



Physical Analysis of VO₂ Films Grown by Atomic Layer Deposition and RF Magnetron Sputtering

Madhavi Tangirala,^{a,b,*} Kai Zhang,^{a,b,**} David Nminibapiel,^{a,b,*} Venkateswara Pallem,^c Christian Dussarrat,^c Wei Cao,^{a,b} Thomas N. Adam,^d Corbet S. Johnson,^d Hani E. Elsayed-Ali,^{a,b} and Helmut Baumgart^{a,b,**,z}

^aDepartment of Electrical and Computer Engineering, Old Dominion University, Norfolk, Virginia 23529, USA

^bApplied Research Center, Newport News, Virginia 23606, USA

^cAmerican Air Liquide, Delaware Research & Technology Center, Newark, Delaware 19702, USA

^dCollege of Nanoscale Science and Engineering, University at Albany, Albany, New York 12203, USA

Among the many vanadium suboxides and different stoichiometries, VO₂ has received considerable attention due to its remarkable metal-insulator transition (MIT) behavior, which causes a significant reversible change in its electrical and optical properties occurring across the phase transition at 67°C. The initially amorphous VO₂ thin films were fabricated by the emerging, Atomic Layer Deposition (ALD) technique with (tetrakis[ethylmethylamino]vanadium) {V(NEtMe)₄} as precursor and H₂O vapor as oxidation agent. For benchmarking we have also used the RF Magnetron Sputtering technique to deposit metallic vanadium thin films, which were later oxidized during furnace annealing. Post annealing of the as-deposited ALD films was performed in order to obtain the technologically important form of crystallized VO₂ thin films using furnace annealing. All film depositions were carried out on native oxide covered (100) Si substrates. The conditions for successful furnace annealing are reported in terms of temperature and annealing gas composition and the physical characterization results are presented.

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VO₂ exhibits many technologically remarkable properties that lie at the core of the renewed interest in this material. In particular, VO₂ shows a semiconductor–metal transition (SMT) or metal-insulator transition (MIT) at ~67°C. This (MIT) phase transition at ~67°C is accompanied by a reversible change in its electrical and optical properties.^{1–3} At low-temperatures below the transition, VO₂ shows a semiconducting phase that has a monoclinic crystal structure. When the temperature rises above the transition temperature, the VO₂ exhibits its metallic phase which has a rutile crystal structure. The MIT of VO₂ is attributed to the combination of Mott-Hubbard transition with Peierls transition.⁴ Electrically, the change in resistivity of bulk VO₂ across the MIT temperature can be as large as four or five orders of magnitude. Optically, crystalline VO₂ thin films exhibit good infrared transmission in the insulating monoclinic phase below the MIT temperature, while the metallic rutile phase is highly reflective in the infrared region.^{5,6}

Based on these temperature dependent optical transmission changes crystalline VO₂ is also known as a thermochromic material, which can be employed as thin films in smart window applications to reduce air condition and heating costs. Because of these physical properties VO₂ films have the potential to be used in nonvolatile resistive memories, switches in microelectronics and optical sensors and smart window applications.

However, the V-O system has been reported to contain about 25 compounds and suboxide phase.^{7,8} It is experimentally challenging to find the optimum combination of different furnace annealing parameters that would result in the accurate mixture of vanadium and oxygen in the desired proportion to obtain the stoichiometric VO₂ phase. Even a 1% change in the oxygen content of the annealing atmosphere in the furnace would further oxidize the initially amorphous vanadium oxide or reduce it and result in undesirable intermediate phases, such as V₆O₁₃, V₃O₇, V₂O₅, which do not exhibit the MIT property. Certain vanadium suboxides or stoichiometries, such as V₂O₃ and VO do in fact also exhibit MIT properties.⁹ However, in our experimental setup we never obtained those stoichiometries,

but only V₆O₁₃, V₃O₇ and V₂O₅ which unfortunately do not show any MIT properties and have no technological device applications. A cursory literature review reveals that in the past VO₂ films have been prepared using many techniques, including Reactive Bias Target Ion Beam Deposition (RBTIBD),² magnetron sputtering,¹⁰ chemical deposition (CVD),¹¹ pulsed laser deposition (PLD)¹² and sol-gel spin coating.¹³

During the past decade the emerging atomic layer deposition (ALD) has been extensively investigated for the deposition of thin films of semiconductors, metals, alloys and oxides, but was barely applied to grow VO₂ films due to the lack of suitable vanadium precursors. However, a newly available chemical precursor (tetrakis [ethylmethylamino] vanadium) [V(NEtMe)₄, TEMAV] supplied by Air Liquide has enabled the synthesis of VO₂ by ALD with this new precursor.¹ For comparison of film properties, such as morphology, microstructure and physical properties, VO₂ films were also fabricated by using RF magnetron sputtering of a metallic vanadium target. Subsequently, the critical post annealing with a specific mixture of N₂ and O₂ was required in order to crystallize the originally amorphous ALD vanadium oxide films and alternatively to oxidize the metallic vanadium magnetron sputtered films.

Experimental

Synthesis of VO₂ using atomic layer deposition.— In this work, TEMAV was employed as vanadium ALD precursor along with water vapor as a source for oxygen. In TEMAV the vanadium atom has an oxidation state of 4⁺ unlike those in previously applied precursors which have 5⁺. Therefore, TEMAV is the preferred ALD precursor, since it facilitates the synthesis of the technologically important VO₂ with V⁴⁺ instead of V₂O₅ with V⁵⁺ ions. V₂O₅ does not show phase transitions. Vanadium oxide films were deposited by thermal ALD with the cross flow reactor Savannah100 from Cambridge Nanotech. Generally, N₂ was used as the inert carrier gas with a flow rate of 20 sccm. The ALD growth temperature of vanadium oxide was set at 120–150°C. The vanadium oxide films were deposited on a native silicon oxide covered Si (100) substrate with the following ALD growth conditions: the pulse time of the ALD precursor # 1 H₂O was 15 ms, the purging time was 10 s, the pulse time of ALD precursor #2

*Electrochemical Society Student Member.

**Electrochemical Society Active Member.

^zE-mail: hbaumgar@odu.edu

Table I. Experimental furnace annealing conditions to crystallize the initially amorphous vanadium oxide thin films deposited by ALD in order to obtain the polycrystalline stoichiometric VO₂ phase. (The gray highlighted rows were the successful annealing conditions.)

Anneal Temp	Air	Annealing time and gas ratio under atmospheric pressure				Annealing time and gas ratio under low vacuum (10 ⁻² Torr)		
		N ₂ (100%)	98.78% N ₂ + 1.22% O ₂	99% N ₂ + 1% O ₂	98.5% N ₂ + 1.5% O ₂	98.2% N ₂ + 1.8% O ₂	99.4% N ₂ + 0.6% O ₂	2.7 × 10 ⁻² Torr (1 sccm O ₂)
420°C	30 min							
420°C		30 min						
420°C				5 min				
420°C					5 min			
420°C						10 min		
420°C							10 min	
425°C			30 min					
430°C				5 min				
450°C	30 min							
450°C		30 min						
450°C				30 min				
450°C					5 min			
450°C						10 min		
450°C							10 min	
500°C								60 min

TEMAV was 50 ms and the purging time was 10 s. The base pressure was 20 mTorr.

All vanadium oxide thin films obtained by ALD are amorphous, as the growth temperature is lower than the crystallizing temperature of VO₂. Therefore, post annealing treatment of ALD deposited thin films is required to produce the technologically important polycrystalline stoichiometric VO₂ structure. Post-deposition annealing is required in order to achieve the important monoclinic crystal structure below the transition temperature and the tetragonal rutile crystal phase above the metal-insulator transition temperature.

Since vanadium can form many other oxide phases (V₂O₅, V₂O₃ etc.), the as-deposited amorphous vanadium oxide ALD films using TEMAV and water precursors were annealed under the systematically varying furnace temperatures and annealing atmosphere gas ratios reported in Table I.

The accurate annealing gas ratio between oxygen and inert nitrogen gas mentioned above is absolutely crucial to obtain stoichiometric crystallized VO₂ while suppressing the undesirable vanadium suboxides. Insufficient oxygen content in the annealing atmosphere will lead to further reduction of the ALD vanadium oxide, while too much oxygen content promotes further oxidation of the ALD film. Table I indicates all experimental annealing conditions that were applied during this study. The complexity and difficulty of the crystallization and reduction task is obvious from the many experimental annealing conditions shown in Table I that did not yield the desired stoichiometric VO₂ phase.

We were successful in achieving stoichiometric polycrystalline VO₂ at 425°C for 30 minutes, using 98.78% N₂ and 1.22% O₂, with a N₂ flow rate of 27 sccm under atmospheric pressure. We also obtained the VO₂ films at a higher annealing temperature of ~450°C for 30 minutes, 99% N₂ and 1% O₂, with a N₂ flow rate of 27 sccm under atmospheric pressure. When the samples were annealed in low vacuum at 10⁻² Torr, we were able to get the desired polycrystalline VO₂ films under the condition of 450°C annealing for 10 min, in 99.4% N₂ and 0.6% O₂, with a N₂ flow rate of 27 sccm. Similarly, annealing at 500°C for 60 min in 100% O₂ with 1 sccm at 2.7 × 10⁻² Torr also achieved the successful results. The low flow rate of 1 sccm of pure O₂ required the longer annealing time of 60 min at 500°C under a lower pressure in order to achieve successful stoichiometric VO₂ crystallization. It was observed that the as-deposited ALD vanadium oxide remains amorphous if it is annealed using 100% inert nitrogen gas (N₂) furnace ambient up to 500°C, which indicates crystallization was inhibited. The stoichiometry and crystallography of the vanadium changes only when the O₂ concentration is ~1%, emphasizing the importance of the correct oxygen ratio to achieve stoichiometric VO₂

thin films. We used two mass flow controllers from Brooks Instrument for oxygen and nitrogen and a Brooks Instrument 0254 control box for accurately mixing and controlling the ratio of the two gases in the furnace atmosphere.

Synthesis of VO₂ by RF magnetron sputtering of metallic vanadium.— For benchmarking VO₂ thin films were also obtained by oxidation of metal vanadium films deposited on Si (100) substrates by using RF magnetron sputtering from AJA International Inc. of metallic vanadium with O₂ at low vacuum condition. Base pressure was set to less than 10⁻⁶ Torr for RF magnetron sputtering. We used a deposition pressure of 3 × 10⁻³ Torr while the sputter deposition was carried out using an argon source for the plasma. The temperature was controlled at 450°C for the sputter deposition of a vanadium film on Si substrates to obtain a uniform fine grain polycrystalline V film. As-deposited thin vanadium films were subsequently annealed for 6 hours under various N₂ to O₂ ratios in order to oxidize vanadium into stoichiometric VO₂ within the temperature range of 450–600°C as listed in Table II.

Film characterization.— The structural properties and morphology of the films before and after annealing were characterized by field-emission electron microscopy (Hitachi FE-SEM), transmission electron microscopy (TEM) using a JEOL JEM 2100F microscope. The crystal structure of the films was measured by X-ray diffraction (XRD) using a Rigaku Miniflex (II) diffractometer with Cu-Kα radiation (λ ~ 1.540598 Å). Film roughness before and after annealing was measured by Atomic Force Microscopy (AFM).

Finally, the composition and the stoichiometry of the films, and the valence state of the vanadium ions were measured by XPS with a Kratos Axis Ultra DLD X-ray Photoelectron Spectrometer (Kratos Analytical Inc.) using a monochromatic Al Kα X-ray source.

Results and Discussion

The composition and the stoichiometry of the as-prepared amorphous vanadium oxide ALD films deposited on the Si substrate were measured by XPS as shown in Figure 1. For the as-synthesized ALD vanadium oxide film, the binding energy of the V2p_{3/2} peaks was fitted as 517.5 eV and 516.1 eV. These two values correspond to the V⁵⁺ and V⁴⁺ oxidation state of vanadium, respectively. This reveals that the as-prepared amorphous ALD vanadium oxide films contained a two phase mixture of 68.7% V₂O₅ and 31.3% VO₂. Prior to performing the XPS measurement the ALD vanadium oxide films were

Table II. Furnace oxidation of RF magnetron sputtered vanadium films to convert into stoichiometric polycrystalline VO₂ films. (The gray highlighted rows were the successful oxidation conditions.)

Sample No.	Ramp time (min)	Oxidation temperature (°C)	Hold time (min)	N ₂ (sccm)	O ₂ (sccm)	Pressure (Torr)
1	45	450	500	21.6	5.4	0.8
2	60	600	240	26.0	7.0	1.0
3	50	600	500	21.6	5.4	0.79
4	120	500	120	60.0	0.0	No Vacuum
5	60	600	240	26.0	0.0	0.89
6	120	600	240	26.0	0.5	0.89
7	120	600	240	26.0	0.1	0.82
8	120	600	240	0.0	0.0	0.84
9	120	600	240	26.0	0.01	0.85
10	120	600	240	26.0	0.03	0.83
11	120	600	240	26.0	0.05	0.83
12	120	600	240	26.0	0.07	0.83
13	60	450	500	26.0	0.05	0.83

exposed to ambient air and XPS analyzes typically the top ~10 nm of the samples. Room temperature oxidation may have occurred in surface regions and may be responsible for the high percentage of V₂O₅ in the mixed phase ALD films.

In order to obtain the stoichiometric VO₂ phase, the amorphous starting material needs to be recrystallized and chemically reduced by furnace annealing at 450°C in an accurately controlled annealing atmosphere. When furnace annealing was performed in regular air at 450°C for 30 min, only V₂O₅ was produced instead of VO₂ as revealed by the XRD plot of Figure 2a. The 2θ diffraction peaks at 20° and 42° are respectively indexed as (001) and (400) planes of V₂O₅ which are in good agreement with the values in the standard card (JCPDS No.41-1426). This means the initially amorphous vanadium oxide in the as-prepared thin film was further oxidized into the V₂O₅ phase. For comparison, when furnace annealing was performed in pure 100% N₂ atmosphere, the ALD vanadium oxide remained amorphous as seen in the XRD plot in Figure 2a by the absence of diffraction peaks. The XRD graph of Figure 2b reveal an XRD peak at 27.8°, which proves the presence of a pure stoichiometric VO₂ phase under the favorable annealing condition of 450°C for 10 minutes with an optimized 1 sccm O₂ flow in a low vacuum at 2.7×10^{-2} Torr.

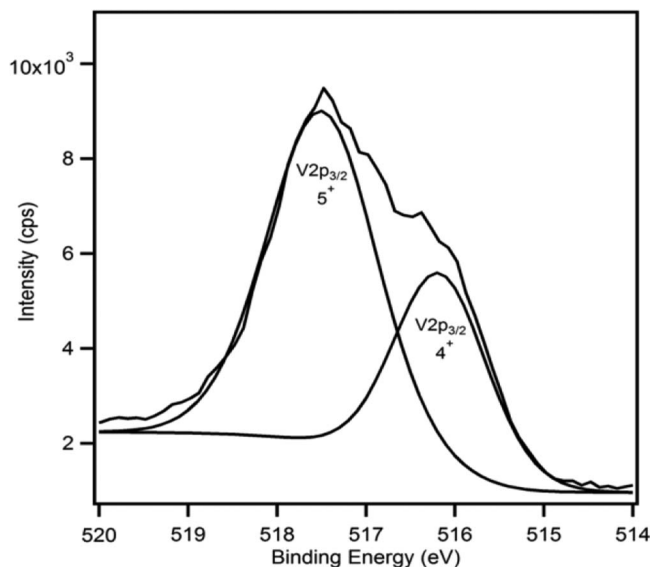


Figure 1. XPS measurement of as-deposited ALD amorphous vanadium oxide films on silicon substrates revealing the presence of 2 valence states of vanadium (+5, and +4) indicating a mixture of 68.7% V₂O₅ and 31.3% VO₂.

Atomic Force Microscopy provides a measure of the surface roughness and surface coverage of the vanadium oxide thin films. Figure 3a shows the smooth surface for the originally amorphous ALD vanadium oxide. In contrast, Figure 3b displays the polycrystalline morphology following crystallization during furnace annealing. The amorphous ALD vanadium oxide film of Figure 3a was found to have an rms roughness of 0.58 nm, while the crystallized film of Figure 3b has an increased rms roughness of 3.64 nm. Figure 3b exhibits island morphology after annealing in contrast to Figure 3a which shows smooth surface morphology before furnace annealing. This corroborates our XRD results delineating the polycrystalline nature of the annealed VO₂ films.

The images in Figure 4 were obtained by cross-sectional Transmission Electron Microscopy (TEM) analysis of VO₂ and V₂O₅ ALD films after annealing at different conditions. We investigated a post-deposition furnace annealing for recrystallization at 425°C in an atmosphere of N₂: 27 sccm blended with O₂ (0.34 sccm) corresponding to a ratio of 1.22% O₂ and 98.78% N₂ following ALD deposition in Figure 4a and 4b. The TEM cross-section reveals significantly larger spherical VO₂ crystallites, whose diameters are limited by the film thickness. The TEM micrographs of Figure 4a and 4b clearly show that the annealed ALD vanadium oxide thin films have been recrystallized into randomly oriented polycrystalline VO₂ films from the initially amorphous phase. The TEM diffraction conditions were set to image the Si crystal lattice planes and therefore do not show the lattice of the VO₂ crystallites in this view. The TEM cross-section measurements reveal the crystallized VO₂ film thickness as 14.26 nm and native oxide as 3.86 nm. The vanadium film was grown with 3500 ALD cycles at 120°C. As a comparison, we also obtained stoichiometric V₂O₅ films through annealing of the initially amorphous ALD vanadium oxide films at 600°C for 6 hours under atmospheric pressure with 60 sccm N₂ and a blend of 0.6 sccm O₂ corresponding to 1.0% as shown in Figure 4c and 4d. Both films started as amorphous ALD mixed phase films grown with 3500 ALD cycles at 120°C of identical thickness. The final different stoichiometries were achieved by deliberate changes in the furnace annealing conditions, because we were interested to investigate the structural differences between these two phases of vanadium oxides at higher TEM magnifications. In spite of starting out with the identical amorphous ALD film thickness grown with 3500 ALD cycles, the final furnace recrystallized film thicknesses differ markedly. The recrystallized stoichiometric vanadium dioxide (VO₂) film ended up with a thickness of 14.3 nm, while the vanadium pentoxide (V₂O₅) resulted in a final furnace annealed and recrystallized film thickness of 89.6 nm. The marked film thickness differences can be explained by the volume expansion upon recrystallization and the fact that the V₂O₅ has more oxygen and vanadium atoms compared to VO₂ and consequently takes up more volume. Figure 4c & 4d reveals TEM cross-sections of pure phase V₂O₅ films recrystallized at the elevated temperature of 600°C. Two different size

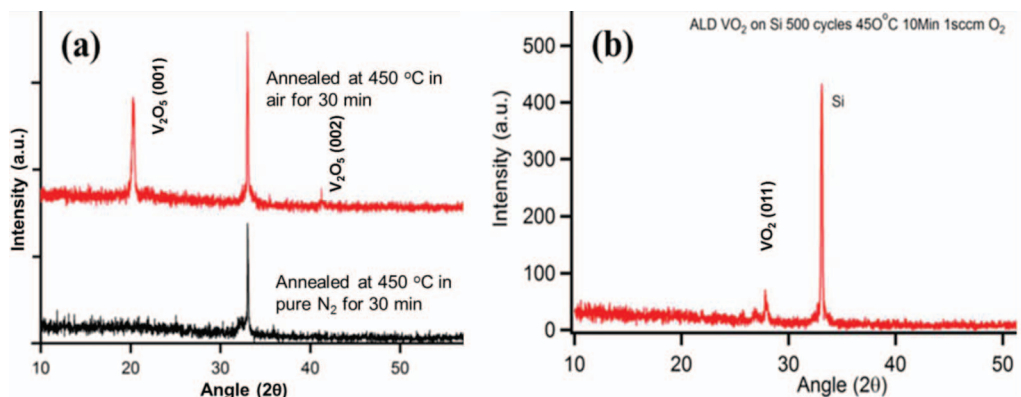


Figure 2. XRD results obtained from the furnace annealed ALD vanadium oxide samples at 450°C when annealed (a) in the presence of regular atmospheric air, and, alternatively, in 100% nitrogen gas for 30 min and (b) in the presence of a 1.2% O₂ and 98.8% pure N₂ gas mixture.

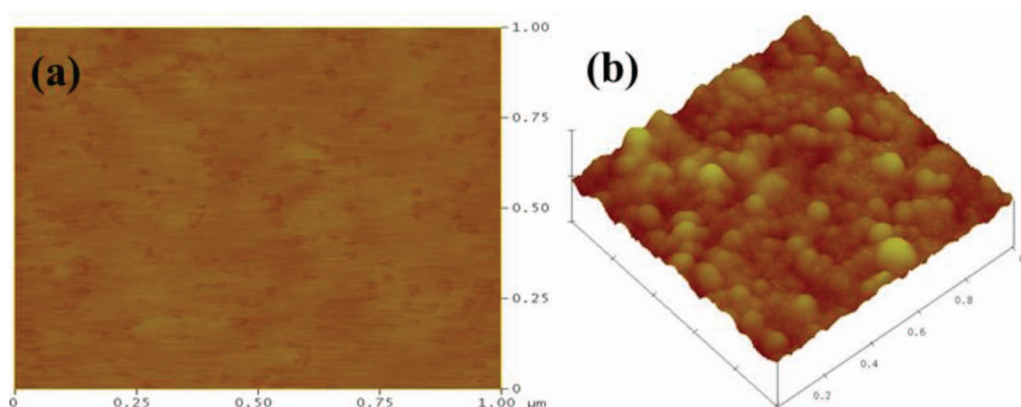


Figure 3. AFM analysis of the surface morphology showing the film roughness of (a) as-deposited amorphous ALD vanadium oxide with an rms roughness of 0.58 nm and (b) of crystallized VO₂ in 3-dimensional view after annealing in 1% O₂ and 99% N₂ at 420°C with a 3.64 nm rms surface roughness.

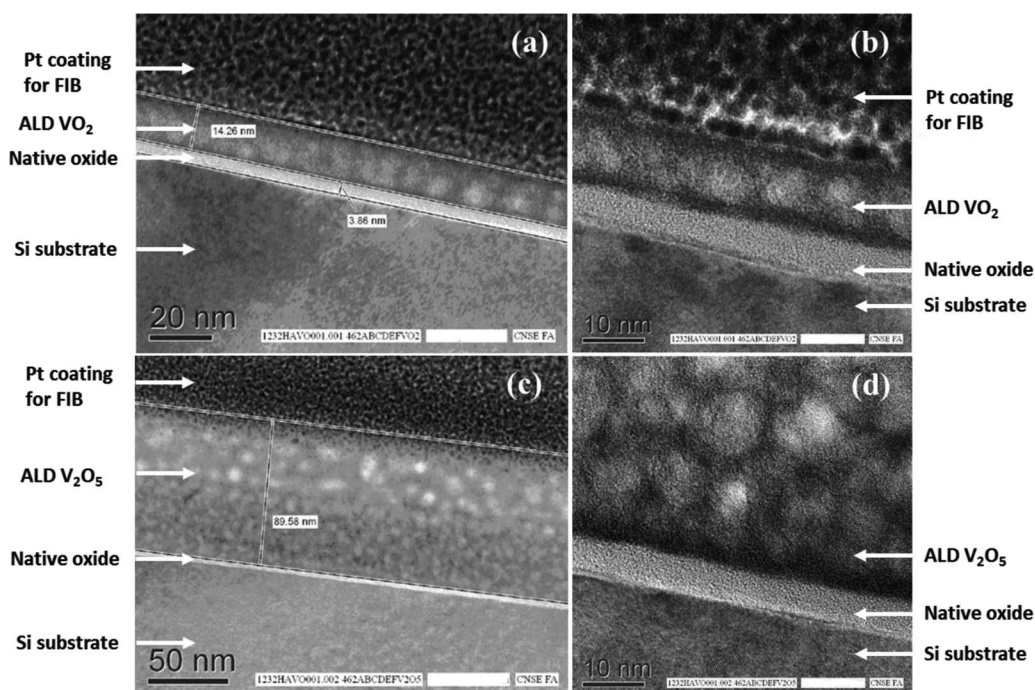


Figure 4. Cross-sectional TEM micrographs of ALD samples (a) low magnification (b) high magnification close up highlighting the spherical grain structure of crystallized stoichiometric VO₂ films. Figure 4 (c) & (d) instead reveals TEM cross-sections of pure V₂O₅ films recrystallized at the elevated temperature of 600°C. Two different size distributions of the resulting V₂O₅ crystallites are visible. The lower half toward the Si substrate exhibits smaller V₂O₅ crystallites, while the upper half of the film exhibits noticeably larger V₂O₅ crystallites.

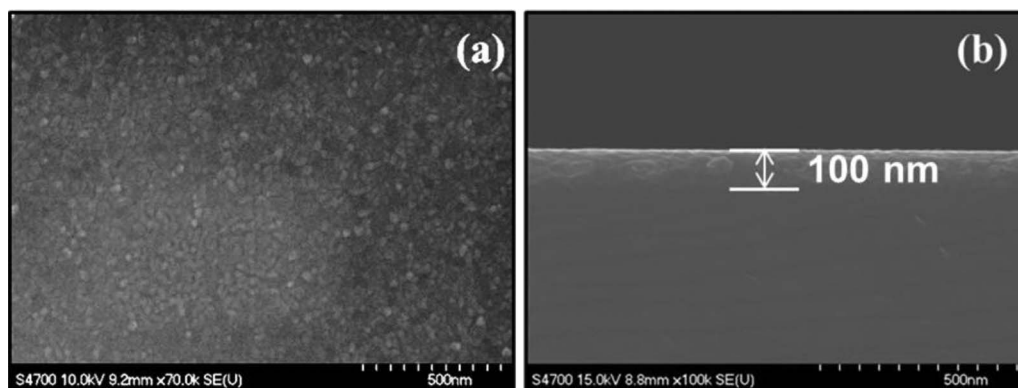


Figure 5. FE-SEM micrographs showing (a) the surface coverage of the vanadium metal film and (b) a cross-sectional view of a cleaved sample revealing a 100-nm thickness sputtered vanadium film.

distributions of the resulting V_2O_5 crystallites are visible. The lower half toward the Si substrate exhibits smaller V_2O_5 crystallites, while the upper half of the film exhibits noticeably larger V_2O_5 crystallites. This is attributed to the diffusion of oxygen through the surface of the much thicker recrystallized V_2O_5 film (89.6 nm) establishing an oxygen gradient. The lower half of this thick V_2O_5 film is expected to be more oxygen depleted, which inhibits the growth of the V_2O_5 crystallites. In the case of the much thinner film of 14.3 nm annealed at lower temperature of 425°C the effect of the oxygen gradient over the film thickness is not as pronounced.

Figure 5 shows the FE-SEM micrographs of the vanadium metal sputtered on silicon substrates. Figure 5a shows the uniform and well covered surface of the fine grain polycrystalline vanadium metal which will be further annealed in a furnace to oxidize it to vanadium dioxide. Figure 5b shows a cleaved cross-sectional view of the vanadium film that was used in determining the thickness of the sputter deposited vanadium film. The measurement revealed about a 100 nm thick polycrystalline vanadium metal film.

FE-SEM micrographs were used to compare the thin film morphologies of samples fabricated by ALD and magnetron sputtering, which have been furnace annealed for crystallization. Figure 6a shows the ALD deposited vanadium oxide film that has been furnace annealed at 450°C for 30 min, while Figure 6b shows the RF magnetron sputtered thin film that was annealed at 450°C for 6 hours. XRD analysis of both films from Figure 6a and Figure 6b revealed that stoichiometric VO_2 films were achieved. The surface coverage of the vanadium dioxide thin films over the silicon substrate looks very uniform in both images. However, it is evident that the crystal grain size is significantly larger for the sputtered thin film in Figure 6b when

compared to the sample deposited using ALD in Figure 6a. This can be explained by the longer annealing time of 6 h at 450°C and the thicker starting film thickness of 100 nm for the sputter deposited pure vanadium films, which enables further solid state grain growth.

Subsequently, the sputtered vanadium films were annealed in order to oxidize them by using different ratios of N_2 and O_2 furnace atmospheres. RF magnetron sputtered vanadium films can be oxidized into stoichiometric films for the specific annealing atmosphere condition of 26 sccm N_2 flow at 0.87–0.89 Torr and 0.05 sccm O_2 flow as revealed in Figure 7a. In contrast, Figure 7b shows that only undesirable V_6O_{13} thin films are obtained by annealing the magnetron sputtered vanadium films only in N_2 gas at a flow of 26 sccm. We observed a significant volume expansion during oxidation of the sputtered polycrystalline vanadium film. An initially 100 nm thick sputtered vanadium film expanded to 1000 nm following oxidation at 600°C for 6 hours. Oxidation of the initially pure vanadium metal film involves this observed volume change of the resulting polycrystalline VO_2 film in similar fashion to the well-known volume expansion of SiO_2 upon oxidation of Si.

RF magnetron sputtered vanadium films were successfully oxidized at 600°C by furnace annealing. As discussed above, any change in the annealing atmosphere for polycrystalline vanadium would result in different vanadium oxide phases. Figure 7a shows the desired polycrystalline VO_2 thin film under the following annealing condition: N_2 flow: 26 sccm, O_2 flow: 0.05 sccm. Figure 7b shows that we obtained only V_6O_{13} upon furnace annealing using pure N_2 flow at 26 sccm at 600°C for 6 hrs. The absence of oxygen in the ambient changed the stoichiometry of the vanadium oxide to the undesirable V_6O_{13} suboxide.

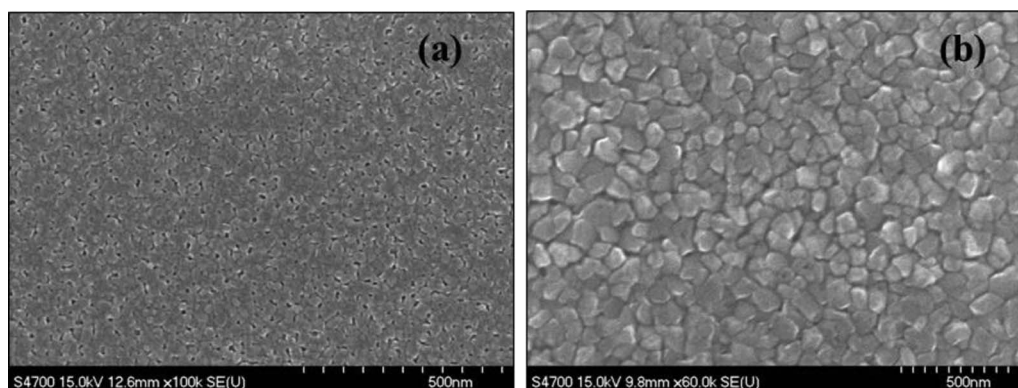


Figure 6. FE-SEM micrograph comparison between ALD deposited and magnetron sputter deposited VO_2 films showing the surface morphology after furnace annealing. (a) ALD film of 14.3 nm thickness furnace annealed at 450°C for 30 min. (b) thick 100 nm RF magnetron sputtered film oxidized at 450°C for 6 h under 26 sccm N_2 and 0.05 sccm O_2 gas mixture.

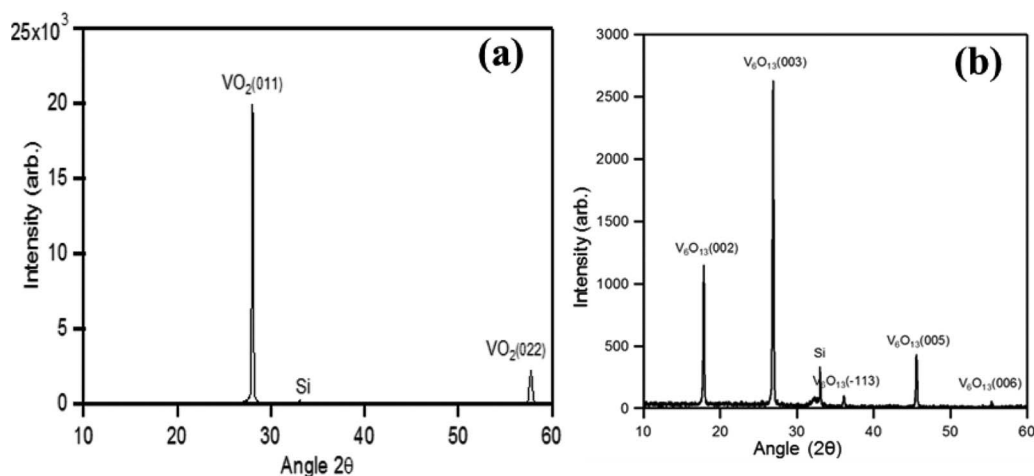


Figure 7. Different XRD results obtained from the furnace annealed samples that were deposited using RF magnetron sputtering at 600°C for 6 h; (a) annealing atmosphere composition of 26 sccm N₂ flow at 0.87–0.89 Torr and 0.05 sccm O₂ that resulted in stoichiometric VO₂ and (b) pure N₂ annealing atmosphere resulting in V₆O₁₃.

Conclusions

Thermal ALD deposition of amorphous vanadium oxide thin films has been demonstrated with TEMAV and H₂O vapor as ALD precursors. The optimized ALD process condition for the synthesis of vanadium oxide worked consistently and yielded amorphous films containing a mixed-phase of 68.7% V₂O₅ and 31.3% VO₂ for our investigation under our specific experimental conditions. It turns out that the ALD synthesis of amorphous vanadium oxide films is very reproducible and thus constitutes the straightforward part of the process. The harder challenge for the synthesis of crystallized stoichiometric VO₂ films lies in the complexities of the subsequent furnace recrystallization processes. Since the V-O phase diagram contains many vanadium oxide phases and suboxides the furnace recrystallization process depends sensitively on the accurate ratio between oxygen gas and inert nitrogen gas in the furnace atmosphere during the annealing in order to achieve the desired stoichiometric VO₂ crystalline phase that exhibits the technologically important MIT phase change property. In summary, we have identified four experimental furnace annealing conditions that yield stoichiometric recrystallized VO₂ films out of the ALD synthesized amorphous mixed phase vanadium oxide films as outlined by the shaded rows in Table I. Furnace annealing was successful in achieving polycrystalline pure phase VO₂ films under the following four conditions: a) at an annealing temperature of ~425°C for 30 minutes, 98.78% N₂ and 1.22% O₂, with a N₂ flow rate of 27 sccm under atmospheric pressure; b) at an annealing temperature of ~450°C for 30 minutes, 99% N₂ and 1% O₂, with a N₂ flow rate of 27 sccm under atmospheric pressure; c) under low vacuum of 1×10^{-2} Torr, at an annealing temperature of 450°C for 10 min, in 99.4% N₂ and 0.6% O₂, with a N₂ flow rate of 27 sccm; d) under low vacuum of 2.7×10^{-2} Torr at an annealing temperature of 500°C for 60 min in 100% O₂ ambient with 1 sccm flow rate. Physical characterization has been performed to compare polycrystalline VO₂ thin films that were deposited using ALD and alternatively RF magnetron sputtering processes. Careful TEM cross-sectional analysis revealed a markedly large difference in volume expansion upon furnace recrystallization between stoichiometric films of VO₂ and V₂O₅. The thicker RF magnetron sputtered and oxidized VO₂ films are subject

to larger volume expansion and exhibit a significantly higher surface roughness compared to ALD recrystallized VO₂ films. For the PVD process starting with a pure vanadium metal film we have identified five furnace annealing conditions resulting in stoichiometric films. The technical details of the successful furnace annealing conditions are summarized in the gray shaded rows of Table II.

Acknowledgments

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