Optical properties of vanadium dioxide thin films on $c$-Al$_2$O$_3$ (001) substrates by in-situ RF magnetron sputtering

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Abstract
Vanadium oxide thin films were deposited on $c$-Al$_2$O$_3$ (001) substrate by in-situ RF magnetron sputtering. Oxygen partial pressure was adjusted to prepare thermochromic VO$_2$ phase. X-ray diffraction patterns and scanning electron microscopy convincingly showed that plate-like V$_2$O$_5$ grains were changed into round-shape VO$_2$ grains as oxygen partial pressure decreased. After the optimized deposition conditions were fixed, the effect of substrate temperature and orientation on the optical properties of VO$_2$ thin films was analyzed.

Key words VO$_2$, Thermochromic, Optical properties, Crystal structure, Microstructure, Thin Films

1. Introduction

Thermochromic materials are capable of reversible change of their optical properties in response to temperature [1]. Such materials have been attracting great attention in applications including smart window coatings for buildings and vehicles to control the solar irradiance automatically. Vanadium oxide (VO$_2$) is a promising candidate for thermochromic application. The crystal exhibits an abrupt metal-insulator transition at a critical temperature $T_c = 68^\circ$C [2,3]. The metal-insulator transition of VO$_2$ is attributed to crystallographic structure change, which is from monoclinic to tetragonal. Below $T_c$, the material is semiconducting and IR transparent; above $T_c$, it is metallic and IR reflecting.

There have been many reports for the fabrication of VO$_2$ by pulsed laser deposition [4-6], sol-gel process [7,8], atmospheric pressure chemical vapor deposition [9,10], and magnetron sputtering [11-13]. Among them, magnetron sputtering method has advantages for high deposition rate and large area deposition. However, deposition of VO$_2$ thin films by magnetron sputtering has been quite difficult due to the very narrow phase existence in the complex V-O system [14,15]. To form a single phase VO$_2$ thin film by reactive magnetron sputtering, oxygen partial pressure should be precisely controlled. While many studies have reported VO$_2$ films by magnetron sputtering methods, few studies have been focused on the effect of crystal structure and microstructure change on the optical properties of VO$_2$ thin films [15,16]. In particular, optical properties of VO$_2$ thin films on $c$-Al$_2$O$_3$ (001) substrate have been scarcely reported [11].

In the current study, thermochromic vanadium oxide thin films were deposited on $c$-Al$_2$O$_3$ (001) substrates by in-situ RF magnetron sputtering. Optimum deposition conditions to prepare highly oriented VO$_2$ thin film were found with changing oxygen partial pressure ($P_O$). The effect of substrate temperature ($T_s$) and orientation on the crystal structure, microstructure, optical transmittance, and transition behavior of VO$_2$ thin films was analyzed.

2. Research Procedure

2.1. Films Preparation

The $c$-Al$_2$O$_3$ (001) single crystal substrates were ultrasonically cleaned with acetone, absolute methyl alcohol, and de-ionized water for 5 minutes, respectively. The VO$_2$ thin films were deposited on $c$-cut sapphire substrates by reactive radio frequency (RF) magnetron sputtering using a V metal target of 2 inch in diameter with 99.9% purity. The RF power, total flow rate, and working pressure were maintained at 150 W, 50 sccm, and 30 mTorr, respectively during the deposition. The $P_O$ was changed from 0.8 to 1.1 sccm (1.6 to 2.2%) to find the optimum condition for obtaining VO$_2$ thin film.
The mass flow controller was applied for the fine control of \( O_2 \) flow ratio. The \( T_s \) was varied from 300\({^\circ}\)C to 400\(^{\circ}\)C. The lowest \( T_s \) to obtain crystalline VO\(_2\) was found to be 300\(^{\circ}\)C.

2.2. Characterizations

The crystal structure and phase composition of the vanadium oxide film was determined using X-ray diffractometry (XRD) in the \( \theta-2\theta \) mode with CuK\( \alpha \) radiation operated at 30 kV and 20 mA in a 2\( \theta \) range of 15–60\(^{\circ}\). To observe the surface microstructure of VO\(_2\) thin films, scanning electron microscopy (SEM) was used. Spectral transmittance was measured using UV-Vis spectrometer at wavelengths between 400 to 2500 nm with a step width of 2 nm. Temperature-dependent transmittance curve (hysteresis curve) was also obtained using UV-Vis spectrometer at wavelength of 2500 nm. From the hysteresis curve, the midpoint of heating curve (T1), midpoint of cooling curve (T2), hysteresis width (T: difference between the T1 and T2), and transmittance difference (\( \Delta T_r = T_r(30^{\circ}C) - T_r(90^{\circ}C) \)) were evaluated. The Tc (minimum of the derivative of the heating curve) was also evaluated.

3. Results and Discussion

The XRD patterns of the vanadium oxide thin films deposited with oxygen partial pressures of 2.2, 2.0, 1.8, and 1.6\% are presented in Fig. 1. The thin films were \textit{in-situ} heated at \( T_s \) of 400\(^{\circ}\)C. It can be seen that the intensity of the VO\(_2\) (020) is gradually increased whereas the intensity of the V\(_2\)O\(_5\) (410) phase is gradually decreased as the \( P_o \) decreased from 2.2 to 1.6\%. Although V\(_2\)O\(_5\) second phase and VO\(_2\) (012) plane was found in the vanadium oxide film deposited with the \( P_o \) of 1.6\%, VO\(_2\) phase was highly oriented with (010) planes parallel to the surface of the substrate. For the VO\(_2\) (020) peak, the full width half maximum (FWHM) value is found to be about 0.19\(^{\circ}\), which corresponds to high crystallinity thick film. The VO\(_2\)(010)/Al\(_2\)O\(_3\)(001) relationship is consistent with previous reports [6, 17].

Fig. 2 shows SEM images of the vanadium oxide thin films deposited with oxygen partial pressures of 2.2 (a), 1.8 (b), 2.0 (c) and 2.2 \% (d). The insets are corresponding spectral transmittance. As the oxygen partial pressure decreased the fraction of plate-like grains were reduced and round-shape grains were increased. According to Figs. 1 and 2, it might be concluded that plate-like grains correspond to V\(_2\)O\(_5\) phase and round-shape grains correspond to VO\(_2\) phase. Spectral transmittances confirm that the thermochromic properties are enhanced as VO\(_2\) phase increases. As the V\(_2\)O\(_3\) phase is the most stable oxide in the V-O system [18-20], oxygen partial pressure should be precisely adjusted to form VO\(_2\) phase.

XRD patterns and SEM images obtained from VO\(_2\) thin films deposited at the \( T_s \) of 300 and 350\(^{\circ}\)C with oxygen partial pressure of 1.6\% are shown in Fig. 3(a). It can be seen that the intensity of the VO\(_2\) (020) peak decreases as the \( T_s \) decreases from 350 to 300\(^{\circ}\)C. Average grain size of the thin films was calculated using Scherrer’s formula [21]:

\[
b = \frac{0.9\lambda}{\beta\cos\theta}
\]

where b is the average grain size, \( \lambda = 1.541 \) Å (X-ray wavelength), and \( \beta \) is the FWHM for the diffraction angle 20. The calculated grain sizes of the VO\(_2\) thin films deposited at the \( T_s \) of 300 and 350\(^{\circ}\)C are 5.8 and 6.8 nm, respectively. SEM images also follow a similar trend to the calculated grain sizes. Both images show uniform-sized nano-grain but the VO\(_2\) thin films deposited at 350\(^{\circ}\)C have relatively large grain sizes than the VO\(_2\) thin films deposited at 300\(^{\circ}\)C. In order to investigate the influence of \( T_s \) on the crystal structure, we obtained subtle XRD patterns of 2\( \theta \) near 39.8, as shown in Fig. 3(b). As \( T_s \) increases from 300 to 350\(^{\circ}\)C, the diffraction peak of VO\(_2\) (020) shift to higher position from 39.84 to 39.92, which correspond to (010) lattice spacing of 4.523 Å and 4.514 Å, respectively. Epitaxial VO\(_2\) thin film deposited on \( c-\)Al\(_2\)O\(_3\) (001) substrate with \( T_s \) of 400\(^{\circ}\)C showed VO\(_2\) (020) position of 2\( \theta \) = 39.98 –
indicating that our VO₂ thin film deposited at the Tₛ of 350°C have similar crystal structure with epitaxial thin film with good crystallinity but the VO₂ thin film deposited at the Tₛ of 300°C is not fully crystallized and have relatively open structures.

Fig. 4 shows the spectral transmittance of the VO₂ thin films deposited at 300°C (a) and 350°C (b) at T < Tₑ (30°C) and T > Tₑ (90°C). The film deposited at 350°C shows higher visible region transmittance and Tr than the film deposited at 300°C due to larger grain size and better crystallinity. However, both films show large transmittance difference between the semiconductor state of
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T < T<sub>C</sub> (30°C) and metal state of T > T<sub>C</sub> (90°C) in the infrared region, which means good thermochromic property.

Hysteresis curves of the VO₂ thin films deposited at 300°C (a) and 350°C (b) are shown in Fig. 5. Table 1 shows the T<sub>1</sub>, T<sub>2</sub>, T<sub>r</sub>, T<sub>Δ</sub>, and T<sub>C</sub> of the VO₂ thin films deposited at 300°C and 350°C in which obtained from Fig. 5. While the VO₂ thin film deposited at 350°C have relatively sharp decrease of transmittance with T<sub>r</sub> of 55.4%, the film deposited at 300°C have broad change of transmittance with decreased T<sub>r</sub> of 45.8%. The T is increased from 9.6 to 11.4°C and the T<sub>C</sub> is decreased from 77.5 to 70.3°C with decreasing T<sub>S</sub>. The VO₂ films deposited at low temperature can lead to the destabilization of low-temperature semiconductor phase and thereby causing reduced T<sub>C</sub> and transition sharpness [15, 22], which is consistent with our results. However, considering the reduced T<sub>C</sub> by the crystalline imperfection, the T<sub>C</sub> of the both films are still larger than the bulk value of ~68°C.

The lattice parameters and thermal expansion coefficients for the rhombohedral Al₂O₃ substrate and monoclinic VO₂ film are shown in Table 2. The lattice parameter a of rhombohedral Al₂O₃ is 4.758 and the lattice parameters a, b and c of monoclinic VO₂ are 5.753, 4.526, and 5.382, respectively. The epitaxial VO₂(010)//Al₂O₃(001) can induce the epitaxial relationship of VO₂(010)//Al₂O₃(001).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Lattice parameters (Å)</th>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>a = 4.758, c = 12.992</td>
</tr>
<tr>
<td>VO₂</td>
<td>a = 5.753, b = 4.526, c = 5.382</td>
</tr>
</tbody>
</table>

![Fig. 4. Spectral transmittance of the VO₂ thin films deposited at 300°C (a) and 350°C (b) at T < T<sub>C</sub> (30°C) and T > T<sub>C</sub> (90°C).](image1)

![Fig. 5. Temperature-dependent transmittance curve (hysteresis curve) of the VO₂ thin films deposited at (a) 300°C and (b) 350°C.](image2)
(100)/(100). As a result, in-plane compressive stress and corresponding out of plane tensile stress can be induced. In the form of thin film, the Tc of VO₂ can be modified by the control of c-axis stress induced by the lattice mismatch between the film and substrate [5,23]. The c-axis compressive stress decreases the Tc, whereas the c-axis tensile stress increases the Tc. The increased Tc of our VO₂ thin film deposited on c-Al₂O₃ (001) might be originated from increased c-axis tensile stress.

As mentioned earlier, the lattice spacing was decreased from 4.523 Å to 4.514 Å with increasing Ts from 300 to 350°C. The decrease in c-axis lattice spacing means c-axis compressive stress, and hence the Tc should be decreased. However, the Tc was increased with great extent of ~7.2°C with increasing Ts from 300 to 350°C, that is opposite tendency compared with previous reports [5, 23]. A more detailed research concerning the correlation between the Ts and the Tc of the VO₂ films deposited on c-Al₂O₃ (001) substrate is under investigation.

4. Conclusions

Vanadium oxide thin films were deposited on c-Al₂O₃ (001) substrate by in-situ RF magnetron sputtering. As the oxygen partial pressure decreased, rod-like V₂O₅ grains were reduced and plate-like VO₂ grains were increased. With increasing substrate temperature, grain size increased and (010) lattice spacing decreased from 4.52 to 4.514 Å. The VO₂ thin films deposited at 300 and 350°C showed large transmittance difference between the semiconductor and metal state in the infrared region, which implies good thermochromic property. While the VO₂ thin film deposited at 350°C had relatively sharp decrease of transmittance, the film deposited at 300°C had broad change of transmittance with decreased Tr due to the crystalline imperfection. The increase in Tc of VO₂ thin film deposited on c-Al₂O₃ (001) substrate compared with bulk VO₂ might be originated from c-axis tensile stress induced by lattice mismatch.

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References


