Facile Phase Control of Multivalent Vanadium Oxide Thin Films (V$_2$O$_5$ and VO$_2$) by Atomic Layer Deposition and Postdeposition Annealing

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ABSTRACT: Atomic layer deposition was adopted to deposit VO$_x$ thin films using vanadyl tri-isopropoxide (VO[O-(C$_3$H$_7$)$_3$])$_3$, VTIP) and water (H$_2$O) at 135 °C. The self-limiting and purge-time-dependent growth behaviors were studied by ex situ ellipsometry to determine the saturated growth conditions for atomic-layer-deposited VO$_2$. The as-deposited films were found to be amorphous. The structural, chemical, and optical properties of the crystalline thin films with controlled phase formation were investigated after postdeposition annealing at various atmospheres and temperatures. Reducing and oxidizing atmospheres enabled the formation of pure VO$_2$ and V$_2$O$_5$ phases, respectively. The possible band structures of the crystalline VO$_2$ and V$_2$O$_5$ thin films were established. Furthermore, an electrochemical response and a voltage-induced insulator-to-metal transition in the vertical metal–vanadium oxide–metal device structure were observed for V$_2$O$_5$ and VO$_2$ films, respectively.

KEYWORDS: atomic layer deposition, vanadium oxide, postdeposition annealing, electrochromism, insulator-to-metal transition

1. INTRODUCTION

Transition metal oxides with partially filled d electron shells have drawn significant attention because of the reversible phase transition between the metal and insulator states, which makes them distinct from conventional insulators or semiconductors. Vanadium, with an electronic configuration of [Ar]3d$^3$4s$^2$, forms multivalent oxides with ionic bonding, for example, VO, V$_2$O$_5$, V$_2$O$_3$, VO$_2$, and V$_2$O$_4$, because of the switchable valence of vanadium ions. Among vanadium oxides with different cation/anion ratios, VO$_2$ and V$_2$O$_5$ are the most extensively studied because of their various applications. Vanadium pentoxide (V$_2$O$_5$), a band insulator with a 3d$^0$ electronic configuration, is the most stable compound and has been receiving attention for its broad application in smart windows and gas sensors because of its electrochemical properties. On the other hand, vanadium dioxide (VO$_2$), a correlated insulator with a 3d$^1$ electron configuration, has the intriguing feature of a sharp change in resistivity and near-infrared (NIR) transmission. VO$_2$ can be applied as a selector for resistive random-access memories (RRAMs), switches and neuro-inspired devices in microelectronics, and thermochromic smart windows. Because vanadium oxides have many applications, it is essential to deposit vanadium oxide thin films with a suitable stoichiometry by controlling the process parameters during deposition or by postdeposition processing. Structural change from V$_2$O$_5$ to V$_2$O$_3$ was demonstrated by a controlled reduction reaction in a H$_2$ atmosphere by R Hampelberg et al. Huang et al. demonstrated the phase evolution from V$_2$O$_5$ to V$_2$O$_3$ by changing the oxygen partial pressure during annealing. Liu et al. proposed a sandwich structure [V$_2$O$_3$–metal (V or W)–V$_2$O$_5$] for the control on VO$_2$ polymorphs. To date, several studies have reported the thin film growth of vanadium oxides with various phases using electrodeposition, electron beam evaporation, sputtering, pulsed laser deposition, chemical vapor deposition (CVD), and atomic layer deposition (ALD). A modified version of CVD, an excellent tool for the formation of thin films owing to its advantages over other growth processes. Its ability to achieve self-limiting growth offers precise control of the film thickness down to the Angstrom level, perfect conformity over a large area, good repeatability, and step coverage for substrates with three-dimensional (3D) nanostructures. The ALD of vanadium oxide (VO$_x$) thin films using several vanadium metal precursors with water (H$_2$O) or oxygen (O$_2$) plasma as the oxidant has been reported. Vanadium oxytrichloride (VOCl$_3$) was used as the metal halide precursor for the ALD of VO$_x$ thin films with H$_2$O as the oxygen source. The introduction of metal–organic ALD precursors instead of an inorganic halide salt is always preferable to avoid the production of corrosive by-products; it
also often reduces the deposition temperature.\(^{36}\) Several metal–organic compounds have been used for VO\(_2\) thin film deposition by ALD with different oxidants, such as bis[2,4-pentanedionato]vanadyl(II) [VO(acac)\(_2\)] with O\(_2\),\(^{37}\) vanadium \(n\)-propoxide with CH\(_3\)COOH,\(^{38}\) tetrakis(dimethylamido)vanadium [V(NMe\(_2\))\(_4\)] with H\(_2\)O or O\(_2\),\(^{39}\) and tetrakis[ethylmethylamido]vanadium [V(NEtMe\(_2\))\(_4\)] with H\(_2\)O.\(^{28,30,31}\) Direct growth of an amorphous VO\(_2\) film by ALD has been recently reported by Peter et al. using V(NEtMe\(_2\))\(_4\) and H\(_2\)O and O\(_2\) plasma for crystalline V\(_2\)O\(_5\) deposition.\(^{29,30}\) A study of the thermal ALD using the same metal precursor with different oxidants has been recently reported by Peter et al. using V(NEtMe\(_2\))\(_4\) and H\(_2\)O, and careful annealing was required to crystallize the VO\(_2\) films.\(^{31}\)

VO(thd)\(_2\) (thd = 2,2,6,6-tetramethylheptano-3,5-dione) was also used as the vanadium source with O\(_2\).\(^{40}\) VO\(_2\) thin films with different phases have reportedly been obtained by ALD using VTIP as the metal precursor and either H\(_2\)O, O\(_2\), or O\(_3\) during deposition.\(^{33,44}\) These two results of electrochemical response and MIT support the possibility of phase control of ALD-VO\(_2\) via postdeposition annealing.

2. EXPERIMENTAL SECTION

Vanadium oxide (VO\(_2\)) thin films were deposited on a laminar-flow-type thermal ALD reactor (CN1, Atomic Classic, Korea) at 135 °C on Si and glass substrates. A continuous flow of N\(_2\) was used as the purge and carrier gas throughout the deposition process. VTIP (V\(^{5+}\)) (EG Chemical, Korea) and deionized water were the ALD precursors acting as V and O sources, respectively. The metal precursor was kept at 40 °C during deposition. The precursor doses and the purging sequence can be represented as VTIP pulse (t\(_1\)) – purge (t\(_2\)) – H\(_2\)O pulse (t\(_3\)) – purge (t\(_4\)) in one ALD cycle, where t\(_1\) and t\(_2\) are the dose times and t\(_3\) and t\(_4\) are the purge times.

The thicknesses of the as-deposited films were obtained by ellipsometry measurements (J.A. Woollam, ESM 300 ellipsometer). To study the selective formation of the crystalline phase of the VO\(_2\) thin films, the as-deposited films were annealed at 300, 400, and 500 °C for 1 h in air or a forming gas atmosphere (FGA, 95% N\(_2\), 5% H\(_2\), 40 sccm) in a box-type furnace (Hantech, C-A14P). The crystallinity of the as-deposited and annealed films was examined by XRD (DARANalytical, XPert Pro MPD) analysis, which was supplemented by cross-sectional high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100F). Scanning electron microscope (SEM, Hitachi, S-4800) and atomic force microscope (AFM, PSIA, XE150) were used to investigate the surface morphology of the as-deposited and annealed films. XPS (Thermo Fisher Scientific, ESCALAB 250, U.K.) measurements were recorded to determine the chemical nature of the VO\(_2\) thin films before and after annealing. The work function of the annealed materials was estimated from valence-band ultraviolet photoelectron spectroscopy (UPS, Thermo Fisher Scientific, ESCALAB 250, U.K.) using the He I (21.22 eV) line. The optical properties were studied using an ultraviolet–visible (UV–vis)–NIR spectrophotometer (Varian, Cary 5000), and the band gaps of the annealed films were calculated from the spectra.

To verify the selective formation of the phase-pure VO\(_2\) film, the as-deposited thin films were annealed at 300, 400, and 500 °C in air or forming gas (FGA, 95% N\(_2\) and 5% H\(_2\), 40 sccm) in a box-type furnace (Hantech, C-A14P). The crystallinity of the as-deposited and annealed films was examined by XRD (DARANalytical, XPert Pro MPD) analysis, which was supplemented by cross-sectional high-resolution transmission electron microscopy (HR-TEM, JEOL JEM-2100F). Scanning electron microscope (SEM, Hitachi, S-4800) and atomic force microscope (AFM, PSIA, XE150) were used to investigate the surface morphology of the as-deposited and annealed films. XPS (Thermo Fisher Scientific, ESCALAB 250, U.K.) measurements were recorded to determine the chemical nature of the VO\(_2\) thin films before and after annealing. The work function of the annealed materials was estimated from valence-band ultraviolet photoelectron spectroscopy (UPS, Thermo Fisher Scientific, ESCALAB 250, U.K.) using the He I (21.22 eV) line. The optical properties were studied using an ultraviolet–visible (UV–vis)–NIR spectrophotometer (Varian, Cary 5000), and the band gaps of the annealed films were calculated from the spectra.

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H2O. This suggests that the oxidant determines the rate of VO
disperse at a higher precursor dose time for the reaction with
surface. Therefore, the GPC exhibited the self-saturation
coverage of the available surface species on the substrate
when the dose time was increased further owing to the complete
the GPC was observed beyond this limiting value even when
GPC of 30 s in Figure 1a, b, respectively, where
pulses for the ALD of VO
processes.27,42

To obtain the optimized ALD reaction conditions, another
important parameter is the purge time after each precursor
dose. An insufficient purge time results in a significantly high
GPC. Figure 1c, d shows the variation in the GPC as a function of
purge time after VTIP and H2O pulses, respectively, at 135
°C. In this study, the VTIP and H2O pulse times were fixed at 2
and 5 s, respectively, as determined from the saturated growth
conditions. In both cases, the GPC first decreased slightly with
increasing purge time, and then saturation occurred. Thus, the
figures show a saturated GPC of ∼0.028–0.029 nm/cycle for
15 s (t1) and 20 s (t2), which are similar to the GPC values
measured during the pulse time study. Henceforth, all VOx thin
films for other characterizations were deposited using a t1 − t2 −
t3 − t4 sequence of 2s−15s−5s−20s at 135 °C.

3.2. Structural Characterizations and Effect of
Postdeposition Annealing. The crystallinity of the as-
grown VOx thin films and the effect of annealing at different
atmospheres and temperatures on the crystal structure were
investigated using the XRD patterns, as shown in Figure 2a, b.
For this study, 25 nm thick films were deposited on Si
substrates. The as-deposited VOx films were amorphous in
nature; thus, no signature peak appears except for the Si
substrate peak.

By contrast, the VOx films heat-treated under air and the
FGA show clear crystalline characteristics. Figure 2a shows the
crystallinity of the VOx thin films annealed at 300, 400, and 500
°C in air for 1 h. The amorphous VOx thin film becomes
crystalline after annealing at 300 °C, where the peaks for the
(001) and (002) planes correspond to orthorhombic V2O5,
which is consistent with the JCPDS file (JCPDS card no. 00-
041-1426). The film also shows a strong c-axis-preferred
orientation along the [001] direction with increasing annealing
temperature from 400 to 500 °C, which was also observed in
previous reports.26

Similarly, the amorphous as-deposited VOx thin films
annealed in the FGA showed a spontaneous change in the
crystal structure to polycrystalline monoclinic VO2 (JCPDS
card no. 041-1426). The film also shows a strong -axis-preferred
orientation along the [001] direction with increasing annealing
temperature from 400 to 500 °C, which was also observed in
previous reports.27,42

To obtain the optimized ALD reaction conditions, another
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Figure 2. XRD patterns of the as-deposited VOx thin films and after postdeposition annealing at 300, 400, and 500 °C for 1 h in (a) air and (b) FGA.

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Figure 3. Surface SEM images of films annealed in air at (a) 300, (b) 400, and (c) 500 °C and annealed in the FGA at (d) 300, (e) 400, and (f) 500 °C. The inset shows the as-deposited VO\textsubscript{x} film.

Figure 4. Surface morphologies of films annealed at (a) 300, (b) 400, and (c) 500 °C in air and at (d) 300, (e) 400, and (f) 500 °C in the FGA and (g) the as-deposited VO\textsubscript{x} film. (h) Variation in the root-mean-square surface roughness (R\textsubscript{q}) with annealing temperature in each atmosphere.

Figure 5. Cross-sectional transmission electron microscopy (TEM) images of (a) V\textsubscript{2}O\textsubscript{5} and (b) VO\textsubscript{2} thin films. The insets show the corresponding selected area electron diffraction (SAED) patterns. Each red circle highlights the observed diffraction spots from (a) V\textsubscript{2}O\textsubscript{5} and (b) VO\textsubscript{2} phases and confirms the c-axis preferred growth for both films.

Figure 3 shows the surface SEM images of the annealed VO\textsubscript{x} thin films, and the inset of Figure 3a shows the image of an as-deposited film. The image shows uniform film deposition on the entire substrate surface, which ensures pinhole-free film formation by ALD. The SEM images also confirm the distinctive effect of annealing under air and the FGA observed in the XRD patterns in Figure 2. Figure 3a–c shows the change in the surface morphology with increasing crystallization of the V\textsubscript{2}O\textsubscript{5} films at different annealing temperatures in air. On the other hand, the VO\textsubscript{x} thin film also appears amorphous after annealing at 300 °C in the FGA (Figure 3d), finally crystallizing at 400 and 500 °C, respectively, as shown in Figure 3e,f. Thus,
these SEM images also verified the XRD results obtained earlier. Note, however, that larger, elongated grains appear in the film annealed at 500 °C under the FGA (Figure 3f), and this observation is inconsistent with the XRD data in Figure 2b. These results suggest that precise temperature control is needed, especially to form the VO2 phase.

The surface roughness of the as-grown and annealed VO2 thin films on Si substrates was investigated using AFM. The surface morphology of all films is shown in Figure 4a–g. The as-deposited film (Figure 4g) and the film annealed at 300 °C in the FGA (Figure 4d) have similar morphologies; both are amorphous, with a very low root-mean-square surface roughness (Rq) of <1 nm (Figure 4h). The air-annealed films show different morphologies owing to an increase in the particle size with increasing annealing temperature. Larger particles were also observed in the VO2 films annealed at 400 and 500 °C in the FGA, which is also consistent with the XRD and SEM results. Figure 4h summarizes the measured surface roughness (Rq), which is higher for the films annealed at high temperature, consistent with the increasing grain size observed from the surface morphology.

The crystalline structure of the annealed thin films was further characterized using TEM. Figure 5a,b shows the cross-sectional images of ~10 nm thick V2O5 and VO2 thin films annealed in air (400 °C) and the FGA (500 °C), respectively, on Si substrates. Here, native oxide was not removed by hydrofluoric (HF) acid dipping. The insets show the SAED patterns. From the lattice fringes in Figure 5a, the measured interplanar distance of 6.7 Å represents the (001) planes of the orthorhombic V2O5 phase. This lattice interplanar spacing was found to be 4.3 Å, which corresponds to the (001) plane of the Si substrate. From the lattice fringes in Figure 5a, the measured interplanar spacing of 4.3 Å, which corresponds to the (001) plane of the Si substrate. From the lattice fringes in Figure 5a, the measured interplanar spacing of 4.3 Å, which corresponds to the (001) plane of the Si substrate. 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shows the Tauc plots of the films annealed at 500 °C in air (V2O5) and the FGA (VO2). The V2O5 thin film exhibits an indirect band gap of ~2.63 eV, whereas the VO2 thin film has a direct band gap of ~0.59 eV, which is consistent with the literature.53-58

On the basis of the above results, the band diagrams of the V2O5 and VO2 thin films can be constructed, as shown schematically in Figure 7d. The Fermi level clearly lies near the conduction band minimum (below ~0.18 eV), which is consistent with the n-type conductivity of V2O5.41 Thus, the position of the conduction band minimum is ~4.64 eV below the vacuum level55,56 compared with ~5.43 eV below for VO2.53 Here, VO2 shows intrinsic characteristics because of the presence of the Fermi level at a position almost exactly between the conduction and valence bands, as obtained from the above results.

3.5. Electrochemical Characteristics of V2O5. The electrochemical performance of the V2O5 thin film was studied by CV measurement. For this measurement, a 30 nm VOx thin film was deposited on an ITO glass substrate by ALD and subsequently annealed at 500 °C in air to obtain the V2O5 phase. The CV measurement was performed using a conventional three-electrode cell, where V2O5/ITO or only ITO, Pt, and Ag/AgCl were used as the working, counter, and reference electrodes, respectively. LiCl solution (1.0 M) was used as the electrolyte.

Figure 8 shows the cyclic voltammograms of the V2O5/ITO sample and of the ITO substrate for five cycles. The CV result of the V2O5/ITO sample exhibits cathodic (Epc) and anodic (Epa) peaks at ~0.04 and ~0.2 V, respectively. These peaks, which appeared during the cathodic and anodic sweeps of the V2O5/ITO film electrode, confirm Li-ion insertion and extraction in the lattice, which can be represented as

\[
\text{V}_2\text{O}_5 + x(\text{Li}^+ + e^-) \rightarrow \text{Li}_x\text{V}_2\text{O}_5 \quad \text{(during cathodic sweep)}
\]

\[
\text{Li}_x\text{V}_2\text{O}_5 \rightarrow \text{V}_2\text{O}_5 + x(\text{Li}^+ + e^-) \quad \text{(during anodic sweep)}
\]

A similar V2O5 behavior was described in the literature,59,60 confirming the efficient electrochemical behavior of the V2O5 thin films obtained by air annealing.

3.6. Voltage-Induced MIT of Ultrathin VO2 Films. To verify the effectiveness of the air and FGA postannealing processes on the voltage-induced MIT in the atomic-layer-deposited VO2 thin films, the electrical characteristics of the VO2 films were analyzed using the geometry of a selector device for RRAM.46,47 Figure 9a shows the current density—voltage (J−V) characteristics of the V2O5 thin film formed by air annealing. The air-annealed film exhibited unstable hysteresis behavior with a small on/off ratio in the first voltage sweep. The Ohmic-like behavior at a high current level is attributed to a conductive filament that formed after the first voltage sweep.
The conducting filaments are likely to be formed by the first voltage sweep in the highly insulating V2O5 layer. The current level gradually decreased as the voltage sweep process was repeated. This behavior is due to a rupture of the conductive filament, resulting from the crystallization of a possible partial amorphous phase or migration of ionic defects. These results are indicative of the unstability of V2O5 thin films by applied bias.

On the other hand, unlike the air-annealed V2O5 thin films, the FGA-annealed VO2 thin films exhibited stable counterclockwise hysteresis behavior up to 20 cycles, as observed in Figure 9b. In the sweeping process from 0 to 5 V, the current shows a sudden increase at 0.31 V (the threshold voltage, \( V_{th} \)), which is attributed to the MIT of VO2 caused by the voltage-induced Joule heating. The on current density, the off current density, and the on/off current ratio were estimated to be 10.82 MA/cm², 0.36 MA/cm², and 29.6, respectively, which are indicative of the unstability of V2O5 thin films by applied bias.

The crystalline VO2 phase with a preferential c-axis orientation was obtained with increasing annealing temperature in air, whereas the crystalline phase of VO2 was formed after annealing at 500 °C in the FGA environment. These results were further verified by other structural characterizations such as cross-sectional TEM, SEM, and AFM imaging and by chemical analysis using XPS. The crystalline V2O5 had a work function of \( \sim 4.82 \) eV, and the valence band maximum was located at \( \sim 2.45 \) eV below the Fermi level, as determined from the UPS spectra; the corresponding values for the VO2 phase were calculated as \( \sim 5.75 \) and 0.27 eV, respectively. The optical band gaps of the V2O5 and VO2 phases were estimated to be \( \sim 2.63 \) and 0.59 eV, respectively, from the transmittance and reflectance data. An electrochemical response and an abrupt, stable MIT were observed for the crystalline V2O5 and VO2 thin films, respectively, demonstrating the versatility of postdeposition annealing for exploring various applications of vanadium oxides. In particular, demonstration of selector devices on the vertical structure will open up the possibility of ALD-VO2 for 3D memory applications.

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