Effects of TiO\textsubscript{2} Interlayers on the Optical Switching of VO\textsubscript{2} Thin Films Grown by Sol-Gel Process

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Abstract: Thermochromic VO\textsubscript{2} and V\textsubscript{x}W\textsubscript{1-x}O\textsubscript{2} films were deposited on TiO\textsubscript{2}/mica substrates. The TiO\textsubscript{2}/mica substrates were fabricated via Sol-Gel process, and the hydrophilicity of the TiO\textsubscript{2}/mica substrate was improved under UV light irradiated. The V\textsubscript{2}O\textsubscript{5} sol was deposited on the TiO\textsubscript{2}/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 VO\textsubscript{2}/TiO\textsubscript{2} grow preferentially along single orientation. V\textsubscript{x}W\textsubscript{1-x}O\textsubscript{2}/TiO\textsubscript{2} composite film is impossible to fabricate single orientation films. TiO\textsubscript{2} interlayers are favorable to compact the VO\textsubscript{2} thin films and reduce the transition temperature. It will make the hysteresis width of V\textsubscript{x}W\textsubscript{1-x}O\textsubscript{2}/TiO\textsubscript{2} composite film reduce to about 4\textdegree C particularly.

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

Many vanadium oxides compounds (such as V\textsubscript{2}O\textsubscript{3}, V\textsubscript{3}O\textsubscript{5}, VO, VO\textsubscript{2}, V\textsubscript{6}O\textsubscript{13}) undergo insulator to metal-phase transitions\textsuperscript{[1-2]}. Among these, VO\textsubscript{2} is one of the most attractive oxides due to its first-order metal-insulator transition at 68\textdegree C closing to the room temperature and its sharp insulator to metal transition. Below 68\textdegree C, VO\textsubscript{2} has a monoclinic structure with the P2\textsubscript{1}/c space group. And above the phase transition temperature, it is turn to a tetragonal lattice with the P4\textsubscript{2}/mm space group. Various deposition techniques have been used to fabricate VO\textsubscript{2} film such as magnetron sputtering deposition\textsuperscript{[3]}, pulsed laser deposition, ion implantation. However, the complex fabrication method and expensive equipment limit the application of VO\textsubscript{2} film in many field, especially in the fabrication of double-layered VO\textsubscript{2} films\textsuperscript{[4]}.

Recently, preparation and performance research of composite films has become hotspot. Qureshi\textsuperscript{[5]} suggested that TiO\textsubscript{2}/VO\textsubscript{2} composite films fabricated by APCVD exhibited thermochromic switching temperature decreasing obviously. The VO\textsubscript{2}/ZnO nanostructure composite films can significantly reduce the phase transition temperature and narrow the width of thermal hysteresis\textsuperscript{[6]}. TiO\textsubscript{2}/VO\textsubscript{2}/TiO\textsubscript{2} sandwich structure film could improve the transmittance and efficiently decrease the reflection in visible region\textsuperscript{[7]}. The TiO\textsubscript{2} buffer layer could enhance the oxidation durability of the VO\textsubscript{2}/TiO\textsubscript{2}/fused quartz film\textsuperscript{[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\textsubscript{t}) is correlated with the change of substrate orientation\textsuperscript{[9]}, and the epitaxial stress\textsuperscript{[10-11]}. Furthermore, although the properties of VO\textsubscript{2}/TiO\textsubscript{2} thin films have been studied, there are much less reports on doping VO\textsubscript{2}/TiO\textsubscript{2} thin films, only a few researches involved.

In this study, VO\textsubscript{2} thin films were grown by means of UV light hydrophilicity on TiO\textsubscript{2}/mica substrate. Though UV light-induced hydrophilicity of TiO\textsubscript{2} layer has been widely used for self-cleaning and anticontamination technologies, it has not been used in fabricating VO\textsubscript{2} thin film. To our knowledge, this is the first report on growth of vanadium oxide using light-induced hydrophilicity in treatment of the TiO\textsubscript{2}/mica substrates. Furthermore, it will improve the homogeneity of inorganic V\textsubscript{2}O\textsubscript{3} sol filmed on some bad hydrophilicity substrate utilizing TiO\textsubscript{2} film as interlayer. It is possible to expand the applied range of forming film by means of inorganic V\textsubscript{2}O\textsubscript{3} sol in the future.

1 Experiment

1.1 VO\textsubscript{2}/TiO\textsubscript{2} composite films Preparation

VO\textsubscript{2}/TiO\textsubscript{2} composite films on muscovite substrate were prepared by the inorganic Sol-Gel method. Acetylacetone,
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 TiO2 precursor was kept in brown glass container.

The muscovite slice was cleaned in HCl and NH3•H2O solution to remove the contamination, then it was washed with anhydrous alcohol and dried under a stream of nitrogen. The TiO2 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℃ in ambient air for 1 h.

To get a uniform V2O5 thin film by spin-coating, we should make the TiO2/mica substrate hydrophilic for the water-soluble VO2 sol. Otherwise the centrifuging VO2 sol could shrink quickly and hardly to form a film. The TiO2/mica substrate was put under the UV light for 40 min to own good hydrophilicity.

V2O5 sol was fabricated using the inorganic Sol-Gel method\[12-13\]: 5.0 g V2O5/(stoichiometric V2O5 and WO2 mixture) powder was heated to 800℃ 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 TiO2/mica substrate was achieved, V2O5 film was deposited on the TiO2/mica substrate by spin-coating (KW-4A) at 1200 r/min for 15 s and dried in the oven at 60℃ for 15 min to remove the residual moisture. Then the VO2/TiO2/mica film were annealed at 500℃ for 1.5 h in a nitrogen atmosphere.

1.2 Characterization

The contact angle of the TiO2/mica substrate was measured using Video-based, contact angle measuring device (Dataphysics, Germany). The crystalline structure of the TiO2 substrate and the obtained double-layered film was identified by X-ray diffractometry (XRD, χ′Pert Philips) with Cu Kα (λ=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 VO2/TiO2 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 TiO2/mica substrate

Figure 1 shows the SEM image of the TiO2/mica sub-
other hand, the porous TiO₂ thin films have big surface-area and effect of capillary\cite{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 VₓW₁₋ₓO₂/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 VₓW₁₋ₓO₂/TiO₂ composite film is strong, orientations of (013) and (2 3 1) 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 interplanner distance equation for VO₂ monocilinic lattice (summarized in table 1):

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

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 μm. The particles are surrounded by the poros existed independently.

SEM (Fig. 4(a)) observation indicate that the surface of the VₓW₁₋ₓO₂/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 μm. The VO₂ film without TiO₂ interlayer showed uniform particles formed on the surface. 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\cite{18}.

### 2.4 FT-IR

Figure 5 (a, b, c) show the temperature evolution of the IR transmittance of the samples (I -III). The $d(T)/d(T)-T$ 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 VₓW₁₋ₓO₂/TiO₂ composite film $T_t$ is decreased to 53.4°C. A large jump in the IR transmittance is...
observed at 51.0°C cooling and 55.8°C on heating. And the hysteresis loop of transmittance decreases to 4.8°C. The decreasing of hysteresis width caused by combination of W doped and TiO₂ interlayer make the grains grow heterogeneous and compact. The switching efficiency is all above 90%, showing that the TiO₂ interlayer has high transmittance in infrared range.

It is known that VO₂ has a metal-insulator transition temperature of 68°C and the structural transition of VO₂ is accompanied by the metal-insulator transition. The thin film with TiO₂ interlayer has a lower Tᵢ 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 VO₂ crystalline structure from TiO₂ interlayer, and it would lead to a higher Tᵢ. Tᵢ of VₓWₓO₂/TiO₂ composite film decreases more than other films due to the comprehensive action of tungsten doped and TiO₂ interlayer(Fig. 5(a)). Our results

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**Fig. 4** SEM images of the samples
(a) VₓWₓO₂/TiO₂ composite film; (b) VO₂/TiO₂/mica film; (c) VO₂/mica film

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

<table>
<thead>
<tr>
<th>Sample</th>
<th>d(110)/nm</th>
<th>2θ(°)</th>
<th>Hysteresis width/°C</th>
<th>T₉₀/%</th>
<th>T₄₀/%</th>
<th>T₉₀-T₄₀</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Ⅰ) VₓWₓO₂/TiO₂ film</td>
<td>0.31953</td>
<td>27.90</td>
<td>7.1</td>
<td>75.6</td>
<td>10.5</td>
<td>92.3%</td>
</tr>
<tr>
<td>(Ⅱ) VO₂/TiO₂/mica film</td>
<td>0.31920</td>
<td>27.84</td>
<td>4.8</td>
<td>70.5</td>
<td>5.6</td>
<td>92.0%</td>
</tr>
<tr>
<td>(Ⅲ) VO₂/mica film</td>
<td>0.32090</td>
<td>27.78</td>
<td>9.4</td>
<td>66.3</td>
<td>4.2</td>
<td>93.7%</td>
</tr>
</tbody>
</table>

a T₉₀ and T₄₀ refer to the transmittance measured at 2.5 μm wavelength at 90 and 40°C, and T₉₀-T₄₀

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**Fig. 5** Hysteresis loops (a), (b), (c) and the corresponding derivative curve (a’),(b’),(c’)
(a) (a’) VₓWₓO₂/TiO₂ composite film; (b) (b’) VO₂/TiO₂/mica film; (c) (c’) VO₂/mica film
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 VₓW₁₋ₓO₂/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.

References:


TiO$_2$中间层对基于溶胶–凝胶法制备的 VO$_2$薄膜光学特性的影响

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摘 要: 为了提高 VO$_2$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–凝胶法在云母基层上制备锐钛型 TiO$_2$薄膜，再在光致亲水性处理的 TiO$_2$/云母基层上涂覆 V$_2$O$_5$以及掺钨 V$_2$O$_5$水溶胶，然后经热处理获得 VO$_2$/TiO$_2$及 V$_x$W$_{1-x}$O$_2$/TiO$_2$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, VO$_2$/TiO$_2$复合薄膜晶体生长为(011)面择优取向；V$_x$W$_{1-x}$O$_2$/TiO$_2$复合薄膜产生多种取向。TiO$_2$中间层有助于使 VO$_2$薄膜生长致密，相变温度降低，更使 V$_x$W$_{1-x}$O$_2$/TiO$_2$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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