputtering deposition^[3], pulsed laser deposition, ion implantation. However, the complex fabrication method and expensive equipment limit the application of VO₂ film in many field, especially in the fabrication of double-layered VO₂ films^[4].

Recently, preparation and performance research of composite films has become hotspot. Qureshi^[5] suggested that TiO₂/VO₂ composite films fabricated by APCVD exhibited thermochromic switching temperature decreasing obviously. The VO₂/ZnO nanostructure composite films can significantly reduce the phase transition temperature and narrow the width of thermal hysteresis^[6]. TiO₂/VO₂/TiO₂ sandwich structure film could improve the transmittance and efficiently decrease the reflection in visible region^[7]. The TiO₂ buffer layer could enhance the oxidation durability of the VO₂/TiO₂/fused quartz film^[8].

Some interlayer could cause internal stresses at the interfaces. And also, it could make the epitaxial films grow to a different orientation. The transition temperature (T_t) is correlated with the change of substrate orientation^[9], and the epitaxial stress^[10-11]. Furthermore, although the properties of VO₂/TiO₂ thin films have been studied, there are much less reports on doping VO₂/TiO₂ thin films, only a few researches involved.

In this study, VO₂ thin films were grown by means of UV light hydrophilicity on TiO₂/mica substrate. Though UV light-induced hydrophilicity of TiO₂ layer has been widely used for self-cleaning and anticontamination technologies, it has not been used in fabricating VO₂ thin film. To our knowledge, this is the first report on growth of vanadium oxide using light-induced hydrophilicity in treatment of the TiO₂/mica substrates. Furthermore, it will improve the homogeneity of inorganic V₂O₅ sol filmed on some bad hydrophilicity substrate utilizing TiO₂ film as interlayer. It is possible to expand the applied range of forming film by means of inorganic V₂O₅ sol in the future.

1 Experiment

1.1 VO₂/TiO₂ composite films Preparation

VO₂/TiO₂ composite films on muscovite substrate were prepared by the inorganic Sol-Gel method. Acetylacetone,

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ethyl alcohol and butyl titanate were mixed at a volume ratio of 5:120:16 to obtain mixture A. Deionized water and ethyl alcohol were mixed at a volume ratio of 1:50, and then stoichiometric nitric acid was added to the above solution to obtain mixture B. In order to maintain the sol transparent and uniform, the pH value was controlled in the range of 3–4 by pouring mixture B to A. Under vigorous stirring conditions for 30 min, the TiO_2 precursor was kept in brown glass container.

The muscovite slice was cleaned in HCl and $\text{NH}_3 \cdot \text{H}_2\text{O}$ solution to remove the contamination, then it was washed with anhydrous alcohol and dried under a stream of nitrogen. The TiO_2 precursor films were coated on the clean mica substrate by dip coating process, and then the films were dried in air. The dip coating process was repeated at a speed of 1 mm/s to control the thickness, the films were then annealed at 510°C in ambient air for 1 h.

To get a uniform V_2O_5 thin film by spin-coating, we should make the TiO_2 /mica substrate hydrophilic for the water-soluble VO_2 sol. Otherwise the centrifuging VO_2 sol could shrink quickly and hardly to form a film. The TiO_2 /mica substrate was put under the UV light for 40 min to own good hydrophilicity.

V_2O_5 sol was fabricated using the inorganic Sol-Gel method^[12-13]: 5.0 g V_2O_5 (stoichiometric V_2O_5 and WO_3 mixture) powder was heated to 800°C in a crucible for 30 min, and then poured into 300 mL deionized water at room temperature. After vigorous stirring for 2 h, deep brownish sols were obtained. After the hydrophilic TiO_2 /mica substrate was achieved, V_2O_5 film was deposited on TiO_2 /mica substrate by spin-coating (KW-4A) at 1200 r/min for 15 s and dried in the oven at 60°C for 15 min to remove the residual moisture. Then the VO_2/TiO_2 /mica film were annealed at 500°C for 1.5 h in a nitrogen atmosphere.

1.2 Characterization

The contact angle of the TiO_2 /mica substrate was measured using Video-based, contact angle measuring device (Dataphysics, Germany). The crystalline structure of the TiO_2 substrate and the obtained double-layered film was identified by X-ray diffractometry (XRD, χ' Pert Philips) with $\text{Cu K}\alpha$ ($\lambda=0.15406$ nm) radiation at a grazing angle of 2° . The film morphology was analyzed using a scanning electron microscope (SEM S-4800, Hitachi). The thermochromic properties of the VO_2/TiO_2 double-layered film were measured using a Tensor 27 (Bruker, Germany) in transmission mode, which equipped with a controllable heating system.

2 Results and Discussion

2.1 Properties of TiO_2 /mica substrate

Figure 1 shows the SEM image of the TiO_2 /mica sub-

strate. The film surface was microstructurally homogenous, with mesoporous, and the grains are in the size range of 20–50 nm. Figure 2 shows the contact angle evolution with UV irradiation time for the TiO_2 /mica substrate. The TiO_2 /mica substrate without UV light irradiation has bad hydrophilicity and the contact angle is about 108.0° . When the UV light irradiated the TiO_2 /mica surface, the contact angle decreased obviously. After putting TiO_2 /mica substrates under UV light for 40 min, the contact angle went down from 108.0° to 8.9° . The results showed that the contact angle of the TiO_2 /mica substrate decreased and the hydrophilicity of the film significantly enhanced with exposing time to UV light. And it is beneficial to the next experiment of coating VO_2 sol film on the TiO_2 /mica substrate.

When the TiO_2 /mica substrates is irradiated by UV light with $\lambda < 380$ nm, an electron is transferred from capacity band to conduction band. Therefore a pairs of electrons and oxidizing holes created on the surface of TiO_2 film. The photogenerated electrons tend to reduce the Ti(IV) cations to the Ti(III) state, and the holes oxidize O^{2-} anions. In this process, the oxygen atoms ejected, creating a group of oxygen vacancies. The water molecules in the environment can occupy these oxygen vacancies, and produce the absorbed OH^- groups on the surface, which increases the hydrophilicity of the TiO_2 film surface^[14-15]. On the

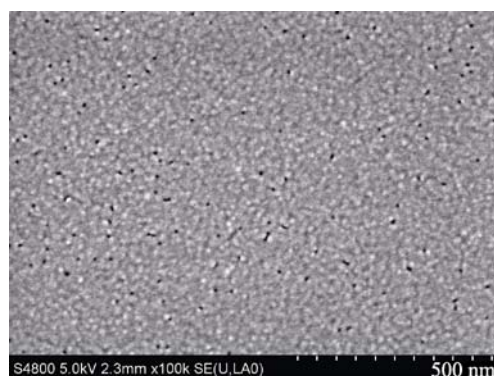


Fig. 1 SEM image of TiO_2 /mica substrate surface

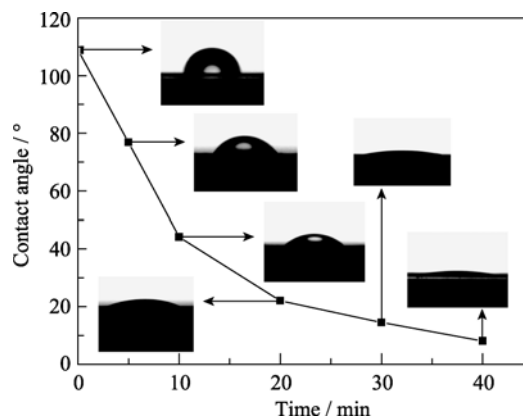


Fig. 2 Contact angle of TiO_2 /mica substrate with UV irradiation time

other hand, the porous TiO₂ thin films have big surface-area and effect of capillary^[16-17], suggesting that the structure of the porous TiO₂ layer leads to more efficient liquid spreading.

2.2 X-ray diffraction

Figure 3(a) shows the XRD patterns of the VO₂/TiO₂ and V_xW_{1-x}O₂/TiO₂ composite films grown on mica substrates, and VO₂/mica for comparison. It can be seen that all the three samples exhibited a single-phase M phase structure. All the XRD patterns have obvious backgrounds from muscovite substrates. And no reflections due to titanium dioxide are observed. Figure 3(b) shows the enlarged patterns for the peaks (011) of three samples. The VO₂/TiO₂ and VO₂ films showed the excellent single orientation. Although the (011) peak of V_xW_{1-x}O₂/TiO₂ composite film is strong, orientations of (013) and ($\bar{2}$ 31) are observed. The details suggest that the W doped VO₂ film depositing on the TiO₂/mica substrate is apt to form multi-orientation. Further studies are needed to explain this experimental phenomenon.

Calculations from XRD patterns using the interplanar distance equation for VO₂ monoclinic lattice(summarized

in table 1.):

$$\frac{1}{d^2} = \frac{h^2}{a^2 \sin^2 \beta} + \frac{k^2}{b^2} + \frac{l^2}{c^2 \sin^2 \beta} - \frac{2lh \cos \beta}{ca \sin^2 \beta}$$

However, it is narrow that the full width at half-maximum (FWHM) of the VO₂ with TiO₂ interlayer at (011) peak, implying slightly better crystallinity of the VO₂/TiO₂/mica film compared to the VO₂/mica film.

2.3 SEM

Typical SEM images of the thin films annealed were shown in Fig.4. The results indicate that the TiO₂ films as interlayer have the important influence on the microstructure images of the VO₂ thin films. Compared with the VO₂ thin film without TiO₂ interlayer (Fig. 4(c)), all of the composite thin films obtained consist of irregular particles and long rod particles. The average spherical grain size of the VO₂/TiO₂/mica film is between 150–300 nm(Fig. 4(b)). The largest dimension of the rod-like particles is between 1–3 μ m. The particles are surrounded by the poros existed independently.

SEM (Fig. 4(a)) observation indicate that the surface of the V_xW_{1-x}O₂/TiO₂ composite film have spherical particles and rod-like particles. The structures are made up of homogeneous connected grains with a range from 50–250 nm. The rod-like particles exhibit compact within a range of 1.5–3 μ m. The VO₂ film without TiO₂ interlayer showed connected and uniform particles formed on the surface. And the rod-like particles are not found. This result indicate that the TiO₂ interlayer have influence on the growth morphology, which promoted priority growth at one orientation of some of the VO₂ particle. It could be explained by the influence of TiO₂ interlayer, which causes the stress exist in the interface. This could make the VO₂ film grow to multi-orientation. The addition of W depressed the growth of VO₂ grain size due to the heterogeneous nucleation mechanism during annealing^[18].

2.4 FT-IR

Figure 5 (a, b, c) show the temperature evolution of the IR transmittance of the samples (I -III). The $d(T_t)/d(T)-T$ curves(Fig. 5a',b',c') of all the samples have been complied with Gaussian distributions by Origin 7.5 software.

The phase-transition temperature (T_t) is commonly about 65°C in the sample II and III. Experiment results show that the T_t of undoped single-layered VO₂ film was 67.8°C(Fig. 5(c)). The hysteresis loop of transmittance was 9.4°C between the heating and cooling branches. For the VO₂/TiO₂ film (Fig. 5(b)), the T_t slightly decreases to 64.5°C which is lower about 3°C than that for VO₂/mica film, and the hysteresis widths decrease to 7.1°C. Figure 5(a) shows the V_xW_{1-x}O₂/TiO₂ composite film T_t is decreased to 53.4°C. A large jump in the IR transmittance is

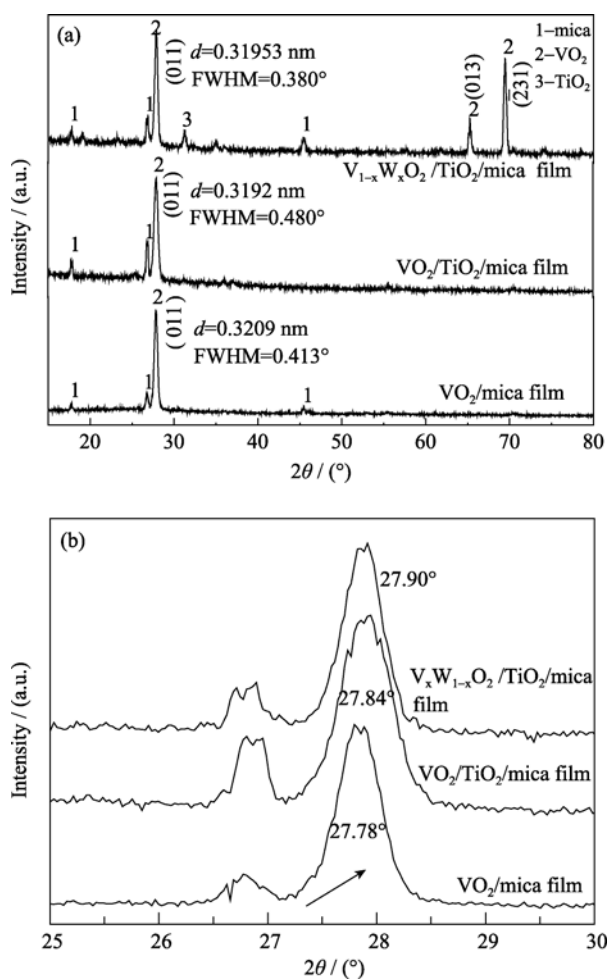


Fig. 3 (a) XRD patterns for three samples; (b) enlarged patterns of the diffraction peaks (011)

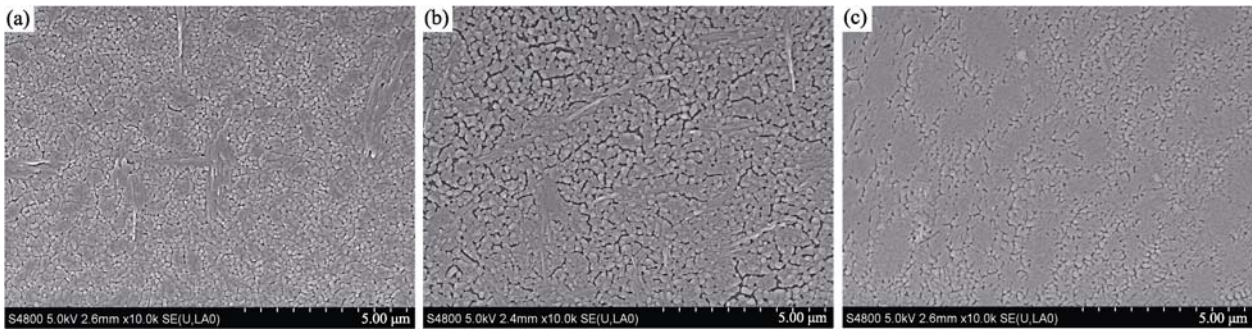


Fig. 4 SEM images of the samples
(a) $V_xW_{1-x}O_2/TiO_2$ composite film; (b) $VO_2/TiO_2/mica$ film; (c) $VO_2/mica$ film

Table 1 Parameters of the lattice and the phase transition in samples (I -III)

Sample	$d(110)/nm$	$2\theta/(^\circ)$	Hysteresis width/ $^\circ C$	$T_{90}/\%$	$T_{40}/\%$	$T_{\Delta T}/T_{40}$
(I) $V_xW_{1-x}O_2/TiO_2$ film	0.31953	27.90	7.1	75.6	10.5	92.3%
(II) $VO_2/TiO_2/mica$ film	0.31920	27.84	4.8	70.5	5.6	92.0%
(III) $VO_2/mica$ film	0.32090	27.78	9.4	66.3	4.2	93.7%

^a T_{90} and T_{40} refer to the transmittance measured at 2.5 μm wavelength at 90 and 40 $^\circ C$, and $T_{\Delta T}=T_{90}-T_{40}$

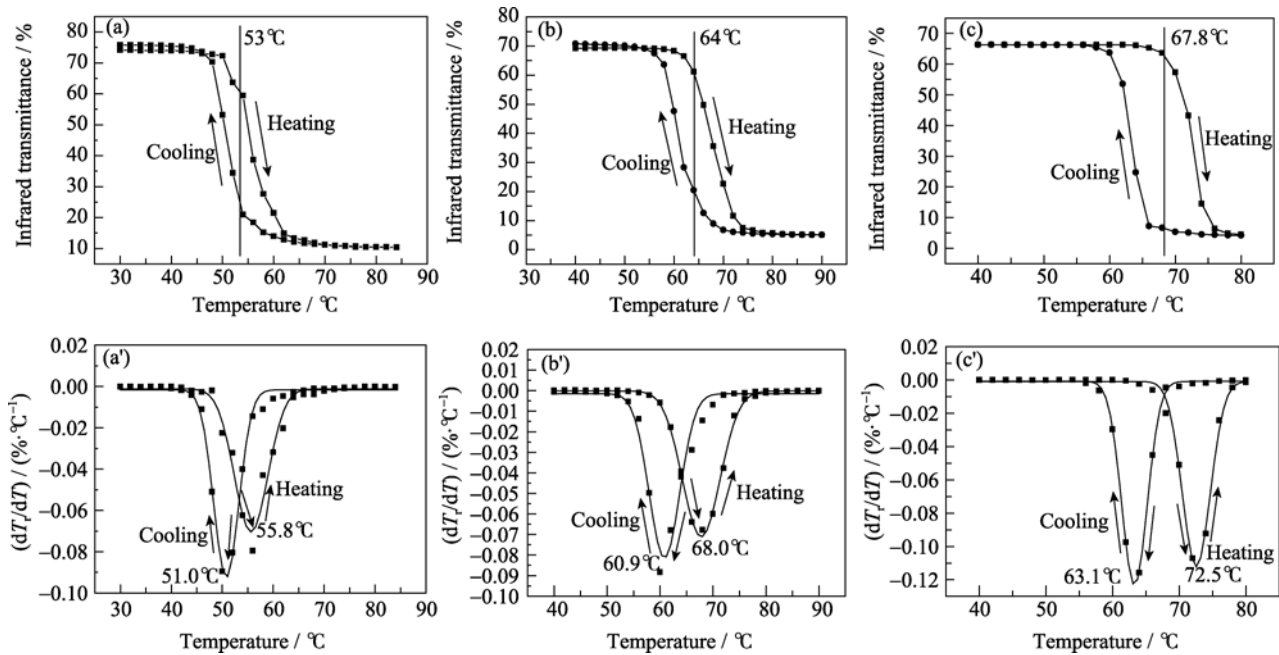


Fig. 5 Hysteresis loops (a), (b), (c) and the corresponding derivative curve (a'),(b'),(c')
(a) (a') $V_xW_{1-x}O_2/TiO_2$ composite film; (b) (b') $VO_2/TiO_2/mica$ film; (c) (c') $VO_2/mica$ film

observed at 51.0 $^\circ C$ cooling and 55.8 $^\circ C$ on heating. And the hysteresis loop of transmittance decreases to 4.8 $^\circ C$. The decreasing of hysteresis width caused by combination of W doped and TiO_2 interlayer make the grains grew heterogeneous and compact. The switching efficiency is all above 90%, showing that the TiO_2 interlayer has high transmittance in infrared range.

It is known that VO_2 has a metal-insulator transition temperature of 68 $^\circ C$ and the structural transition of VO_2 is

accompanied by the metal-insulator transition. The thin film with TiO_2 interlayer has a lower T_t than that without interlayer probably because of the in-plane tensile stress induced by the lattice mismatch between the film surface and substrate^[10-11]. It is different from the previous report^[8] which indicated Ti ion diffused and doped into VO_2 crystalline structure from TiO_2 interlayer, and it would lead to a higher T_t . T_t of $V_xW_{1-x}O_2/TiO_2$ composite film decreases more than other films due to the comprehensive action of tungsten doped and TiO_2 interlayer(Fig. 5(a)). Our results

show that Ti doped into VO₂ film can be suppressed by Sol-Gel method. Furthermore, a large and sharp change in the IR transmittance was observed, indicating the high quality of the thin films.

3 Conclusion

The TiO₂ film as interlayer was prepared by the Sol-Gel method, VO₂ film was fabricated on the TiO₂/mica substrate after UV light irradiate the TiO₂ film. The V_xW_{1-x}O₂/TiO₂ composite film has a smaller and compacter grain size compared to the undoped film, as shown in the SEM photos. The VO₂/TiO₂/mica film with good crystallinity showed in the XRD. W-doped VO₂ film depositing on the TiO₂/mica substrate was apt to form multi-orientation. The hysteresis width became narrow in the VO₂/TiO₂/mica due to the stress existing in the interface. The combination of W doped and TiO₂ interlayer made the hysteresis width narrower.

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TiO₂ 中间层对基于溶胶-凝胶法制备的 VO₂ 薄膜 光学特性的影响

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摘 要: 为了提高 VO₂ 薄膜的热致相变性能, 采用复合结构与掺杂相结合的方法, 首先通过溶胶-凝胶法在云母基底上制备锐钛型 TiO₂ 薄膜, 再在光致亲水性处理的 TiO₂/云母基底上涂覆 V₂O₅ 以及掺钨 V₂O₅ 水溶胶, 然后经热处理获得 VO₂/TiO₂ 及 V_xW_{1-x}O₂/TiO₂ 复合薄膜。采用 X 射线衍射仪(XRD)、场发射扫描电子显微镜(FESEM)、傅立叶变换红外光谱仪(FTIR)研究薄膜的物相、表面形貌以及热致相变特性。结果表明, VO₂/TiO₂ 复合薄膜晶体生长为(011)面择优取向; V_xW_{1-x}O₂/TiO₂ 复合薄膜产生多种取向。TiO₂ 中间层有助于使 VO₂ 薄膜生长致密, 相变温度降低, 更使 V_xW_{1-x}O₂/TiO₂ 复合薄膜滞后温宽降至约 4℃。

关 键 词: 氧化钒薄膜; 复合薄膜; 溶胶-凝胶法; 光致亲水; 热致相变

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