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Properties of VO_2 Films Sputter-Deposited from V_2O_5 Target

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Rutile VO_2 is a thermochromic material that exhibits a reversible metal-insulator phase transition upon thermal cycling. A new deposition process of rutile VO_2 from a V_2O_5 target was developed using reactive oxygen instead of hydrogen. Adjusting the substrate temperature and the oxygen flow ratio changes the compositions and phases of the as-deposited films into rutile VO_2 under optimum deposition conditions on the Si and thick glass substrates. Crystalline phases analyzed by X-ray diffraction shows the relationship among V_4O_9, V_6O_{13}, and VO_2 films prepared under different deposition conditions. Analysis by AFM shows that VO_2 films grown at higher substrate temperatures have larger grain size. The optical switching property of VO_2 was measured at a wavelength of 1.5 μm and transition temperature around 45°C was also measured. Inhomogeneity and the strained structure of the film are suggested to be the reasons of transition temperature lower than typical reported value because the impurity in the target is too low to be detected quantatively by ICP.
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KEYWORDS: Vanadium dioxide, optical switching, metal-insulator transformation, thermochromism, rf sputtering

1. Introduction

Rutile VO_2 is a well known thermochromic material because it exhibits a reversible phase transition around 68°C:[1,2] high-temperature phase is tetragonal and its low-temperature phase is monoclinic.[1,2] This reversible phase transition exhibits high cyclability because it is associated only with local movement of atoms. The local movement of atoms also results in great changes in optical and electrical properties. The literature shows a fourth order change in resistivity[3] and a large change in transmittance in the IR spectrum region during the phase change in single crystal rutile VO_2. Reversible changes enable VO_2 to be electrical or thermochromic switches.

Several approaches to deposit rutile VO_2 films have been reported, such as sputter deposition,[4–11] evaporation,[12,13] pulse laser deposition,[14] and sol–gel coating.[15–18] Magnetron sputtering has been one of the most reliable techniques for producing large-area uniform films with micrometer thickness, and vanadium, V_2O_3 or V_2O_5 has been typically used as the target material to deposit rutile VO_2. The reactive gas and the range of the flow ratio during sputtering vary with the targets. Reactive oxygen is required if vanadium or V_2O_3 target is used, while hydrogen is reported to be necessary for reduction of oxygen during sputtering from a V_2O_5 target.[4] The range of the flow ratio of oxygen/argon is narrow during deposition when a metallic vanadium target is used as the target. Furthermore, serious oxidation on the surface of target make the deposition of VO_2 impossible. The preparation of VO_2 with a V_2O_3 target allows a wider range of flow ratio but the cost of a V_2O_3 target is much higher while its stability is lower than that of V_2O_5. V_2O_5 is one of the best choices of target material because of its low cost and high stability in air. However, sputtering with reactive hydrogen at a high substrate temperature requires special safety precautions during processing.

The study aims to deposit VO_2 films from V_2O_5 target without hydrogen as a reducing agent and to explore the structure and properties of such films. Depositing rutile VO_2 from a V_2O_5 target with reactive oxygen was successfully demonstrated. Furthermore, rutile VO_2 films were grown not only on Si substrate but also on glass substrates by the same method and the relationships among the deposition process, thermochromic properties and the microstructure were discussed.

2. Experimental

V_2O_5 targets were prepared by powder compaction and then sintered in air at 650°C for 30 min and cooled down to room temperature in air. Films were deposited by rf magnetron sputtering with a target of diameter of 2-inches. The distance between the substrate and the target for sputtering was 10 cm. The vacuum chamber was evacuated to 10^{-5} Torr and then back-filled with a mixture of Ar and oxygen to a certain total gas pressure. Ar and oxygen were pre-mixed in a small chamber at a positive pressure before being led into a vacuum chamber to maintain a sputtering pressure. The process pressure was measured using a capacitance manometer (MKS Baratron gauge). During deposition, the total gas pressure was kept at 12.5 mTorr. The substrate temperatures (T_s) were varied from 300 to 500°C at a power of 60 or 120 W under an oxygen flow ratio (R_{fo}) of 0.042 to 0.1, where $R_{fo} = (f_{O_2})/(f_{O_2} + f_{Ar})$ and f is the flow rate of the gas in sccm. Well cleaned fused silica glasses, Si(001) or thick SiO_2 on Si(001) were used as the substrates. Substrates were heated by irradiation lamps during sputtering. The temperature was measured *in-situ* by using a thermocouple. Before the film sample was prepared, the target was pre-sputtered for 4 h. Some films were deposited during pre-sputtering at a substrate of temperature 400°C for comparison. The thickness of the deposited films was kept constant at 100 ± 30 nm.

X-ray diffraction (XRD) patterns were recorded by a diffractometer (D/max-IIB, Rigaku) in the 2θ range 10–50°. Surface morphology and microstructure were elucidated by atomic force microscopy (AFM). The light source used to measure the transmittance at different temperatures was a semiconductor laser with a wavelength of 1.5 μm.

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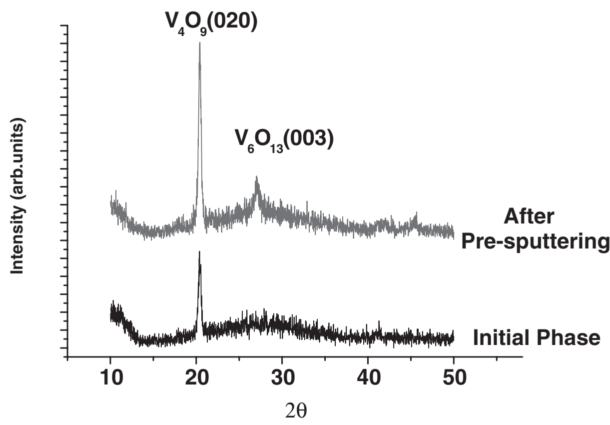

Fig. 1. XRD patterns of as-deposited films on Si(001) before and after pre-sputtering at $T_s = 400°C$ ($R_{fo} = 0.4$).

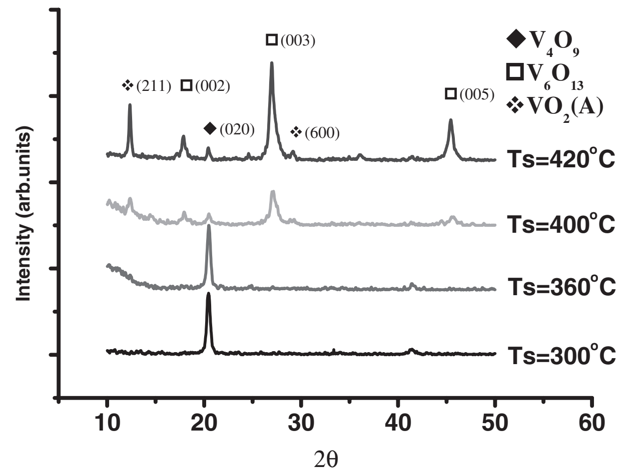

Fig. 3. XRD patterns of as-deposited films on Si(001) at, (a) 300°C, (b) 350°C, (c) 400°C, and (d) 420°C ($R_{fo} = 0.3$).

3. Results and Discussions

The phases of the as-deposited films during pre-sputtering ($R_{fo} = 0.4$) are shown in Fig. 1. The initial phase of the as-deposited film at a substrate temperature of 400°C is V_4O_9. V_6O_{13} then appears gradually during pre-sputtering which lasts for several hours. During pre-sputtering, the color of the target gradually becomes darker and finally keeps to dark gray, indicating a serious loss of oxygen since the color of V_2O_5 is yellowish, while color of V_2O_3 is blackish. Target composition, or more specifically the oxidation state of vanadium, reaches equilibrium as the mixture of V_4O_9 and V_6O_{13} is generated. No phase with less-oxygen further appears. The preparation of sample starts with target in this state.

The phase of the as-deposited films without any reactive oxygen ($R_{fo} = 0$) is amorphous ($T_s = 400°C$ and $T_s = 450°C$), whose colors are all blackish, as shown in Fig. 2. After these films are post annealed in Ar at 450°C, the phases of these films remain all amorphous. Amorphous structure of these films implies that composition of these films are not stoichiometric and the oxygen contents are less than that of VO_2, because, with addition of reactive oxygen under the same sputtering conditions, films show up with known crystalline phases, including V_4O_9, V_6O_{13}, VO_2(A) and even rutile VO_2. The VO_2(A) is a meta-stable phase of VO_2.[21)]

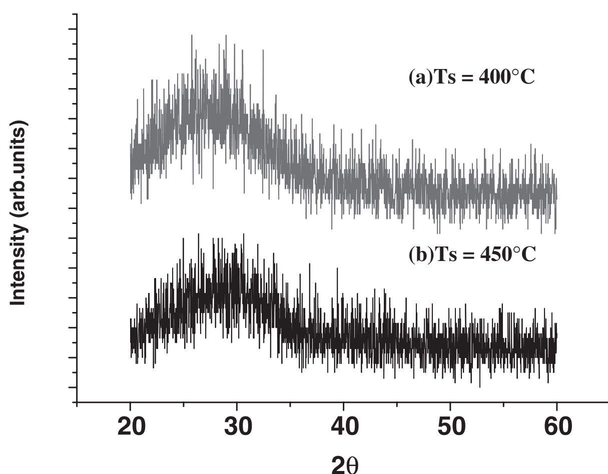

Fig. 2. XRD patterns of as-deposited films on Si(001) without reactive oxygen at (a) 400°C, and (b) 450°C.

The temperature of the substrate is an important parameter for controlling the oxygen content of the as-deposited films. In the same ambience, as Fig. 3 shows, increasing substrate temperature (T_s) results in a change of phase of the as-deposited film. When the substrate temperature is only 320°C, the phase of the film is solely V_4O_9. The phases V_6O_{13} and VO_2(A) appear at substrate temperatures higher than 400°C, implying that the substrate temperature affects not only phase formation but also the sputtering yield of oxygen. As substrate temperature increases, the sputtering yield of oxygen becomes lower, leading to the formation of phases with less oxygen. Restated films prepared under the same oxygen flow ratio and at a higher substrate temperatures show phases of less oxygen. Beside the oxygen content in the films, the substrate temperature also dominates the formation and crystallization of the phases. For example, activation energy for forming V_6O_{13} and VO_2(A) exceeds activation energy required for forming V_4O_9 because the former two only appear at high substrate temperatures.

Oxygen flow ratio is an important parameter for controlling oxygen content of the as-deposited film. The films with the phases shown in Fig. 4(a) are all prepared at $T_s = 450°C$ under different oxygen flow ratio. V_6O_{13} and VO_2(A) are formed at $R_{fo} = 0.1$. Phases with less oxygen appear gradually as the oxygen flow ratio is reduced. Rutile VO_2 and metastable VO_2(A) phases coexist when (R_{fo}) is down to 0.042. Only rutile VO_2 phase appears, as Fig. 5 shows, when the substrate temperature is increased to 500°C at the same oxygen flow ratio. At $T_s = 500°C$, 60 W under an oxygen flow ratio between 0.06 and 0.042, only rutile VO_2 phase appears on the Si substrate, while a mixture of rutile VO_2 and other phases appear under other deposition conditions. On Si(001), SiO_2 and fused silica glass substrates at $T_s = 450°C$, the texture of rutile VO_2 is (011). Planes (001), (211) and (212) of VO_2 phase appear on Si(001) as T_s is increased to 500°C. Quantitatively, the degree of preferred orientation (*DPO*):

$$DPO(hkl) = I_{(hkl)}/\Sigma I_{\text{all planes}} \times 100\% \quad (1)$$

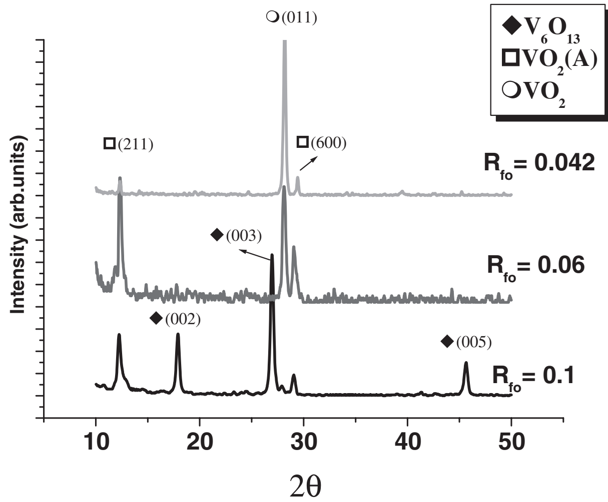

Fig. 4. XRD patterns of as-deposited films on Si(001) at 450°C, (a) $R_{fo} = 0.1$, (b) $R_{fo} = 0.06$, and (c) $R_{fo} = 0.042$.

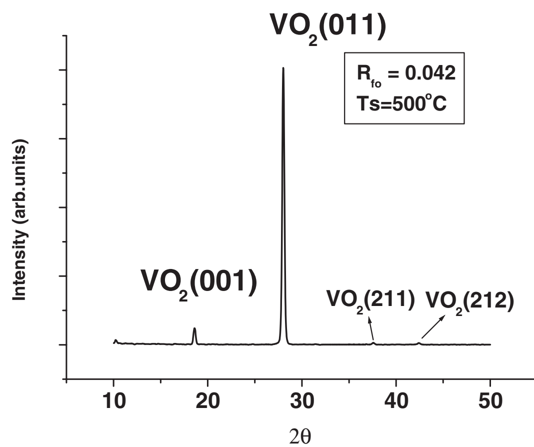

Fig. 5. The XRD patterns of single phase VO_2 deposited on Si(001) at 500°C and $R_{fo} = 0.042$.

The *DPO* of plane (011) is 95% and that of plane (001) is 5%.

As a simple approximation, the relative amount of each phase can be represented by the relative intensity (*Ir*):

$$Ir(\text{A–B}) = (\Sigma I_{\text{all peaks of phase A}} / \Sigma I_{\text{all peaks of phases B}}) \quad (2)$$

Ir can represent the relative quantity of each phase.

For samples prepared at $T_s = 450°C$ under an oxygen flow ratio from $R_{fo} = 0.1$ to 0.06, $Ir(V_6O_{13}–VO_2(A))$ decreases from 3 down to 0. Decreasing the amount of oxygen suppresses the formation of V_6O_{13}, and the fraction of V_6O_{13} in the as-deposited film decreases gradually while the portion of $VO_2(A)$ increases. To our knowledge, this metastable $VO_2(A)$ phase was obtainable only by the hydrothermal method.[21–23] The $VO_2(A)$ phase is consisted of VO_6 octahedra structure. As the oxygen flow ratio decreases, $VO_2(A)$ appears earlier than rutile VO_2, implying that more oxygen during sputtering increases the internal stress in the as-deposited film and results in the formation of the $VO_2(A)$ metastable phase. No $VO_2(A)$ is found in the sample prepared at $T_s = 500°C$ even at $R_{fo} = 0.06$. Oxygen content of films prepared at $T_s = 450°C$ is less than that of the samples prepared at $T_s = 450°C$ because, as shown before, films deposited at higher substrate temperatures but in the same ambient atmosphere have less oxygen than these prepared at lower substrate temperatures. Besides, a higher substrate temperature may promote atomic diffusion to relax the as-grown stress in the as-deposited film and to reach thermodynamic equilibrium.

The grain sizes of the single phase rutile VO_2 film prepared at $T_s = 500°C$ and $R_{fo} = 0.06$, as shown at the right part of Fig. 6, are from 300 to 800 nm. However, a multiphase sample with coexisting rutile VO_2 and $VO_2(A)$ phases prepared under the same conditions and at $T_s = 450°C$, as shown at the left part of Fig. 6, shows grain sizes from 100 to 300 nm with an average of 250 nm. The average grain size of the mixed phase sample prepared at 500°C is about 450 nm, larger than the average grain size of films prepared at 450°C, showing that substrate temperature is associated not only with the formation of phases but also with the grain size of as-deposited films.

The measured transmittance at a wavelength of 1.5 μm at different temperatures is shown in Fig. 7. This sample was deposited on Si(001) at 500°C at $R_{fo} = 0.042$. The transmittance is derived by the following formula:

$$\text{Transmittance } (\%) = \frac{T_f}{T_s} \quad (3)$$

T_f and T_s are the transmittance of the substrate with and

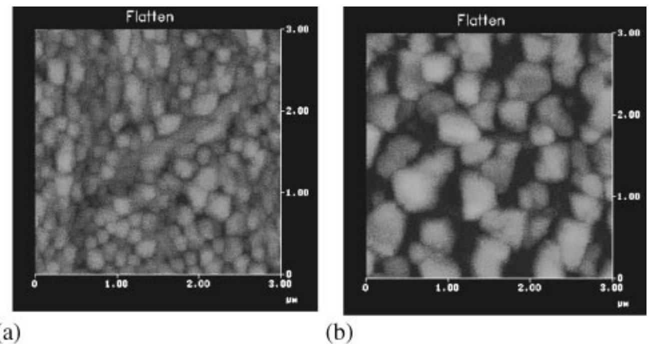

Fig. 6. AFM photography of films deposited on Si(001) at (a) 450°C, and (b) 500°C ($R_{fo} = 0.06$).

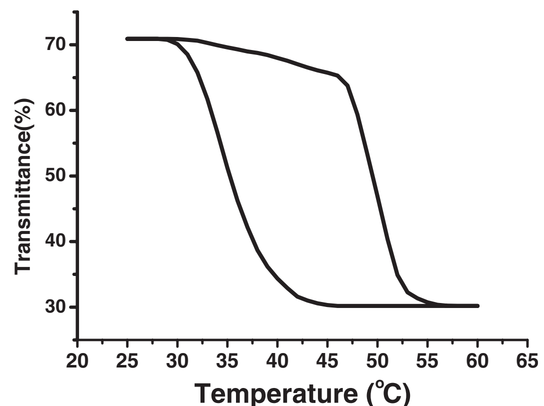

Fig. 7. Measured transmittance vs temperature for film deposited on Si(001) at $T_s = 500°C$ and $R_{fo} = 0.042$.

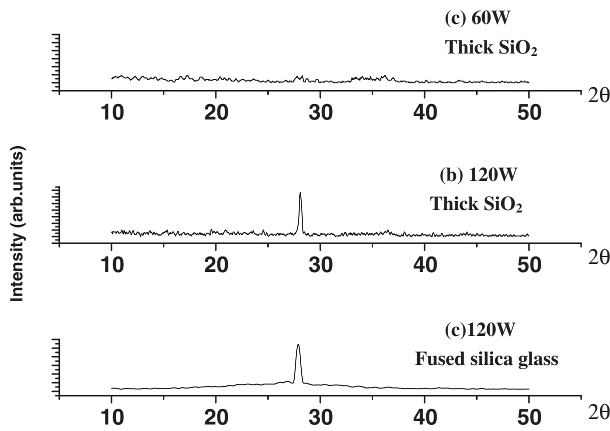

Fig. 8. XRD patterns of as-deposited films on (a) fused silica glass with at 120 W, (b) thick SiO_2 with at 120 W, and (c) thick SiO_2 with at 60 W ($T_s = 450°C$ $R_{fo} = 0.042$).

without a film on it. The transmittance falls sharply at 50°C and returns to its initial value as the measurement temperature decreases to room temperature, but with a hysteresis that spans about 15°C at the mid-portion of difference of transmittance. The transient temperature T_1 and T_2 are the temperatures of mid-point of the change in transmittance during heating and cooling. As reported by Goodenough,[1] the transition temperature of pure rutile VO_2 is about 67°C but transient temperatures T_1 and T_2 differ among the reports. $T_1 - T_2$ of un-doped VO_2 are about 73–60°C,[2] 67–25°C,[20] 90–45°C,[17] 53–45°C.[20] Large differences between transient temperatures for different samples mean that the transient temperatures and the hysteresis width of the rutile VO_2 film depend strongly on preparation process and the substrates. For our sample, T_1 and T_2 are 50 and 35°C and they are much lower than the typical value 67°C. ICP analysis reveals that the ratio of vanadium to the most possible impurity, sodium, is 14 to 0.02, respectively. Many other impurities are too low to be detected quantitatively, implying that impurities are not the cause of the lower transient temperature. Rather, the lower transition temperature may arise from inhomogeneity and the strained structure of the film[4,19,20] because the sample was not post-annealed.

Beside on Si substrate, rutile VO_2 was also deposited successfully on thick SiO_2 on Si(001) and fused silica glasses as shown in Fig. 8. SiO_2 on Si(001) substrate was prepared by growing SiO_2 to a thickness of 500 nm on Si wafer. However, sputtering power strongly affects the deposition of rutile VO_2 on the SiO_2 substrate. In Fig. 8, the film prepared at 60 W shows an amorphous state [Fig. 8(b)] while film prepared at 120 W [Fig. 8(c)] is single-phase rutile VO_2. Under the same deposition conditions, crystalline rutile VO_2 film can be grown on Si(001) substrate but it is amorphous on SiO_2 substrate when the sputtering power is 60 W, implying that Si substrate with a (001) texture promotes the formation of rutile VO_2, and high power is required to overcome the threshold energy of the formation of crystalline VO_2 on amorphous SiO_2 substrates.

4. Conclusions

Sputter-deposition of rutile VO_2 using a V_2O_5 target with the reactive oxygen is proven to be a promising technique. As single phase rutile VO_2 film can be formed by modifying the substrate temperature, oxygen flow ratio and sputtering power. Under the same deposition condition, a higher substrate temperature (T_s) causes a lower oxygen content of as-deposited film and promotes the formation of those phases which require higher crystallization energy such as rutile VO_2. As the oxygen flow ratio is reduced at the same substrate temperature, the order of phase formation is V_4O_9, V_6O_{13}, VO_2(A) and finally rutile VO_2. The transient temperatures of the film prepared at $T_s = 500°C$ at an oxygen flow ratio $R_{fo} = 0.06$ are lower than the typical reported values. Lower transient temperatures may arise from inhomogenity and the strained structure of the film because no post annealing was performed. The minimum sputtering power required to deposit rutile VO_2 differs with the substrate when all other deposition conditions are held the same, implying that the substrate strongly affects the threshold crystallization energy of rutile VO_2.

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