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## Physical Analysis of VO<sub>2</sub> Films Grown by Atomic Layer Deposition and RF Magnetron Sputtering

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Among the many vanadium suboxides and different stoichiometries, VO<sub>2</sub> 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 VO<sub>2</sub> thin films were fabricated by the emerging, Atomic Layer Deposition (ALD) technique with (tetrakis[ethylmethylamino]vanadium) {V(NEtMe)<sub>4</sub>} as precursor and H<sub>2</sub>O 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 VO<sub>2</sub> 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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VO<sub>2</sub> exhibits many technologically remarkable properties that lie at the core of the renewed interest in this material. In particular, VO<sub>2</sub> 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.<sup>1–3</sup> At low-temperatures below the transition, VO<sub>2</sub> shows a semiconducting phase that has a monoclinic crystal structure. When the temperature rises above the transition temperature, the VO<sub>2</sub> exhibits its metallic phase which has a rutile crystal structure. The MIT of VO<sub>2</sub> is attributed to the combination of Mott-Hubbard transition with Peierls transition.<sup>4</sup> Electrically, the change in resistivity of bulk VO<sub>2</sub> across the MIT temperature can be as large as four or five orders of magnitude. Optically, crystalline VO<sub>2</sub> 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.<sup>5,6</sup>

Based on these temperature dependent optical transmission changes crystalline VO<sub>2</sub> 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 VO<sub>2</sub> 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.<sup>7,8</sup> 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 VO<sub>2</sub> 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 V<sub>6</sub>O<sub>13</sub>, V<sub>3</sub>O<sub>7</sub>, V<sub>2</sub>O<sub>5</sub>, which do not exhibit the MIT property. Certain vanadium suboxides or stoichiometries, such as V<sub>2</sub>O<sub>3</sub> and VO do in fact also exhibit MIT properties.<sup>9</sup> However, in our experimental setup we never obtained those stoichiometries,

but only V<sub>6</sub>O<sub>13</sub>, V<sub>3</sub>O<sub>7</sub> and V<sub>2</sub>O<sub>5</sub> which unfortunately do not show any MIT properties and have no technological device applications. A cursory literature review reveals that in the past VO<sub>2</sub> films have been prepared using many techniques, including Reactive Bias Target Ion Beam Deposition (RBTIBD),<sup>2</sup> magnetron sputtering,<sup>10</sup> chemical deposition (CVD),<sup>11</sup> pulsed laser deposition (PLD)<sup>12</sup> and sol-gel spin coating.<sup>13</sup>

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 VO<sub>2</sub> films due to the lack of suitable vanadium precursors. However, a newly available chemical precursor (tetrakis [ethylmethylamino] vanadium) [V(NEtMe)<sub>4</sub>, TEMAV] supplied by Air Liquide has enabled the synthesis of VO<sub>2</sub> by ALD with this new precursor.<sup>1</sup> For comparison of film properties, such as morphology, microstructure and physical properties, VO<sub>2</sub> films were also fabricated by using RF magnetron sputtering of a metallic vanadium target. Subsequently, the critical post annealing with a specific mixture of N<sub>2</sub> and O<sub>2</sub> 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 VO<sub>2</sub> 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<sup>+</sup> unlike those in previously applied precursors which have 5<sup>+</sup>. Therefore, TEMAV is the preferred ALD precursor, since it facilitates the synthesis of the technologically important VO<sub>2</sub> with V<sup>4+</sup> instead of V<sub>2</sub>O<sub>5</sub> with V<sup>5+</sup> ions. V<sub>2</sub>O<sub>5</sub> does not show phase transitions. Vanadium oxide films were deposited by thermal ALD with the cross flow reactor Savannah100 from Cambridge Nanotech. Generally, N<sub>2</sub> 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 H<sub>2</sub>O was 15 ms, the purging time was 10 s, the pulse time of ALD precursor #2

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**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 VO<sub>2</sub> 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 <sup>-2</sup> Torr)		
		N <sub>2</sub> (100%)	98.78% N <sub>2</sub> + 1.22% O <sub>2</sub>	99% N <sub>2</sub> + 1% O <sub>2</sub>	98.5% N <sub>2</sub> + 1.5% O <sub>2</sub>	98.2% N <sub>2</sub> + 1.8% O <sub>2</sub>	99.4% N <sub>2</sub> + 0.6% O <sub>2</sub>	2.7 × 10 <sup>-2</sup> Torr (1 sccm O <sub>2</sub> )
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 VO<sub>2</sub>. Therefore, post annealing treatment of ALD deposited thin films is required to produce the technologically important polycrystalline stoichiometric VO<sub>2</sub> 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 (V<sub>2</sub>O<sub>5</sub>, V<sub>2</sub>O<sub>3</sub> 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 VO<sub>2</sub> 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 VO<sub>2</sub> phase.

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

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 VO<sub>2</sub> by RF magnetron sputtering of metallic vanadium.*— For benchmarking VO<sub>2</sub> 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 O<sub>2</sub> at low vacuum condition. Base pressure was set to less than 10<sup>-6</sup> Torr for RF magnetron sputtering. We used a deposition pressure of 3 × 10<sup>-3</sup> 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 N<sub>2</sub> to O<sub>2</sub> ratios in order to oxidize vanadium into stoichiometric VO<sub>2</sub> 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

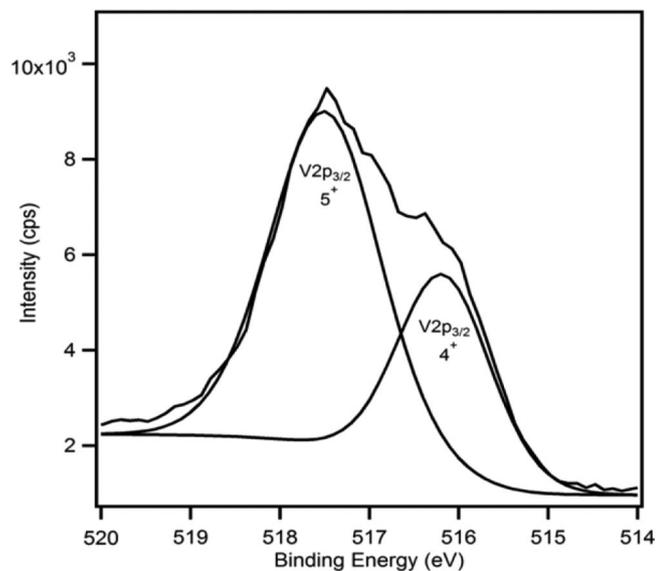
The composition and the stoichiometry of the as-prepared amorphous vanadium oxide ALD films deposited on the Si substrate were measured by XPS as shown in Figure 1. For the as-synthesized ALD vanadium oxide film, the binding energy of the V2p<sub>3/2</sub> peaks was fitted as 517.5 eV and 516.1 eV. These two values correspond to the V<sup>5+</sup> and V<sup>4+</sup> oxidation state of vanadium, respectively. This reveals that the as-prepared amorphous ALD vanadium oxide films contained a two phase mixture of 68.7% V<sub>2</sub>O<sub>5</sub> and 31.3% VO<sub>2</sub>. 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 VO<sub>2</sub> films. (The gray highlighted rows were the successful oxidation conditions.)**

Sample No.	Ramp time (min)	Oxidation temperature (°C)	Hold time (min)	N <sub>2</sub> (sccm)	O <sub>2</sub> (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 V<sub>2</sub>O<sub>5</sub> in the mixed phase ALD films.

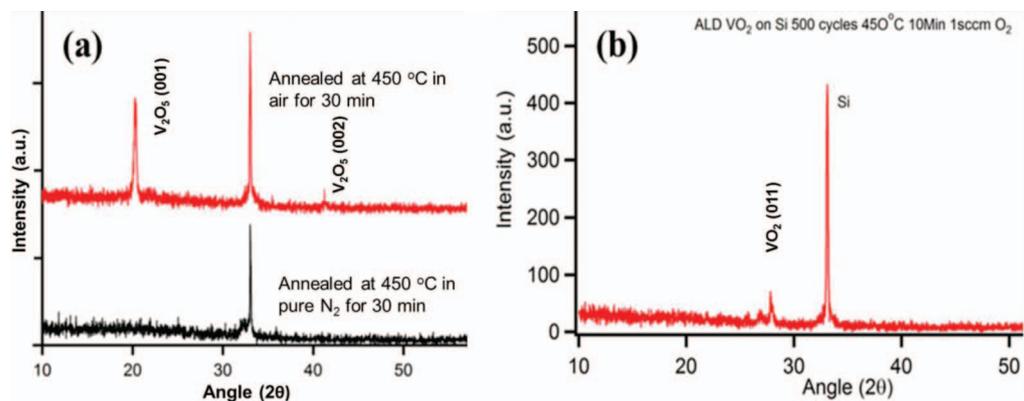
In order to obtain the stoichiometric VO<sub>2</sub> phase, the amorphous starting material needs to be recrystallized and chemically reduced by furnace annealing at 450°C in an accurately controlled annealing atmosphere. When furnace annealing was performed in regular air at 450°C for 30 min, only V<sub>2</sub>O<sub>5</sub> was produced instead of VO<sub>2</sub> 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 V<sub>2</sub>O<sub>5</sub> 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 V<sub>2</sub>O<sub>5</sub> phase. For comparison, when furnace annealing was performed in pure 100% N<sub>2</sub> 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 VO<sub>2</sub> phase under the favorable annealing condition of 450°C for 10 minutes with an optimized 1 sccm O<sub>2</sub> flow in a low vacuum at  $2.7 \times 10^{-2}$  Torr.



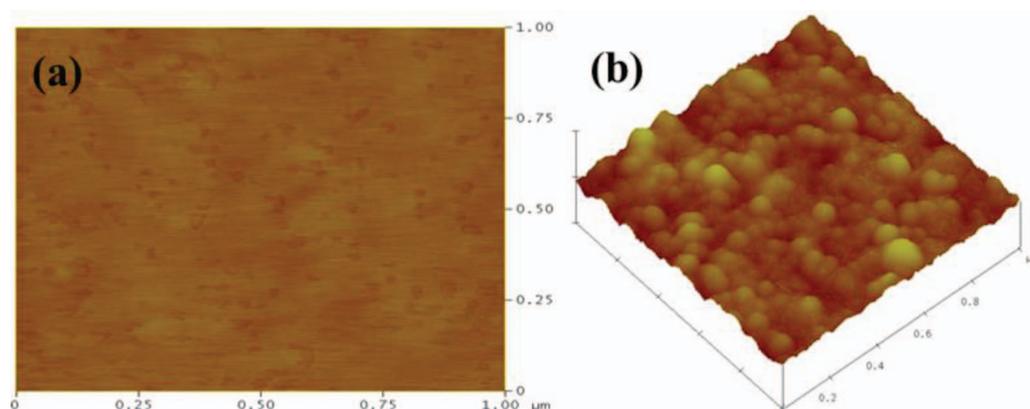
**Figure 1.** XPS measurement of as-deposited ALD amorphous vanadium oxide films on silicon substrates revealing the presence of 2 valence states of vanadium (+5, and +4) indicating a mixture of 68.7% V<sub>2</sub>O<sub>5</sub> and 31.3% VO<sub>2</sub>.

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 VO<sub>2</sub> films.

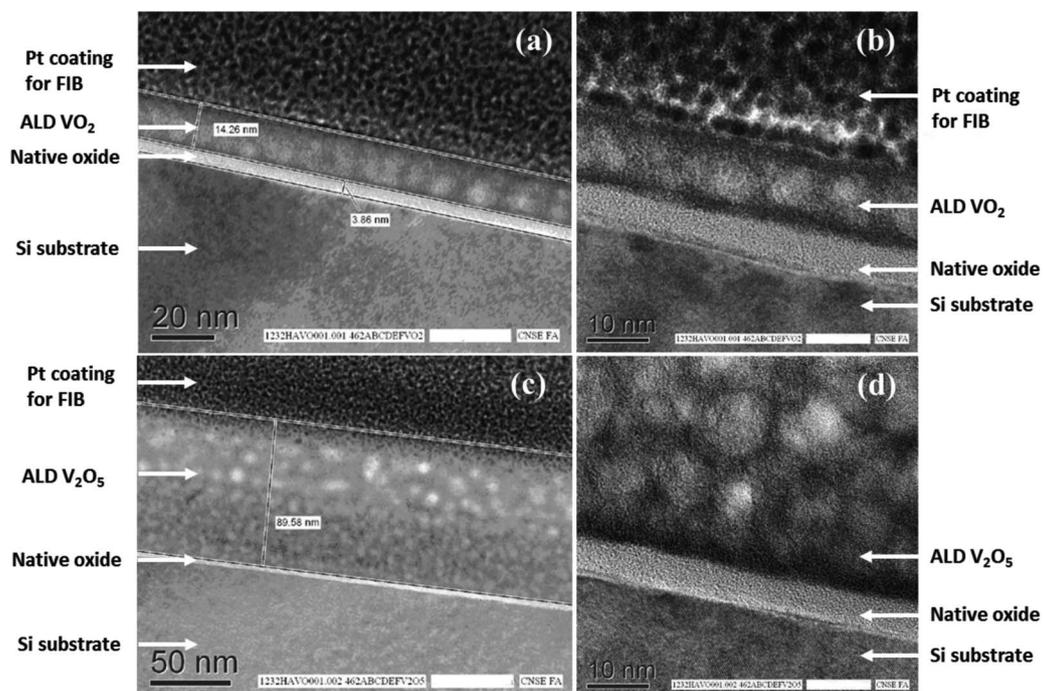
The images in Figure 4 were obtained by cross-sectional Transmission Electron Microscopy (TEM) analysis of VO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub> ALD films after annealing at different conditions. We investigated a post-deposition furnace annealing for recrystallization at 425°C in an atmosphere of N<sub>2</sub>: 27 sccm blended with O<sub>2</sub> (0.34 sccm) corresponding to a ratio of 1.22% O<sub>2</sub> and 98.78% N<sub>2</sub> following ALD deposition in Figure 4a and 4b. The TEM cross-section reveals significantly larger spherical VO<sub>2</sub> 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 VO<sub>2</sub> 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 VO<sub>2</sub> crystallites in this view. The TEM cross-section measurements reveal the crystallized VO<sub>2</sub> 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 V<sub>2</sub>O<sub>5</sub> films through annealing of the initially amorphous ALD vanadium oxide films at 600°C for 6 hours under atmospheric pressure with 60 sccm N<sub>2</sub> and a blend of 0.6 sccm O<sub>2</sub> 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 (VO<sub>2</sub>) film ended up with a thickness of 14.3 nm, while the vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) 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 V<sub>2</sub>O<sub>5</sub> has more oxygen and vanadium atoms compared to VO<sub>2</sub> and consequently takes up more volume. Figure 4c & 4d reveals TEM cross-sections of pure phase V<sub>2</sub>O<sub>5</sub> films recrystallized at the elevated temperature of 600°C. Two different size



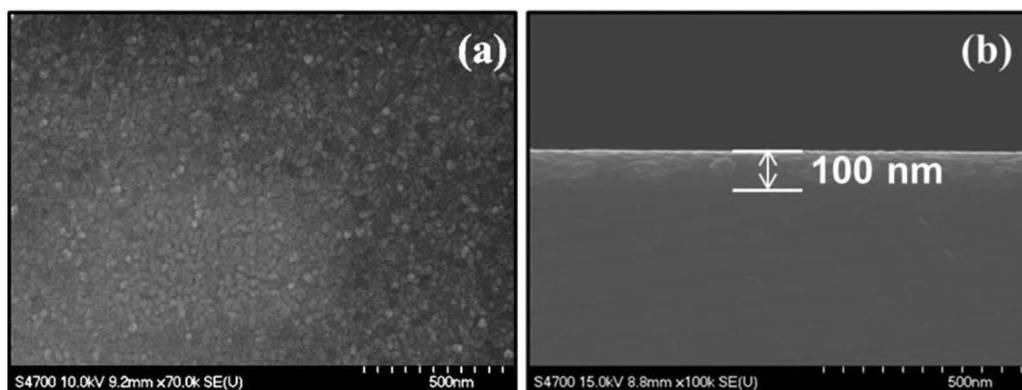
**Figure 2.** XRD results obtained from the furnace annealed ALD vanadium oxide samples at 450°C when annealed (a) in the presence of regular atmospheric air, and, alternatively, in 100% nitrogen gas for 30 min and (b) in the presence of a 1.2% O<sub>2</sub> and 98.8% pure N<sub>2</sub> gas mixture.



**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 VO<sub>2</sub> in 3-dimensional view after annealing in 1% O<sub>2</sub> and 99% N<sub>2</sub> 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 VO<sub>2</sub> films. Figure 4 (c) & (d) instead reveals TEM cross-sections of pure V<sub>2</sub>O<sub>5</sub> films recrystallized at the elevated temperature of 600°C. Two different size distributions of the resulting V<sub>2</sub>O<sub>5</sub> crystallites are visible. The lower half toward the Si substrate exhibits smaller V<sub>2</sub>O<sub>5</sub> crystallites, while the upper half of the film exhibits noticeably larger V<sub>2</sub>O<sub>5</sub> 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.

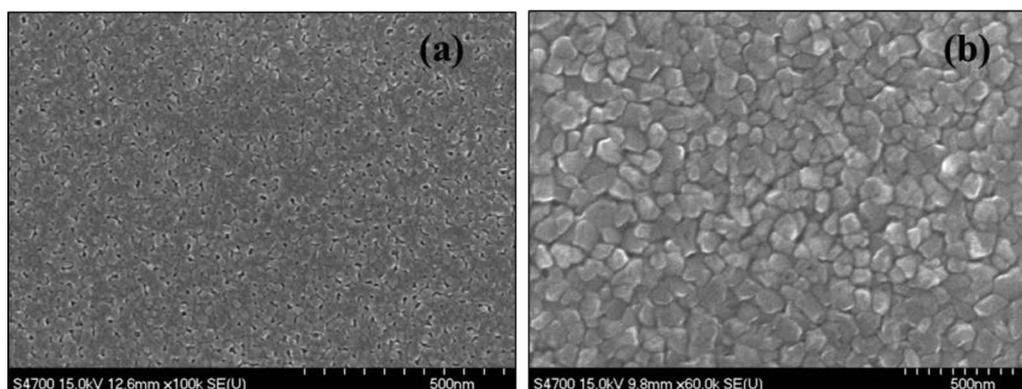
Figure 5 shows the FE-SEM micrographs of the vanadium metal sputtered on silicon substrates. Figure 5a shows the uniform and well covered surface of the fine grain polycrystalline vanadium metal which will be further annealed in a furnace to oxidize it to vanadium dioxide. Figure 5b shows a cleaved cross-sectional 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

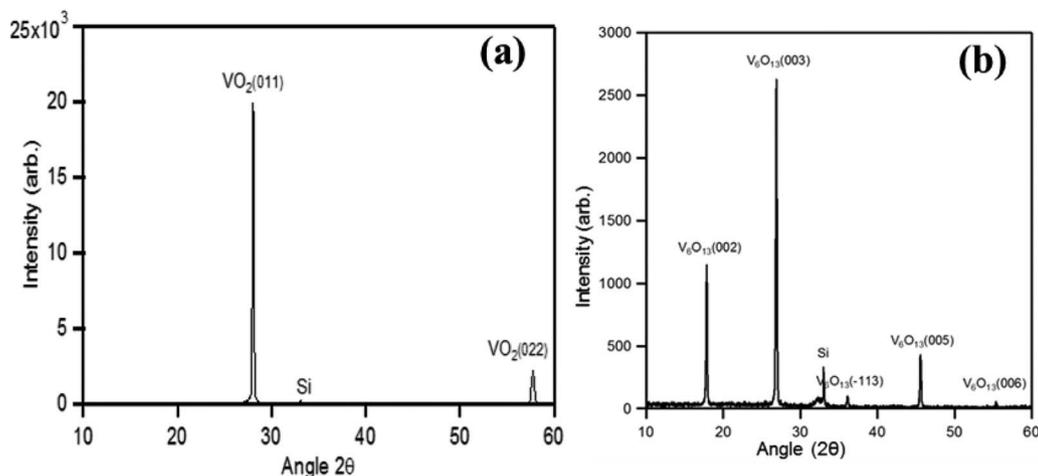
compared to the sample deposited using ALD in Figure 6a. This can be explained by the longer annealing time of 6 h at 450°C and the thicker starting film thickness of 100 nm for the sputter deposited pure vanadium films, which enables further solid state grain growth.

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 N<sub>2</sub> flow at 0.87–0.89 Torr and 0.05 sccm O<sub>2</sub> that resulted in stoichiometric VO<sub>2</sub> and (b) pure N<sub>2</sub> annealing atmosphere resulting in V<sub>6</sub>O<sub>13</sub>.

### Conclusions

Thermal ALD deposition of amorphous vanadium oxide thin films has been demonstrated with TEMAV and H<sub>2</sub>O 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% V<sub>2</sub>O<sub>5</sub> and 31.3% VO<sub>2</sub> 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 VO<sub>2</sub> 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 VO<sub>2</sub> 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 VO<sub>2</sub> 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 VO<sub>2</sub> films under the following four conditions: a) at an annealing temperature of ~425°C for 30 minutes, 98.78% N<sub>2</sub> and 1.22% O<sub>2</sub>, with a N<sub>2</sub> flow rate of 27 sccm under atmospheric pressure; b) at an annealing temperature of ~450°C for 30 minutes, 99% N<sub>2</sub> and 1% O<sub>2</sub>, with a N<sub>2</sub> flow rate of 27 sccm under atmospheric pressure; c) under low vacuum of  $1 \times 10^{-2}$  Torr, at an annealing temperature of 450°C for 10 min, in 99.4% N<sub>2</sub> and 0.6% O<sub>2</sub>, with a N<sub>2</sub> flow rate of 27 sccm; d) under low vacuum of  $2.7 \times 10^{-2}$  Torr at an annealing temperature of 500°C for 60 min in 100% O<sub>2</sub> ambient with 1 sccm flow rate. Physical characterization has been performed to compare polycrystalline VO<sub>2</sub> 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 VO<sub>2</sub> and V<sub>2</sub>O<sub>5</sub>. The thicker RF magnetron sputtered and oxidized VO<sub>2</sub> films are subject

to larger volume expansion and exhibit a significantly higher surface roughness compared to ALD recrystallized VO<sub>2</sub> 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.

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### References

- G. Rampelberg, M. Schaeckers, K. Martens, Q. Xie, D. Deduytsche, B. De Schutter, N. Blasco, J. Kittl, and C. Detavernier, *Appl. Phys. Lett.*, **98**, 162902 (2011).
- K. G. West, J. Lu, J. Yu, D. Kirkwood, W. Chen, Y. Pei, J. Claassen, and S. A. Wolf, *J. Vac. Sci. Technol. A*, **26**, 133 (2008).
- P. A. Premkumar, M. Toeller, I. P. Radu, C. Adelman, M. Schaeckers, J. Meerschaut, T. Conard, and S. Van Elshocht, *ECS Journal of Solid State Science and Technology*, **1**(4), 169 (2012).
- R. M. Wentzcovitch, W. W. Schultz, and P. B. Allen, *Phys. Rev. Lett.*, **72**, 3389 (1994).
- M. A. Mamun, S. K. Kittiwatanakul, K. Zhang, H. Baumgart, J. Lu, S. Wolf, and A. Elmstafa, *Supplemental Proceedings of TMS 141<sup>st</sup> Annual Meeting*, **2**, 753 (2012).
- K. Zhang, M. Tangirala, D. Nminibapiel, W. Cao, V. Pallem, C. Dussarrat, and H. Baumgart, *ECS Trans.*, **50**, 175 (2013).
- H. A. Wriedt, *Bull. Alloy Phase Diagrams*, **10**, 271 (1989).
- H. A. Wriedt, in *Phase Diagrams of Binary Vanadium Alloys*, J. F. Smith, Editor, p. 175, ASM International, OH, USA (1989).
- Z. Yang, C. Ko, and S. Ramanathan, *Annu. Rev. Mater. Res.*, **41**, 337 (2011).
- D. Brassard, S. Fourmaux, M. Jean-Jacques, J. C. Kieffer, and M. A. El Khakani, *Appl. Phys. Lett.*, **87**, 051910 (2005).
- H. K. Kim, H. You, R. P. Chiarello, H. L. M. Chang, T. J. Zhang, and D. J. Lam, *Phys. Rev. B*, **47**, 12900 (1993).
- K. Nagashima, T. Yanagida, H. Tanaka, and T. Kawai, *J. Appl. Phys.*, **100**, 063714 (2006).
- M. Pan, H. Zhong, S. Wang, J. Liu, Z. Li, X. Chen, and W. Lu, *J. Cryst. Growth*, **265**, 121 (2004).