Atomic layer deposition of vanadium oxide thin films from tetrakis(dimethylamino)vanadium precursor

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Atomic layer deposition (ALD) of vanadium oxide (VOx) thin films, using tetrakis(dimethylamino)vanadium as the vanadium precursor, is comprehensively reported in this work. The vanadium precursor is highly volatile and can be used at room temperature for deposition. Either H2O or O3 can be used as the coreactant for depositing VOx at 50–200 °C. However, partial precursor decomposition is suggested for the deposition temperature higher than 160 °C. The as-deposited VOx films are pure, smooth, and amorphous, and can be crystallized into monoclinic VO2 phase by postdeposition annealing under N2 ambient. The minimum annealing temperature for film to crystallize is found, by in situ high-temperature X-ray diffraction experiments, at around 550–600 °C. In situ quartz crystal microbalance experiments are performed to further analyze the surface reaction mechanism involved in this ALD process.

I. INTRODUCTION

Vanadium oxide (VOx) has been extensively studied for many decades, due to its polymorphism and wide applications in a variety of fields.1 The properties of VOx are closely related to its stoichiometry, crystal structure, and morphology.1 Among various VOx compounds, VO2 and V2O5 are particularly important for studying. Vanadium atoms in VO2 and V2O5 are in their +4 and +5 oxidation states, respectively. VO2 is featured for its well-known metal-insulator transition near 67 °C.2 This transition leads to an abrupt reduction in resistivity and infrared transmission, and therefore renders VO2 promising for nanoelectronic switches,3 transistors,4 and optical devices.5 V2O5 also has a fairly wide scope of applications. Examples include cathode materials for lithium-ion batteries6 and sodium-ion batteries,7 active materials for supercapacitors,8,9 charge-injection-layer materials for field-effect transistors,10 and catalysts for organic synthesis.11

Synthesis techniques for VOx thin films are of great importance to realize the material applications. Over the years, various preparation approaches have been developed for VOx thin films, such as sol–gel,12 spray pyrolysis,13 electrodeposition,14 evaporation,15 magnetron sputtering,16 pulsed laser deposition,17 chemical vapor deposition,18 and atomic layer deposition (ALD).6,8,19–32 Among these approaches, ALD is of particular interest for preparing thin films. ALD employs alternate saturated self-limiting surface chemistry reactions, and allows one to deposit thin films in a well-controlled layer-by-layer fashion.33 The properties of ALD films, such as composition, crystal structure, and morphology, are highly consistent, reproducible, and uniform over large area, and meanwhile the thickness of deposited films can be precisely controlled at an atomic level by digitally adjusting the total ALD cycles. Moreover, ALD also allows for conformal thin-film coating on high aspect-ratio 3D structures, which is essential

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for realizing the above-mentioned high-performance batteries/supercapacitors applications, as well as various other applications.

ALD of VO₂ has been reported using several types of vanadium precursors. Vanadyl triisopropoxide was a commonly used vanadium precursor and was applied for both thermal (with water or ozone) and plasma-enhanced ALD processes. A similar precursor, vanadium n-propoxide, could also be used along with acetic acid to produce ALD V₂O₄. Also, VOCl₃ could be used with water to deposit VO₂. Postdeposition annealing was also attempted to crystallize the deposited VO₂ thin films. The base pressure of the deposition chamber was ~0.3 Torr during the step of purging with N₂. All the N₂ was purified through a Gatekeeper inert gas purifier. The deposition temperature was varied from 50 to 200 °C. Flow-through mode was used for all the ALD processes. A long purging time of 100 s was used after each precursor dose, allowing for a complete removal of the by-products as well as unreacted excess precursors. Si wafer and fused silica substrates were used for deposition studies. Both the substrates were treated with ultraviolet/ozone for 5 min before deposition, and the native oxide on Si was not intentionally removed.

B. Characterizations of precursor and VO₂ films

Thermogravimetric (TG) analyses were performed on a Mettler-Toledo TGA-2 system (Schwerzenbach, Switzerland) under N₂ ambient inside a glovebox. Approximately 10 mg of V(dma)₄ sample was used for each measurement. 50 sccm of N₂ gas was used as the flow gas, and the temperature ramping rate was set as 10 °C/min. Both open-cup and close-cup modes were used for the TG measurements. Under close-cup condition, the sample crucible was covered by a lid with a pinhole of 1 mm diameter, which could slow down the release of V(dma)₄ vapor and allow the precursor to be exposed to a higher temperature for evaluating its thermal stability.

The thickness of the deposited VO₂ films was measured by X-ray reflectometry (XRR) using a Göbel mirror Cu Kα radiation (D8 Advance, Bruker Corporation, Karlsruhe, Germany). The film composition was analyzed by X-ray photoelectron spectroscopy (XPS) using monochromated Al Kα radiation. A Thermo Fisher Scientific, East Grinstead, United Kingdom. The pass energies for survey and high-resolution scans were 50 and 20 eV, respectively. To remove the adventitious carbon on sample surface, 20 s of 2 keV Ar⁺ sputtering was performed prior to each XPS measurement. X-ray diffraction (XRD) was used to analyze the film crystallinity. Regular XRD experiments were performed on the same Bruker diffractometer as for XRR. In situ high-temperature XRD (HTXRD) was performed on a Rigaku SmartLab diffractometer (Rigaku Corporation, Tokyo, Japan) equipped with an Anton-Paar oven under N₂ ambient. The HTXRD spectra were taken at temperatures ranging from 200 to 800 °C in steps of 50 °C. The temperature ramping rate was set as 10 °C/min, and additional 10 min waiting time was set to stabilize the
temperature before taking each spectrum. Atomic force microscopy (AFM; MultiMode 8, Bruker Corporation, Santa Barbara, California) and scanning electron microscopy (SEM; SUPRA55, Carl Zeiss AG, Oberkochen, Germany) were used to examine the film surface morphology. QCM was used to in situ investigate the reaction mechanism. The QCM consisted of a gold-covered quartz crystal sensor with an oscillation frequency of ~6 MHz, and the change of the frequency was monitored by an Inficon SQC-310 controller (East Syracuse, New York).

III. RESULTS AND DISCUSSION

TG analysis was used to evaluate the volatility and thermal stability of the vanadium precursor V(dma)$_4$. The TG experiments were performed under both open-cup and close-cup conditions. As shown in Fig. 1, the curves exhibited only a single step of weight loss, indicating a favorable single-step evaporation process upon heating. In particular, the TG weight loss started at a fairly low temperature under open-cup condition (1% weight loss at 70 °C) and completed at ~160 °C, with only ~2.5% in residual mass at the end of temperature ramping. This suggested that V(dma)$_4$ is a highly volatile compound with sufficient thermal stability to serve as a suitable precursor for ALD. Moreover, V(dma)$_4$ is comparatively much more volatile than V(NEtMe)$_4$, a previously reported$^{28}$ vanadium precursor which has a similar chemical structure as V(dma)$_4$. The TG weight loss for V(NEtMe)$_4$ was reported to finish at ~210 °C, and its evaporation temperature was set as 65 °C during ALD.$^{28}$ In our case, V(dma)$_4$ completed weight loss at a much lower temperature around 160 °C, and therefore we expected (validated later) that room temperature should be enough to provide sufficient V(dma)$_4$ vapor for ALD. Thus, no additional heating is needed for this precursor, which can greatly simplify the design of ALD reactors for future large-scale applications. On the other hand, it was also suggested that V(dma)$_4$ might partially decompose during high-temperature ALD (>190 °C), since the TG curve under close-cup condition showed an appreciably higher residual mass (8% above 200 °C), which was likely from the thermal decomposition.

ALD of vanadium oxide thin films were performed following the procedure described in the Experimental Section. As we previously demonstrated for the deposition at 50 °C,$^{32}$ single doses for both V(dma)$_4$ and H$_2$O were sufficient to, respectively, provide enough precursor exposures to saturate the ALD surface reactions. We therefore continued to use single doses for the precursors in this study. The equivalent exposures for single doses were roughly 0.02 and 0.05 Torr s for V(dma)$_4$ and H$_2$O, respectively. Single dose was also used for O$_3$, which corresponded to 0.03 Torr s in exposure, assuming negligible decomposition of O$_3$ during delivering. The temperature dependence of the VO$_x$ film growth rate is plotted in Fig. 2. The growth rates remained fairly constant up to 120 °C, but substantially increased above 160 °C, which was likely due to partial thermal decomposition at higher temperatures. Below 120 °C, the VO$_x$ growth rate using O$_3$ as the oxygen source was ~0.045 nm/cycle, which was ~50% higher than the growth rate using H$_2$O (~0.030 nm/cycle).

The chemical composition of the deposited VO$_x$ films were examined by XPS. The XPS signals were collected on the VO$_x$ samples with 20 s of Ar$^{+}$ sputtering to remove the adventitious carbon on surface. Figure 3 displays a set of representative spectra for a 15 nm film deposited at 120 °C using H$_2$O as the coreactant. The survey spectrum [Fig. 3(a)] shows that the deposited film contained the elements of V, O, C, N, and Ar, where the impurities of C and N were likely from the amino ligand of V(dma)$_4$, and Ar was from the sputtering cleaning process. High-resolution XPS scans for V, O, C, and N were also performed, and the spectra are shown in Figs. 3(b)–3(e). The elemental atomic percentages of the films deposited under various conditions were further extracted from the

![FIG. 1. TG curves of V(dma)$_4$ performed under open-cup and close-cup conditions.](https://www.cambridge.org/core/terms).
XPS data and listed in Table I. For all these deposition conditions, both the C and N impurity levels were fairly low (<3 at.%), suggesting that the deposited VO\(_x\) films were fairly pure. The atomic ratios of O/V were also included in Table I. Pure VO\(_2\) and V\(_2\)O\(_5\) should have O/V ratios of 2 and 2.5, respectively. However, the measured ratios were all between 2 and 2.5, without any clear trends on the deposition conditions. Similar results were also obtained with the use of V(NEtMe)\(_4\) as the vanadium precursor. It should be noted that the film oxygen content could also be affected by post oxidation after the films were exposed to air, and also, incorporation of water and/or unreacted hydroxyl groups during deposition could deviate the oxygen content from ideal stoichiometry as well. Deconvolution of the high-resolution V 2\(\text{p}_{3/2}\) spectrum [Fig. 3(b)] suggested the presence of both V\(^{4+}\) (516.2 eV) and V\(^{5+}\) (517.6 eV) in the film, but further attempts to quantify the V\(^{4+}\)/V\(^{5+}\) ratio were found to involve too much uncertainty to draw any solid conclusions.

All the as-deposited VO\(_x\) films were amorphous, as there were no peaks in their XRD spectra. The films were also quite smooth. As examined by AFM, the rms roughness was only ~0.32 nm for the films (approximately 10 nm in thickness) deposited with water at 50 or 120 °C. The films deposited with ozone was slightly rougher, with the rms roughness around 1.0 nm for the films deposited at 50 or 80 °C. Representative AFM images are shown in Fig. 4. Notice that no grain-like features were observed by AFM, which was consistent with the amorphous nature of these films.

Postdeposition annealing was attempted to crystallize the amorphous VO\(_x\) films. As suggested by previous reports, we performed the annealing under N\(_2\) ambient, aiming to form crystalline VO\(_2\) films. Several ALD VO\(_x\) films deposited with H\(_2\)O at 50 °C on fused silica substrates were used for this annealing study. The film thickness ranged from 30 to 60 nm, with no observable difference in this study. After 2 h annealing at 800 °C under N\(_2\), we found that the amorphous VO\(_x\) films indeed converted to a monoclinic phase of VO\(_2\) (PDF#44–0252). The XRD spectra of the film before and after the annealing are comparatively shown in Fig. 5. On the other hand, the film showed severe agglomeration after the annealing; the film became discontinuous and formed submicron-sized islands (Fig. 6). To better understand the temperature effect during annealing, we performed in situ HTXRD for these ALD VO\(_x\) films. An amorphous ALD VO\(_x\) film (approximately 60 nm in thickness) was heated from room temperature to 800 °C with a temperature ramping rate of 10 °C/min. During the heating process, XRD spectra were taken in steps of 50 °C from 200 °C.

As the results shown in Fig. 7, the XRD spectra started to show pronounced crystalline VO\(_2\) peaks at 600 °C, suggesting that the film crystallization probably occurred at 550–600 °C. Based on the HTXRD results, we performed another ex situ annealing experiment at 600 °C. As the results shown in Fig. 7, the XRD spectra started to show pronounced crystalline VO\(_2\) peaks at 600 °C, suggesting that the film crystallization probably occurred at 550–600 °C. Based on the HTXRD results, we performed another ex situ annealing experiment at 600 °C. However, the annealed film was still discontinuous, with almost identical island morphology as after 800 °C annealing [Fig. 6(b)]. As Peter et al. and Rampelberg et al. both pointed out, besides annealing temperature, O\(_2\) partial pressure was also a critical factor to maintain the continuity of VO\(_x\) films after annealing. We therefore
suspected that the lack of O$_2$ control in our annealing ambient was perhaps the reason for agglomeration, although further experiments are needed to confirm this.

On the other hand, understanding surface reaction mechanism is of great importance for an ALD process. To elucidate the mechanism involved in this VO$_x$ ALD process, we further performed in situ QCM experiments to monitor the growth behavior of VO$_x$ using H$_2$O as the oxygen source. The QCM experiments were performed at 50 °C using the same recipe as that for the film depositions. The dosing times for V(dma)$_4$ and H$_2$O were both 1 s, and the purging times after each precursor dose were all 100 s. Figure 8(a) displays the mass gain on the QCM sensor during 50 cycles of ALD. The mass gain showed a generally linear behavior with deposition time, suggesting a well-behaved linear growth for this ALD process. To further analyze the mass gain, an enlarged view for three consecutive ALD cycles was representatively plotted in Fig. 8(b). The mass gain showed a jump increase when V(dma)$_4$ or H$_2$O was dosed into the chamber, and then gradually decayed and flattened out during the following purging step. The jump increase should correspond to the chemical reactions occurred on the surface, and the following decay process was likely due to the desorption of the physisorbed excess V(dma)$_4$ or H$_2$O, or the byproduct dimethylamine molecules. Since we used a fairly low deposition temperature of 50 °C, the molecule desorption rate was relatively slow. It should be noted that the spike-like signals when dosing V(dma)$_4$ were probably interfered with the temperature effect, since the high-pressure assisting gas could suddenly fluctuate the sensor temperature and change the apparent mass reading on QCM. However, this temperature effect should last only for a few seconds in our system [control experiments were performed without supplying V(dma)$_4$], and, therefore, the following decay, which lasted for several tens of seconds, was indeed caused by the change of mass on the QCM sensor.

From the QCM curve [Fig. 8(a)], we further extracted the mass changes for each ALD cycle ($m_0$) and each vanadium half cycle ($m_1$), and plotted $m_0$ and $m_1/m_0$ ratios in Fig. 8(c). The mass gain for each ALD cycle ($m_0$) was quite constant at around 1.37 ± 0.13 Hz, which again indicated a constant per cycle growth rate for this ALD process. The $m_1/m_0$ ratio was also quite constant at...
around 1.01 ± 0.05, which suggested that the surface reaction chemistry was consistent over the entire deposition time. The $m_1/m_0$ ratio can be further used to analyze the surface reaction mechanism. As dimethylamino metal precursors are commonly suggested to follow ligand-exchange mechanisms, we first assume that this ALD VO$_x$ process follows a simple ligand-exchange mechanism, and the associated two half-cycle reactions are rewritten as the following:

$$-(\text{OH})_y + V(\text{N(CH}_3)_2)_4(g) \rightarrow$$

$$-O_yV(\text{N(CH}_3)_2)_{4-y} + y\text{NH(}\text{CH}_3)_2(g), \quad (1a)$$

$$-O_yV(\text{N(CH}_3)_2)_{4-y} + 2\text{H}_2\text{O(g)} \rightarrow$$

$$-(\text{VO}_2)(\text{OH})_y + (4-y)y\text{NH(}\text{CH}_3)_2(g), \quad (1b)$$

where the symbols “$-$” and “(g)” denote the surface and gaseous compounds, respectively. In Eq. (1a), a V(dma)$_4$ molecule reacts with $y$ number of surface hydroxyl groups, and affords $y$ numbers of V–O bonds on surface and $y$ numbers of gaseous dimethylamine molecules. Notice that $(4-y)$ number of dimethylamino ligands are still attached on the vanadium at the end of the first (vanadium) half cycle. These attached dimethylamino ligands will react with H$_2$O in the second (water) half cycle, following Eq. (1b), and afford surface hydroxyl groups at the end. Thus, according to Eqs. (1a) and (1b), the mass gain ratio, $m_1/m_0$, should be equal to $(227 - 45y)/83$. Plugging in the experimental data, $y$ is calculated as 3.18, implying that 3.18/4 (or ∼80%) of dimethylamino groups are released in the vanadium half cycle. It should be noted that the surface dimethylamino groups can also possibly undergo partial decomposition to form methyleneamino groups, as observed for other dimethylamino metal precursors. If we arbitrarily assume that this decomposition is 100% in our case, the equations should be rewritten as the following:

$$-(\text{OH})_y + V(\text{N(CH}_3)_2)_4(g) \rightarrow$$

$$-O_yV(N = CH_2)_{4-y} + (4-y')CH_4(g) + y'\text{NH(}\text{CH}_3)_2(g), \quad (2a)$$

$$-O_yV(N = CH_2)_{4-y} + 2\text{H}_2\text{O(g)} \rightarrow$$

$$-(\text{VO}_2)(\text{OH})_y + (4-y')\text{NH} = \text{CH}_2(g), \quad (2b)$$

where $y'$ is used to distinguish from $y$ as previously used in Eqs. (1a) and (1b). With similar analysis as above, $y'$ is calculated as 2.73, corresponding to ∼68% of dimethylamino groups released in the vanadium half cycle. The real case for $y$ (or $y'$) should be expected to be between 2.73 and 3.18. To find out the exact percentage of decomposition, one would probably need some other in situ techniques, such as in situ XPS. But, nevertheless, the value for $y$ (or $y'$) is fairly high (roughly 3), implying that approximately three surface hydroxyl groups are needed to react with each V(dma)$_4$ molecule in the vanadium half cycle.
analyze the surface reaction chemistry during ALD. The in situ mechanism study using QCM was also performed to no longer continuous and formed submicron-sized islands. Annealing under N\textsubscript{2} ambient could crystallize the as-deposited films to monoclinic VO\textsubscript{2} phase. In situ HTXRD characterizations were performed on the ALD VO\textsubscript{2} films. The deposited films were found fairly pure, with the impurity levels for C and N both below 3 at.%. All the as-deposited films were amorphous and smooth. Postdeposition annealing under N\textsubscript{2} ambient could crystallize the as-deposited films to monoclinic VO\textsubscript{2} phase. In situ HTXRD suggested that the minimum temperature needed for film crystallization was at around 550–600 °C. However, annealing (at either 600 or 800 °C) could lead to severe film agglomeration, and as a result, the annealed films were no longer continuous and formed submicron-sized islands. In situ mechanism study using QCM was also performed to analyze the surface reaction chemistry during ALD. The QCM results showed that the VO\textsubscript{2} film growth followed a consistently linear growth, and each V(dma)\textsubscript{4} molecule was suggested to react with approximately three surface hydroxyl groups in the vanadium half cycle during ALD.

IV. CONCLUSIONS

In summary, we performed a comprehensive study of ALD for VO\textsubscript{2} thin films using tetrakis(dimethylamino) vanadium [i.e., V(dma)\textsubscript{4}] as the vanadium precursor. The V(dma)\textsubscript{4} precursor was highly volatile, and therefore no additional precursor heating was needed for deposition. Both H\textsubscript{2}O and O\textsubscript{3} were investigated as the coreactant for depositing VO\textsubscript{2}. The deposition temperature was explored from 50 to 200 °C. The film growth rates remained fairly constant up to 120 °C, but substantially increased above 160 °C, which was likely due to partial thermal decomposition at higher temperatures. Below 120 °C, the VO\textsubscript{2} growth rate using O\textsubscript{3} was ~0.045 nm/cycle, and the growth rate using H\textsubscript{2}O was ~0.030 nm/cycle. Careful material characterizations were performed on the ALD VO\textsubscript{2} films. The deposited films were suggested to react with approximately three surface hydroxyl groups in the vanadium half cycle during ALD.

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