Wafer-size VO$_2$ film prepared by facile water-vapor assisted thermal oxidation of metallic vanadium film

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Abstract

The growth of wafer-scale and uniform monoclinic VO$_2$ film with excellent phase transition property was a challenge if considering the multivalent nature of vanadium atom and the various phase structures of VO$_2$ compound. Direct oxidation of metallic vanadium film by annealing in oxygen gas or in air was suggested to be an easy way for VO$_2$ film preparation, while the oxidation parameters including the gas pressure, annealing temperature and time, were extremely sensitive due to the critical preparation window, since any parameter deviation would make the final product in a mess. Here we proposed a facile water-vapor assisted thermal oxidation of metallic vanadium film at ambience pressure and achieved a homogeneous single phase VO$_2$ film with excellent MIT properties. Results indicated that by introducing the water vapor during the annealing process, the oxidation window was greatly broadened and the obtained monoclinic VO$_2$ film showed the resistance change as large as 4 orders of magnitude, which was attributed to the improved crystallinity and the higher oxygen stoichiometry. The current wet oxidation route not only demonstrated that the common water vapor could be used as a modest oxidizing agent, but also showed the unique advantage for large size VO$_2$ film preparation, which was meaningful for practical devices applications in the future.

Keywords

VO$_2$ films, metal-insulator transition, wet oxidation, wafer scale
1. Introduction

As a prototypical transition oxide, vanadium dioxide (VO$_2$) shows a pronounced metal-insulator transition (MIT) behavior at the critical temperature of about 68°C, accompanying by a sharp resistance variation up to five orders of magnitude and a distinct infrared switching effect within sub-picosecond time range. These considerable MIT behaviors make VO$_2$ material many potential applications in smart windows, optical switching devices, infrared laser protection and memory devices.

Since the performance of VO$_2$ based device is directly associated with its MIT behavior, high quality VO$_2$ thin film growth has attracted much interest for many years. While it is known that the quality of VO$_2$ film is very sensitive to oxygen stoichiometry due to the multivalent states of Vanadium ions, which is easy to cause the Magnéli phases such as V$_n$O$_{2n-1}$(3≤n≤9) and seriously degrades the MIT property. Many methods have been adopted to grow high quality VO$_2$ epitaxial film, such as Molecular Beam Epitaxy (MBE), Pulsed Laser Deposition (PLD) and so on. While for the preparation of wafer-scale and monoclinic VO$_2$ film with excellent MIT behavior, it is still a challenge if considering the pure phase structure and uniformity. Although it was claimed that molecule beam epitaxy technology was able to grow wafer-size VO$_2$ film, the process was complex and quite expensive, which was not suitable for quantity device fabrication.

Thermal oxidation of metallic vanadium film in oxygen gas or in air was considered to be a cheap way for VO$_2$ film preparation, while the oxidation parameters, such as the gas pressure, annealing temperature and time, were extremely sensitive due to the critical growth window. C.G. Granqvist group reported the VO$_2$ films by thermal oxidation of vanadium in SO$_2$ gas since they considered that the oxidation agent was milder than pure oxygen. While the toxic gas used in the experiment and much higher temperature required for the annealing treatment (600~650°C) were obvious disadvantages. Thermal oxidation approaches by water vapor was reported to be effective for metal oxidation treatment due to the oxygen partial pressure modulation ability within a controllable temperature range. While till now, there
was no report about the water-vapor-assisted oxidation for large-size VO$_2$ film preparation directly from metallic vanadium film.

In this work, we achieved a facile water-vapor assisted thermal oxidation of metallic vanadium film at ambience pressure and obtained a homogeneous single phase structure VO$_2$ film with excellent MIT properties. The phase transition behaviors of the obtained VO$_2$ films with or without water vapor were systematically investigated. The electronic structures were also characterized by synchrotron radiation based techniques. Results indicated that the water-vapor played very important roles for the thermal oxidation of metallic V film to the final pure VO$_2$ film, which not only broaden the growth window, but also enhanced the uniformity and MIT performance for the obtained large-size VO$_2$ thin film, demonstrating the unique advantage of this wet-oxidation method for scalable VO$_2$ film preparation.

2. Experimental Section

In general, metallic vanadium thin films are easily deposited by thermal evaporation or magnetron sputter. Thus, in the current experiment, we just deposited the precursor metallic V thin film on 2-inch c-cut sapphire wafers by thermal evaporation technique. The growth rate was calibrated by a quartz based thickness monitor (Inficon SQM-160) and the final film thickness was kept at ~30nm and 200nm respectively.

To conduct the water-vapor effects on the oxidation of metallic vanadium film, a home-made water-vapor assisted furnace system was established as shown in Figure 1. Argon gas as the carrier gas was controlled by the flow-meter and piped into a half-filled water flask to produce bubbles. The water flask was kept in a water bath, which was heated to produce the water vapor. The amount of water vapor content transported into the furnace was modulated by both the water bath temperature and argon flux$^{28}$. The as-fabricated metallic films were oxidized in the above furnace system at different temperatures ranging from 450 to 650$^\circ$C by introducing a flow of 0.1–0.8 liter per minute (LBM) argon gas with and without water vapor, respectively. During the wet-
oxidation, the water flask half-filled with deionized water was kept in the water bath with the temperature of 50~70°C. After oxidized in the water vapor for about two hours, the sample was cooling naturally to 150°C before taken out of the furnace.

![Figure 1](image.png)

Figure 1. The scheme for the water-vapor assisted oxidation furnace system. Argon gas flux controlled by the MFC was used as the carrier gas. The water flask half-filled with deionized water was kept in the water bath for water vapor production.

3. Results and Discussion

After the 30-nm VO₂ samples were prepared by wet oxidation with different temperatures (carrier gas~0.8 LBM, water bath~50 °C ), the crystal structures were characterized by XRD and the results were shown in Fig. 2(a). It was observed that except the diffraction peak from Al₂O₃ (0001) substrate, the unique peak around 2θ=39.89° was assigned to the diffraction from monoclinic VO₂ (020) (JCPDS card #82-0661). This observation showed the wet-oxidation treatment can produce high quality VO₂ film with pure phase and the obtained film was grown with the preferred orientation. Fig. 2(b) showed the related Raman spectra for the obtained 30-nm VO₂ samples. The strong Raman peaks at 194, 224, 308, 388, and 615 cm⁻¹ were observed, which confirmed the formation of pure monoclinic VO₂ films by the water-vapor assisted oxidation from metallic V film. While it should be noticed that the Raman
scattering intensity was associated with the obtained samples at different temperatures. When the wet-oxidation was conducted at 550°C, the sample showed the most pronounced Raman peaks, which should be related to the preferred VO$_2$ film with the highest quality.

In order to examine the chemical state of the obtained VO$_2$ films, the X-ray photoelectron spectroscopy (XPS) tests were performed as shown in Fig. 3(a-c). From the XPS peaks of V2p$_{3/2}$ and O1s peaks for the VO$_2$ samples after wet-oxidized with different temperatures, it was confirmed that the metallic V precursor films were successfully oxidized by water vapor. While from the V2p$_{3/2}$ peak shapes for the samples at 450°C and 650°C, it could deduce that there should exist some V$^{3+}$ state in the film due to the broaden peak profiles, though the V$^{4+}$ state was dominated. For the optimized sample prepared at 550°C, the detailed XPS peak fitting were shown in Fig. 3(b-c). The O1s peak located at 530eV should be from the O-V bonds, while the 531.5eV peak was assigned to the surface absorbed –OH species. The V2p$_{3/2}$ peak was dominated by V$^{4+}$ state at 516.1eV$^{39}$, which indicated the pure VO$_2$ film formed. The peak with higher binding energy (∼517.2eV) was related to the V$^{5+}$ state, which was assigned to the surface oxidation at the top-layer. The dominated V$^{4+}$ chemical states of the obtained VO$_2$ film by wet-oxidation were also verified by the synchrotron based absorption near-edge structure (XANES) spectra in Fig. 3(d).
edge X-ray showed almost the same profiles, which were consistent with the previous reports for VO$_2$ compound$^{40,41}$. While it should be pointed out that for the VO$_2$ film at

![Figure 3. (a-c) The XPS test for the VO$_2$ film prepared by wet-oxidation at different temperatures. (d) The synchrotron based XANES tests for the samples.](image)

the growth temperature of 450°C, there is an obvious decrease of the relative intensity ratio of the $t_{2g}$ and $e_g$ peaks in O K-edge curve, showing the existence of V$^{3+}$/V$^{4+}$ mixed state. Anyway, all of the above spectroscopic measurements confirmed that pure phase and well stoichiometric structure of monoclinic VO$_2$ film can be effectively produced by the facile wet-oxidation with water-vapor.

The surface morphologies of the VO$_2$ samples by wet-oxidation were also examined as shown in Fig.4. For the metallic V film, it showed quite smooth surface with very small grains. While after wet-oxidized at 450°C, the produced VO$_2$ film had enlarged particle size on the surface. Further increasing the oxidation temperature to
550°C, the VO₂ film was still continuous and the surface particles grown much larger. However, if the temperature was 650°C, the obtained film was broken with many holes on the surface, which indicated the film was discontinuous. Thus from the SEM observation, it was suggested that wet-oxidation at 550°C should be the suitable condition for VO₂ film preparation with high quality.

The resistance measurements as the function of temperature (or R-T curve) for the obtained 30-nm VO₂ films by wet oxidation at different temperatures were also conducted as shown in Fig. 5(a). It can be observed that as the temperature increased from 450°C to 550°C, the R-T curve became sharper and the resistance ratio between the insulating metallic phases across the MIT transition was improved. While if further
Figure 5. (a) The resistance measurements as the function of temperature (R-T curve) for 30nm VO$_2$ film by wet-oxidation; (b) The R-T curves for the optimized VO$_2$ films by wet-oxidation and by normal oxidation treatment without water-vapor; (c) The resistance ratio between the insulating monoclinic VO$_2$ film and rutile phase ($R_M/R_R$) as the function of oxidation temperature. The wet-oxidation induced VO$_2$ films showed better quality and the oxidation temperature window was greatly broadened (from 30°C to ~90°C) if keeping the $R_M/R_R$ value up to $10^3$. (d) By wet-oxidation route, 200nm VO$_2$ film showed the $R_M/R_R$ value up to four order of magnitudes. The insert showed the related differential curves.

Increasing the wet oxidation temperature up to 600°C, the R-T curve was degraded. Accordingly, the variations of R-T curves further confirmed the optimized wet-oxidation temperature of 550°C, which showed the most pronounced MIT characterization. Fig. 5(b) showed R-T curves for the prepared VO$_2$ film by wet-oxidation and by normal oxidation treatment without water-vapor. Both of the samples were obtained under the optimized conditions. It was obvious that the wet-oxidation induced VO$_2$ film demonstrated much better quality if considering the sharp MIT curve and the great resistance change up to four orders of magnitudes.
In addition, we also found that the annealing temperature window was greatly broadened to produce pure VO$_2$ film by wet-oxidation treatment in Fig. 5 (c), if comparing with the traditional oxidation method in air or in oxygen gas. For traditional oxidation way, VO$_2$ film could be only obtained by very harsh conditions and the annealing temperature window was only ~30°C if the resistance change was up to three orders of magnitudes across the phase transition. While by wet-oxidation in water vapor, the oxidation temperature window was broadened up to 90°C, which made it easier to control the growth conditions. By this wet-oxidation method, we could produce thick VO$_2$ film with very high quality. Fig. 5(d) showed the R-T curve for the obtained 200 nm VO$_2$ film by wet oxidation. The sample demonstrated quite sharp MIT properties and the resistance change was up to four order of magnitudes. From the related differential curves as shown in the insert, the critical temperatures were determined to be 69°C for the heating process and 63°C for the cooling process, respectively, which were quite consistent with previous reports$^{28, 42}$.

Wet-oxidation route can also prepared uniform VO$_2$ film with large-size. Fig. 6 (a) showed the prepared 2-inch metallic V precursor film. Fig. 6 (b) and 6(c) showed the 30nm VO$_2$ film by traditional oxidation method without water vapor and by wet-oxidation route respectively. Though after optimizations, both methods could oxidize the metallic V film to VO$_2$ film, while it was clear that the uniformity of the 2-inch film was quite different. The 2-inch VO$_2$ film by traditional oxidation way showed inferior uniformity, while the wet-oxidation induced VO$_2$ film was much more uniform, even from the eye-sight view.

To further examine the uniformity of the obtained 30nm VO$_2$ film prepared by wet-oxidation, we measured the surface distribution of resistance values before and after the MIT process in Fig. 6(d) and 6(e). It was observed that the insulating monoclinic VO$_2$ film had the resistance values of about 0.5~2 MΩ within the 2-inch surface at room temperature, while the resistance was sharply decreased to 160~400Ω
Figure 6. (a) The prepared metallic V precursor film with 2-inch size; (b) The 30nm VO$_2$ film by traditional oxidation method without water vapor; (c) The 30nm VO$_2$ film prepared by wet-oxidation route; (d) and (e) The surface resistance distribution for the wet-oxidation induced 30nm VO$_2$ film before and after the phase transition, confirming the uniformity of the obtained 2-inch VO$_2$ film.

over the whole surface. The resistance change during the MIT process was always over three orders of magnitudes for the whole 2-inch sample, indicating the excellent uniformity and high quality of the obtained VO$_2$ sample.

In fact, this wet-oxidation by water vapor was also suitable for large-size VO$_2$ film on silicon substrate (Supplementary Figure 1S), though there existed quite large lattice mismatching and high quality VO$_2$ film growth on Si substrate was always difficult previously. By this wet-oxidation, very uniform VO$_2$/Si(001) film with 2-inch size was prepared, while the normal oxidation method induced film was inhomogeneous as shown in Figure S1(a, b). The quite sharp R-T curve and the distinct Raman spectra in Figure S1(c, d) further confirmed the high quality of the prepared VO$_2$/Si(001) film with 2-inch by water-vapor oxidation. In addition, large size and
uniform VO$_2$/mica film with excellent flexibility was also prepared by this water-vapor oxidation method (Supplementary Figure 2S), demonstrating this universal VO$_2$ film preparation technique.

From the experimental results, it was inferred that the wet-oxidation, or the water vapor assisted oxidation process demonstrated various advantages if comparing with traditional oxidation way. Since V atoms show multi-valance states from 0, +1, +2…+5 valence states, it was very sensitive to the oxidation conditions, which determined the final vanadium oxides. While it was suggested that water-vapor could be acted as a modest oxidizing agent, which was not active enough to oxidize V$^{4+}$ ions to V$^{5+}$ states, thus there existed an ideal self-adjustment of oxygen pressure when annealing the metallic V precursor in water-vapor$^{39-40}$.

In fact, the reaction between water vapor and metallic V film can be written as: $2\text{H}_2\text{O} (\text{g}) + \text{V} = 2\text{H}_2 (\text{g}) + \text{VO}_2$. While the traditional oxidation route by oxygen gas is: $\text{O}_2 + \text{V} = \text{VO}_2$. Accordingly, from the view point of thermo-dynamics, these reactions can be estimated by the system Gibbs free energy: $\Delta G = \Delta H - T \Delta S$. By using the general software HSC CHEMISTRY 6.0, we have calculated the Gibbs free energy for the reactions between water vapor/oxygen gas and metallic V film (Supplementary Table 1S). From the $\Delta G$ values for the final products of VO$_2$ and V$_2$O$_5$ with the temperature of 550°C as summarized in Table 1, it was deduced that for the reaction between water vapor and metallic V at 550°C, the final product would prefer to form VO$_2$, while not V$_2$O$_5$ compound, since the $\Delta G$ value to form VO$_2$ was -39.9 kcal, which was quite smaller than that of V$_2$O$_5$ ( $\Delta G$ = -21.4 kcal). However, for the traditional oxidation route

|                  | $\Delta G$ (VO$_2$)@550°C | $\Delta G$ (V$_2$O$_5$)@550°C |
|------------------|--------------------------|-------------------------------|
| H$_2$O(g) + V    | -39.9 kcal               | -21.4 kcal                    |
| O$_2$(g)+V       | -136.6 kcal              | -142.3 kcal                   |
by oxygen gas, the $\Delta G$ values for VO$_2$ and V$_2$O$_5$ formation were quite close, or even the $\Delta G$ value for V$_2$O$_5$ was smaller, which indicated that the reaction preferred to V$_2$O$_5$ formation. Since the final product by the oxidation of metallic V film had no obvious selection to VO$_2$ compound, it was difficult to prepare pure VO$_2$ with high quality by this reaction. This results were quite consistent with our experimental observations that the oxidation temperature window was quite narrow and the obtained 2-inch VO$_2$ film was not uniform by the traditional oxidation route in oxygen gas or in air.

In addition, it was reported that the reaction of H$_2$O molecules with the surface of oxides was more easily to occurrence than oxygen molecules in a dry environment at high temperature, which was usually known as the over-reduced environment. Thus it was deduced that during the wet-oxidation process at high temperature, H$_2$O molecules was adsorbed and chemically dissociated into OH$^-$ and H$^+$ on the oxides surface, perhaps due to the possible catalyst effect of vanadium oxides. Then the O-H bonds were further broken to form free oxygen ions to serve as the oxidizing agent, while some H atoms diffusion in the VO$_2$ crystal lattice would be favor to remove some crystal defect such as the oxygen vacancies, which further improve the quality of VO$_2$ film.

4. Conclusions

In summary, we have successfully prepared high quality VO$_2$ film with large-size by facile wet-oxidation technique. In this route, the water-vapor was used as a modest oxidizing agent and metallic V precursor film could be effectively oxidized to monoclinic VO$_2$ film with pure phase. Comparing with traditional oxidation method for VO$_2$ film preparation, the proposed wet-oxidation way not only improved the VO$_2$ film quality and uniformity, but also broadened the annealing temperature window greatly, which make the wafer-size VO$_2$ film preparation more easier and effective. It was suggested that the advantages of wet-oxidation method were mainly lying on the facile oxidation ability of water as well as the easy facility. The current studies supply a simple VO$_2$ film preparation with large-size, which should be meaningful for further
VO₂ based devices applications in the future. Furthermore, this simple and reproducible wet-oxidation technique demonstrates that the common water vapor can be used as a modest oxidizing agent, which should be applicable for prepare some other transition metallic oxides with multi-valance states.

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**Competing Interests**

The authors declare that they have no competing financial interests.

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