Growth without Postannealing of Monoclinic VO$_2$ Thin Film by Atomic Layer Deposition Using VCl$_4$ as Precursor

Wen-Jen Lee * and Yong-Han Chang

Department of Applied Physics, National Pingtung University, Pingtung 90003, Taiwan; crocodile710280@gmail.com
* Correspondence: wenjenlee@mail.nptu.edu.tw; Tel.: +886-8-7663800

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Abstract: Vanadium dioxide (VO$_2$) is a multifunctional material with semiconductor-to-metal transition (SMT) property. Organic vanadium compounds are usually employed as ALD precursors to grow VO$_2$ films. However, the as-deposited films are reported to have amorphous structure with no significant SMT property, therefore a postannealing process is necessary for converting the amorphous VO$_2$ to crystalline VO$_2$. In this study, an inorganic vanadium tetrachloride (VCl$_4$) is used as an ALD precursor for the first time to grow VO$_2$ films. The VO$_2$ film is directly crystallized and grown on the substrate without any postannealing process. The VO$_2$ film displays significant SMT behavior, which is verified by temperature-dependent Raman spectrometer and four-point-probing system. The results demonstrate that the VCl$_4$ is suitably employed as a new ALD precursor to grow crystallized VO$_2$ films. It can be reasonably imagined that the VCl$_4$ can also be used to grow various directly crystallized vanadium oxides by controlling the ALD-process parameters.

Keywords: vanadium dioxide; atomic layer deposition; vanadium oxide; vanadium tetrachloride; semiconductor-to-metal transition

1. Introduction

Vanadium dioxide (VO$_2$) has attracted extensive research interest during the past decades owing to its unique behavior, called semiconductor-to-metal transition (SMT) or insulator-to-metal transition (IMT), which accompanies the reversible and ultrafast phase transition between monoclinic VO$_2$ [VO$_2$(M)] and tetragonal rutile VO$_2$ [VO$_2$(R)] at temperatures around 340 K (~67 °C) [1–5]. Thus, the optical and electrical properties of VO$_2$ can be switched by controlling the SMT behavior of VO$_2$ [6,7]. Numerous factors for adjusting the SMT behavior of VO$_2$ have already been established that include impurity doping [8], stoichiometry [9], strain [10], grain boundary [11], oxygen vacancy [12], applied external electrical field [13], and light irradiation [14]. Therefore, the VO$_2$ has been widely investigated as a key material for applications in the smart thermochromic windows [15], two-terminal electronic devices [16], electric-field-effect three-terminal devices [17,18], integrated optical circuits [19], electronic oscillators [20], metamaterials [21], memristive devices [22], programmable critical thermal sensors [23], gas sensors [24], and so forth.

Various techniques had been employed for preparing VO$_2$ films, including the sol–gel method [22,23], electron-beam evaporation [25,26], sputtering [5,17], pulsed laser deposition (PLD) [27,28], molecular beam epitaxy (MBE) [16,29], chemical vapor deposition (CVD) [30–34], and atomic layer deposition (ALD) [35–50]. Among them, ALD is an excellent technique which has drawn much attention due to its many advantages, including preparation of the highly conformal thin films with almost 100% step coverage, accurate control of film thickness at the atomic scale,
low growth temperature, and wide-area uniformity. These features make ALD a powerful technique for the fabrication of emerging nanostructures and nanodevices [51–53].

Generally, organic vanadium compounds are employed as ALD precursors and reacted with H\textsubscript{2}O or O\textsubscript{3} to grow vanadium oxide thin films, such as tetrakis(ethylmethylamino)vanadium (TEMAV) [35–42], vanadyl isopropoxide (VTIP) [43–46], and vanadyl triisopropoxide (VTOP) [47–50]. However, the organic precursors (TEMAV, VTIP, and VTOP) are only suitable for low process temperatures in ALD because the decomposition temperatures of TEMA, VTIP, and VTOP are about 175 \degree C [35,40], 200 \degree C [43], and 180 \degree C [49,50], respectively. When the process temperature is higher than the decomposition temperature of the precursor, the growth mechanism of film will be changed from ALD to CVD-like mode [35,40,43,49,50]. In this case, the film is grown by CVD instead of ALD. This is why the low temperature of 120–170 \degree C is usually used for the film growth of ALD using TEMA, VTIP, or VTOP as precursor. However, the low process temperature is not enough to grow crystalline films. Therefore, the as-deposited vanadium oxide films grown by ALD from organic vanadium precursors are generally reported to have amorphous structures with no significant SMT behavior and a postannealing process is necessary for converting the amorphous to crystalline VO\textsubscript{2}. Previous studies have reported that postannealing in N\textsubscript{2}, He, O\textsubscript{2}, or N\textsubscript{2}/O\textsubscript{2} mixed gas with a low O\textsubscript{2} partial pressure resulted in crystalline monoclinic VO\textsubscript{2} for the temperature range of 425–585 \degree C [35–42]. Since the extra postannealing process is necessary to obtain a crystalline VO\textsubscript{2}, it results in higher manufacturing costs and increases the failure possibilities of the process and products.

This work reports that a directly crystalline VO\textsubscript{2} film has been successfully grown by ALD using vanadium tetrachloride (VCl\textsubscript{4}) and H\textsubscript{2}O as precursors at a reaction temperature of 350 \degree C without any postannealing process. It is noticed that the inorganic VCl\textsubscript{4} is used as an ALD precursor for the first time, although a few papers reported that the VCl\textsubscript{4} had been used in traditional chemical vapor deposition (CVD) techniques [30–32]. The VO\textsubscript{2} film has a significant SMT behavior with a VO\textsubscript{2}(M)-to-VO\textsubscript{2}(R) phase-transition temperature of about 61 ± 1 \degree C, which is verified from temperature-dependent Raman spectra and sheet-resistance variations of VO\textsubscript{2} film. Besides, the VO\textsubscript{2} film exhibits two orders of magnitude change in sheet resistance across the semiconductor-to-metal transition although the film thickness is only 30 nm. The results demonstrated that crystalline VO\textsubscript{2} films can be directly grown by ALD using VCl\textsubscript{4} and H\textsubscript{2}O as precursors without any postannealing process, presenting a new selection of precursors for the ALD process to grow the crystalline VO\textsubscript{2} films.

2. Materials and Methods

In this work, VO\textsubscript{2} films were grown on native silicon-oxide-covered Si (100) substrates by ALD at 350 \degree C with 1000 reaction cycles. VCl\textsubscript{4} and H\textsubscript{2}O were employed as precursors to grow the VO\textsubscript{2} films, and Ar was used as purge gas. The reservoirs of the VCl\textsubscript{4} and H\textsubscript{2}O precursors were kept at the temperatures of 30 and 25 \degree C, respectively. The dosing rates of VCl\textsubscript{4} and H\textsubscript{2}O were 0.288 and 0.296 cc/pulse, respectively, as determined by the reservoir temperature and vapor injection time. The flow rate of Ar was 5 sccm, as controlled by a mass flow controller (MFC, SEC-4400M, HORIBA STEC, Kyoto, Japan). An eight-step sequence of gas injection was applied in an ALD cycle, as combined four conventional gas-injection steps and four additional pump-down steps. The pump-down steps can effectively evacuate excess precursors and byproducts to obtain high-quality films with low Cl impurity contents and ensure the achievement of “true ALD mode” growth [54,55]. The time for each step in an ALD cycle was 0.1, 1, 0.5, 1, 0.5, 1, 0.5, and 1 s for VCl\textsubscript{4} vapor injection, pump-down, Ar purge, pump-down, H\textsubscript{2}O vapor injection, pump-down, Ar purge, and pump-down, respectively.

The crystalline structures of the VO\textsubscript{2} films were examined by an X-ray diffractometer (XRD, D8 Advance Eco, Bruker, Karlsruhe, Germany) at 30 and 90 \degree C. The surface morphologies of the film were observed with a high-resolution scanning electron microscope (SEM, SU8000, Hitachi, Tokyo, Japan). In addition, in order to obtain real surface morphology of the film, the SEM analysis was performed without any conductive coating on the VO\textsubscript{2} film surface. The cross-sectional microstructures of the VO\textsubscript{2}...
films were observed by a high-resolution transmission electron microscope (TEM, JEM-2100F, JEOL, Tokyo, Japan). The film thickness was measured from the cross-sectional TEM micrograph and the growth rate of the VO<sub>2</sub> film was estimated from an equation of “growth rate = (film thickness/numbers of ALD cycles)”. The chemical composition of the VO<sub>2</sub> film was analyzed by a high-resolution X-ray photoelectron spectrometer (XPS, Quantera SXM, ULVAC-PHI, Chigasaki, Japan). In addition, the XPS analysis was performed on the VO<sub>2</sub> film surface before and after Ar ion etching with an etching depth of about 2 nm. The temperature-dependent Raman spectra of the VO<sub>2</sub> film were examined at temperatures between 30 and 80 ºC by a micro Raman spectrometer (Raman, UniRAM II, Uninanotech, Yongin, Korea) with a temperature-controllable sample stage. The temperature-dependent sheet resistance of the VO<sub>2</sub> film was measured at temperatures between 30 and 90 ºC by a Keithley 2614B SourceMeter (Keithley, Solon, OH, USA) under a four-point probing configuration with a temperature-controllable sample stage.

3. Results and Discussion

Figure 1 shows the XRD patterns of VO<sub>2</sub> film measured at 30 and 90 ºC, which demonstrate the structural transition of VO<sub>2</sub> film from monoclinic (30 ºC) to tetragonal rutile (90 ºC) phase. The VO<sub>2</sub> film measured at 30 ºC (Figure 1a) displays that two XRD peaks located at 2θ of 27.9º and 55.4º can be indexed to the (011) and (220) planes of monoclinic VO<sub>2</sub>(M) (JCPDS no.: 82–0661), respectively. When the temperature is raised to 90 ºC (Figure 1b), two XRD peaks located at 2θ of 27.6º and 55.4º are detected, which can be assigned to the (110) and (211) planes of tetragonal rutile VO<sub>2</sub>(R) (JCPDS no.: 79–1655), respectively. In addition, because the VO<sub>2</sub> film is grown on Si substrate, an obvious XRD peak of Si (113) at 2θ of 51.9º has also been detected (Supplementary materials: Part 1). Figure 1c is a comparison of Figure 1a,b, which clearly shows an XRD peak shift of VO<sub>2</sub>(M) (011) to VO<sub>2</sub>(R) (110) peak in 26º ≤ 2θ ≤ 30º and the XRD peak of Si substrate does not shift. The XRD peak-shifting behavior is a diagnostic feature for the phase transition of VO<sub>2</sub> film from monoclinic to tetragonal rutile structure. Previously, the similar XRD peak-shifting phenomenon had also been reported by Wu et al. [56] for confirming the phase transformation of monoclinic VO<sub>2</sub> to tetragonal rutile VO<sub>2</sub>.

![Figure 1. XRD patterns of VO<sub>2</sub> film measured at (a) 30 ºC and (b) 90 ºC. (c) A comparison of (a) and (b).](image-url)

Figure 2 shows the SEM and TEM analyzed results for surface and cross-sectional microstructures of the VO<sub>2</sub> film, respectively. The SEM image of surface morphology of the VO<sub>2</sub> film (Figure 2a) displays a conformal VO<sub>2</sub> film with bigger grains surrounded by small grains; the grain sizes of big and small grains are about 78 ± 14 and 40 ± 6 nm, respectively. According to the cross-sectional TEM bright-field and dark-field images (Figure 2b,c), it can be clearly observed that the VO<sub>2</sub> film is grown on a native oxide layer (SiO<sub>x</sub>) of Si substrate and constructed from columnar grains. The thickness of the VO<sub>2</sub> film is about 30 nm, and displays its growth rate at about 0.03 nm/cycle. Moreover, the VO<sub>2</sub>
grains are directly crystallized and grown on the top surface of the native oxide layer, which is verified by the high-resolution TEM (HR-TEM) image of the VO2/SiOx/Si interface (Figure 2d). The HR-TEM image also reveals a clear lattice fringe of about 0.32 nm, corresponding to the (011) plane of VO2(M). The selected-area electron-beam diffraction (SA-EBD) pattern obtained by focusing the electron beam on an individual VO2 grain is shown in Figure 2e; the SA-EBD pattern can be indexed to monoclinic VO2(M) in agreement with the XRD results.

Figure 2. Microstructure analyses of VO2 film. (a) An SEM top-view image. TEM cross-sectional (b) bright-field and (c) dark-field images. (d) A high-resolution TEM (HR-TEM) image of the VO2/SiOx/Si interface. (e) The selected-area electron-beam diffraction (SA-EBD) pattern obtained by focusing the electron beam on an individual VO2 grain.

Figure 3 shows the V2p, O1s, and Cl2p XPS spectra for original (before etching) and after argon-ion etching surface of VO2 film. In addition, the chemical composition of VO2 film calculated from XPS spectra are shown in Table 1. The V and O concentrations of VO2 film are about 25.7 at.% and 74.3 at.%, respectively, for the film before surface etching and are about 33.1 at.% and 66.9 at.%, respectively, for the film after surface etching. The results clearly indicate that the original surface of the VO2 film has a higher oxygen concentration because the VO2 film was exposed to air (oxygen-rich) environment, resulting in absorption of oxygen and a native oxide layer (overoxidation layer) forming on the surface of the VO2 film [26,33,34,41,43,57,58]. After argon-ion etching, surface contamination and the native oxide layer of the VO2 film had been removed, and the atomic proportion of V:O atom was about 1:2 in agreement with the stoichiometry of VO2. Besides, no Cl impurity had been detected in the VO2 film, demonstrating the Cl concentration in the VO2 film was lower than the detection limit of XPS (approximately 0.1 at.%). It is noteworthy that this work successfully achieved VO2 film with high purity (Cl impurity <0.1 at.%) by using a low growth temperature of 350 °C, which can be attributed to the additional pump-down steps in the ALD reaction cycles effectively evacuating excess precursors and byproducts [54]. In a previous study, Cheng et al. reported that implementation of pump-down steps into the gaseous-pulse cycle of ALD can effectively reduce the Cl residues. They used TiCl4 as ALD precursor to grow TiN films by using conventional four-step ALD and modified six-step ALD (adding two pump-down steps). Their results showed that the Cl residues of TiN films can be decreased from about 7.7 at.% to 2.3 at.% at the growth temperature of 300 °C [54].

In Figure 3a, the V2p3/2 peak of the original VO2 film (before surface etching) can be fitted with two peaks at binding energy of about 517.2 and 515.6 eV, which can be assigned to V5+ and V4+, respectively [26,33,34,39,41,43,57,58]. Musschoot et al. [43] and Sliversmit et al. [57] reported that the V5+ signal is mainly contributed from the native oxide layer (overoxidation layer) of VO2 film. After surface etching (to remove the native oxide layer), the V2p3/2 peak has a maximum at 515.6 eV (assigned to V4+), which primarily confirms VO2 stoichiometry. In Figure 3b, the O1s XPS peaks are located at binding energy of about 529.8 and 530.5 eV for the original and after-surface-etching VO2 film, showing a peak-shifting phenomenon. The similar peak-shifting phenomenon of O1s XPS peak for VO2 film after surface etching by argon ion sputtering had also been observed by Musschoot et al. [43].
Figure 3. (a) V2p, (b) O1s, and (c) Cl2p XPS spectra for original (before etching) and after argon-ion etching surface of VO$_2$ film.

Table 1. Chemical composition of VO$_2$ thin film analyzed by XPS.

<table>
<thead>
<tr>
<th>Elemental Content</th>
<th>Before Surface Etching</th>
<th>After Surface Etching</th>
</tr>
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<tbody>
<tr>
<td>V (at.%)</td>
<td>25.7</td>
<td>33.1</td>
</tr>
<tr>
<td>O (at.%)</td>
<td>74.3</td>
<td>66.9</td>
</tr>
<tr>
<td>Cl (at.%)</td>
<td>&lt;0.1</td>
<td>&lt;0.1</td>
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Figure 4a,b show the selected temperature-dependent Raman spectra of the VO$_2$ film for heating and cooling cycles, respectively. It is noticed that the full temperature-dependent Raman spectra of the VO$_2$ films for temperatures between 30 and 80 °C in heating and cooling cycles are shown in Figures S1 and S2, respectively. As shown in Figure 4, four Raman peaks at 194, 224, 305, and 616 cm$^{-1}$ are associated with the monoclinic phase VO$_2$ [25,26,59–61]. The peaks of 194, 305, and 616 cm$^{-1}$ are assigned to $A_g$ phonon vibration modes [25,26,59,60] and the peak of 224 cm$^{-1}$ can be assigned to $A_g + B_g$ mode [61]. The low-frequency phonons at 194 and 224 cm$^{-1}$ relate to lattice motion involving V–V bonds, while the other peaks are attributed to V–O bonds [26,59–61]. Peaks located at 301, 520, and 935–990 cm$^{-1}$ are contributed from the silicon substrate that compared with the Raman spectrum of the silicon substrate (Figure 5). Moreover, the phonon intensities of 194, 224, and 616 cm$^{-1}$ gradually disappear as the temperature increases and display the reversibility during the cooling cycle. However, the peak intensity of 305 cm$^{-1}$ does not show an evident change due to an overlap signal between 305 and 301 cm$^{-1}$ for VO$_2$ and silicon substrate, respectively.
Figure 4. Temperature-dependent Raman spectra of the VO$_2$ film: (a) heating cycle, (b) cooling cycle, and relative Raman intensity of the $A_g$ phonon mode at (c) 194, (d) 224, and (e) 616 cm$^{-1}$.

Figure 5. Raman spectrum of the silicon substrate.

Furthermore, the plots of normalized Raman intensity variations for the $A_g$ phonon vibration mode at 194, 224, and 616 cm$^{-1}$ are shown in Figure 4c, d, e, respectively. The normalized Raman intensity of VO$_2$ film was calculated from the equation below:

$$I_{NRI} = \frac{I_T - I_{80}}{I_{30} - I_{80}}$$

where $I_{NRI}$ is the normalized Raman intensity, $I_T$ is the Raman intensity measured at indicated temperature ($T$), $I_{30}$ and $I_{80}$ are the Raman intensities measured at 30 and 80 °C, respectively. It can be seen clearly that the plots of Raman intensity vibrations show a hysteresis feature for Raman shift at 194, 224, and 616 cm$^{-1}$. The phase transition temperatures of VO$_2$ film estimated by the differential curves (as inserts) are about 65, 63.9, and 64.5 °C for 194, 224, and 616 cm$^{-1}$ in the heating process, respectively. In the cooling process, the phase transition temperatures of VO$_2$ film are about 57.6, 56.6, and 58.7 °C for 194, 224, and 616 cm$^{-1}$, respectively. Therefore, the overall SMT temperatures
estimated from the middle of the hysteresis curves are about 61.3, 60.25, and 61.6 °C for 194, 224, and 616 cm\(^{-1}\), respectively.

The temperature-dependent sheet-resistance (SR) variation of VO\(_2\) film is shown in Figure 6, displaying a thermal hysteresis variation. Besides, the SR variation has approached two orders of magnitude across the semiconductor-to-metal transition (SMT) of the VO\(_2\) film (SR changed from \(2.2 \times 10^4\) to \(2.7 \times 10^2\) Ω/□ for the temperature raised from 40 to 80 °C) so that the value of the resistance ratio agrees with the typical VO\(_2\) film thickness less than 50 nm (typically, the resistance ratios of most VO\(_2\) films across the SMT are in the range of \(10^2\)–\(10^3\) for thickness <50 nm) [29]. Furthermore, a sharp drop of SR can be clearly observed in the heating cycle, determining a phase transition temperature of about 63 °C, and a sharp rise of SR in the cooling cycle with a phase transition temperature of about 56 °C can be also seen in Figure 6. Therefore, the SMT temperature estimated from the middle of thermal hysteresis SR variation is about 60.0 °C.

![Figure 6. Temperature-dependent sheet-resistance variation of the VO\(_2\) film.](image)

There are several parameters that may affect the temperature-dependent electrical properties of VO\(_2\), such as changes in impurity content, stoichiometry, strain, oxygen vacancies, and the presence of grain boundaries [8–12]. In this work, the SMT temperature of VO\(_2\) film evaluated from the temperature-dependent Raman spectra and sheet-resistance variation is about 61 ± 1 °C, slightly different from the well-known 340K (~67 °C), which can be reasonably attributed to the influence of grain boundary density because the VO\(_2\) film has a polycrystalline structure with considerable grain boundaries.

4. Conclusions

In conclusion, the VCl\(_4\) is successfully employed as a new ALD precursor to grow a VO\(_2\) film on the Si (100) substrate. Besides, without any postannealing process required, the as-deposited VO\(_2\) film is directly crystallized and provides a significant SMT property. Moreover, it can be reasonably imagined that the VCl\(_4\) can be used not only to grow crystalline VO\(_2\) films, but also to grow other different vanadium oxides (VO\(_x\), \(x \neq 2\)) by controlling the ALD-process parameters (such as process temperature, VCl\(_4\)/H\(_2\)O ratio, and so forth). It is just like this that the VCl\(_4\) had been used as a precursor for atmospheric pressure CVD to grow different vanadium oxides (VO\(_2\) and V\(_2\)O\(_5\)) by controlling process parameters of temperature and VCl\(_4\)/H\(_2\)O ratio [30–32]. We anticipate this work to be a starting point for using VCl\(_4\) as a precursor to grow various directly crystallized vanadium oxides by ALD without any postannealing process.

Supplementary Materials: The following are available online at http://www.mdpi.com/2079-6412/8/12/431/s1,
Part 1: A brief report provided by Bruker Corporation for explaining “Why Si (113) peak appears in GIXRD profile?”
Part 2: Full temperature-dependent Raman spectra of the VO\(_2\) films. Figure S1: Raman spectra of the VO\(_2\) film measured at indicant temperature for heating cycle (temperature from 30 to 80 °C), Figure S2: Raman spectra of the VO\(_2\) film measured at indicant temperature for cooling cycle (temperature from 78 to 35 °C).
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Conflicts of Interest: The authors declare no conflict of interest.

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