Tunable Electrical Properties of Vanadium Oxide by Hydrogen-Plasma-Treated Atomic Layer Deposition

Helen Hejin Park, Thomas J. Larrabee, Laura B. Ruppalt, James C. Culbertson, and S. M. Prokes

†Electronics Science and Technology Division, U.S. Naval Research Laboratory (NRL), 4555 Overlook Avenue, SW, Washington, District of Columbia 20375, United States
‡American Society for Engineering Education (ASEE) Postdoctoral Fellow at NRL, 4555 Overlook Avenue, SW, Washington, District of Columbia 20375, United States
§Sotera Defense Solutions, 2121 Cooperative Way, Suite 400, Herndon, Virginia 20171, United States

ABSTRACT: In this study, a plasma-modified process was developed to control the electrical properties of atomic layer deposition (ALD)-grown vanadium dioxide (VO₂), which is potentially useful for applications such as resistive switching devices, bolometers, and plasmonic metamaterials. By inserting a plasma pulse with varying H₂ gas flow into each ALD cycle, the insulator-to-metal transition (IMT) temperature of postdeposition-annealed crystalline VO₂ films was adjusted from 63 to 78 °C. Film analyses indicate that the tunability may arise from changes in grain boundaries, morphology, and compositional variation despite hydrogen not remaining in the annealed VO₂ films. This growth method, which enables a systematic variation of the electronic behavior of VO₂, provides capabilities beyond those of the conventional thermal ALD and plasma-enhanced ALD.

INTRODUCTION

Vanadium dioxide (VO₂) has the ability to reversibly transform from an insulator at lower temperatures to a metal at higher temperatures, with the insulator-to-metal transition (IMT) occurring at about 68 °C.¹ The abrupt electrical resistivity drop, up to 5 orders of magnitude, arises from a change in the VO₂ phase, with the low-temperature monoclinic structure transitioning to a tetragonal rutile structure above the IMT. Furthermore, the IMT itself can be shifted over a limited range by varying the properties of the film, including stoichiometry, microstructure, grain orientation, and strain.²−⁶ Such fundamental features make VO₂ attractive for numerous applications that require or benefit from tunable conductivity, including resistive memories and switches,⁷−⁹ bolometers,¹⁰ plasmonic metamaterials,¹¹ and Mott-field transistors.¹² Various growth techniques for VO₂ thin films have been reported in the literature, including magnetron sputtering,¹³ liquid injection chemical vapor deposition,¹⁴ molecular beam epitaxy (MBE),¹⁵ pulsed laser deposition (PLD),¹⁶,¹⁷ and atomic layer deposition (ALD).¹³,¹⁸−²⁰ Although some physical vapor deposition techniques have demonstrated tuning of the electrical properties of VO₂ by varying the oxygen flow rate during the growth or by ex situ hydrogen incorporation,¹⁵−¹⁷,²¹ a method to easily control the electrical properties has not yet been well established for vanadium oxide grown by ALD, a deposition technique that is highly desirable for applications requiring conformal thin-film growth.

The material properties of thin films grown by conventional thermal ALD and plasma-enhanced ALD (PEALD) are generally varied by controlling the deposition parameters, such as the growth temperature, precursor dosing and purging conditions; postannealing conditions; and extrinsic doping/alloying.²²−²⁵ An alternative approach is to alter the conventional ALD sequence by incorporating additional reactive plasma/metal precursor steps into the growth cycle, which has been shown to modify the electrical properties of ALD-grown ZnO thin films.²⁶

In this article, we report a plasma-modified ALD method that incorporates hydrogen plasma treatment steps into the growth sequence of vanadium oxide, allowing a simple and fine variation of the electrical properties, which is not generally achieved by conventional thermal ALD or PEALD. Plasma steps with increasing H₂ gas flow rates are shown to increase the resistivity and the IMT temperature of ALD VO₂ thin films, and film analyses suggest that these changes may be associated with growth-induced changes in morphology and grain structure or with stoichiometry modification arising from oxygen deficiency.

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RESULTS AND DISCUSSION

As shown in the Raman spectra in Figure 1a, the as-deposited vanadium oxide films are amorphous for both plasma-treated and untreated cases, where the strong peak at ~520 cm⁻¹ arises from the Si substrate. Following the 480 °C postdeposition annealing in N₂, the films are converted to crystalline VO₂ (Figure 1b), where all non-Si peaks correspond to VO₂ vibrations.27,28 The Raman spectra are consistent across both treated and untreated films, indicating that similar, phase-pure polycrystalline VO₂ films were formed regardless of the variation in the H₂ flow rate, and the H₂-plasma exposure did not damage the deposited VO₂.

In Figure 2a, electrical resistivity (ρ) is plotted against temperature (T) for VO₂ treated with different hydrogen flow rates of 30, 50, and 100 sccm in the H₂/Ar gas plasma mixture and compared with untreated VO₂ grown by thermal ALD. All films were annealed in nitrogen following deposition and are crystalline. The derivative [d(log ρ)/dT] versus temperature curves are plotted in Figure 2b, where the minimum and maximum values indicate the IMT and metal-to-insulator transition (MIT) temperatures during heating and cooling, respectively. The transition temperatures are plotted against H₂ gas flow rate in the inset of Figure 2b, where it can be seen that the MIT temperature generally increases with increasing hydrogen flow rate, while the MIT temperature is roughly constant, resulting in an increased hysteresis at higher hydrogen flow rates. At the maximum hydrogen flow rate used here, 100 sccm, the VO₂ IMT temperature was ~78 °C, a 15 °C increase from the IMT temperature of ~63 °C observed for the thermally grown film. With increasing hydrogen flow, the resistivities in both the insulating and metal phases increased as well. The resistivity at high temperatures increased by approximately 2 orders of magnitude as the hydrogen flow rate was increased from 30 to 100 sccm, whereas the resistivity increased by less than an order of magnitude at low temperatures (Figure 2a).

This results in a smaller insulator-to-metal resistance ratio (Rᵢ/Rₘ) at higher H₂ gas flow rates, with Rᵢ/Rₘ decreasing by an order of magnitude, from 3.2 × 10² at a H₂ flow of 30 sccm to 3.8 × 10¹ at a H₂ flow of 100 sccm. The as-deposited amorphous films showed only a slight decrease in resistivity from 6.4 to 0.7 Ω cm with increasing temperature, suggesting no significant IMT behavior.

A variety of mechanisms have been shown to influence the temperature-dependent electrical properties of VO₂ thin films, including variations in stoichiometry, strain, oxygen defect density, and the presence of grain boundaries.2,6,9,30 The X-ray photoelectron spectroscopy (XPS) images of the O 1s, V 2p₅/₂, and V 2p₃/₂ peaks for the treated and untreated vanadium oxide films, which were postannealed in nitrogen, are shown in Figure 3. A compositional analysis of vanadium oxides via XPS is challenging because films readily oxidize in air, forming a layer of V₂O₅ on the surface, and Ar⁺ bombardment reduces the surface due to preferential oxygen sputtering.11,12 However, it has been reported that a representative film for comparative purposes can be obtained with careful etching using slow ions;31 therefore, samples were slowly sputtered with Ar ions for 10 s until the C 1s peak could no longer be detected. To estimate the compositional trends, the O 1s and V 2p regions were fitted together using a Shirley background, and the
The oxygen-to-vanadium (O/V) atomic % ratio was computed by integrating the fitted peak intensities and scaling by appropriate sensitivity factors. As depicted in the inset of Figure 3, the O/V atomic % ratio appears to decrease slightly as the H₂ flow rate is decreased from 100 to 30 sccm, suggesting an increase in oxygen deficiency and a corresponding metal enrichment with decreasing H₂ gas flow for the annealed films. The correlation of decreasing IMT temperature with increasing oxygen vacancies among the plasma-treated annealed films is in agreement with the trends observed in previous reports for VO₂ films grown by PLD, MBE, and sputtering. 15−17 Although the as-deposited films do not show any noticeable trend correlated with the plasma treatments, the annealed films in general tend to have a higher oxygen content compared to that of the as-deposited films, which may be due to the trace amount of oxygen in the annealing atmosphere.

Variations in the VO₂ film morphology due to the plasma treatment are evident in the atomic force microscopy (AFM) topographs of Figure 4, where the N₂-annealed films exhibit decreasing surface roughness with increasing H₂ gas flow. The root-mean-square roughness (σRMS) of 12.3 nm for the untreated film decreases to 4.6 nm for the smoothest case, and is obtained with a hydrogen flow of 100 sccm. Along with the decreasing roughness, the larger, more anisotropic, long, thin grains of the thermally grown VO₂ film gradually become smaller and more isotropic with increasing hydrogen flow. The average grain sizes are estimated at 217 ± 116 nm for the thermally grown film and 217 ± 188, 188 ± 73, and 166 ± 61 nm for the treated films with H₂ flow rates of 30, 50, and 100 sccm, respectively. The decreasing grain size of crystals implies more grain boundaries and thus a lower carrier mobility, which would contribute to the overall resistivity increase observed with a higher H₂ gas flow rate. 3,4,33 Previous reports suggest that the IMT transition behavior, such as the transition sharpness, transition amplitude, and hysteresis width, can be strongly influenced by the density and orientation of grain boundaries. 34−36 A decrease in the grain boundary density can

![Figure 3. XPS of annealed vanadium oxide films treated with different flow rates of hydrogen plasma and a film grown by thermal ALD. The inset shows plot of oxygen to vanadium (O/V) atomic % ratio vs H₂ flow rate comparing as-deposited (black squares) and annealed (red circles) films.](image)

![Figure 4. AFM images and root-mean-square roughness (σRMS) values of annealed VO₂ films treated with different flow rates of hydrogen plasma and a film grown by thermal ALD.](image)
release internal stress, leading to a higher transition amplitude and a smaller hysteresis width.37 However, Raman peak positions between the plasma-treated annealed films shift by less than 1 cm\(^{-1}\) (Figure 1), suggesting that any stress differences in the films are too small to make much difference in the IMT behavior. A tendency of a sharper transition, a higher transition amplitude, and a smaller hysteresis width (Figure 2) is observed with increasing grain size, which agrees well with some previous reports.34–36 However, there is a much larger change in the hysteresis width and a smaller change in the grain size compared to those of these reports, suggesting that although grain size may play some role in influencing the IMT, it cannot be the only reason and the observed change must be due to a combination of morphological and chemical effects.

Plasma–surface interactions are varied and complex, making it difficult to precisely identify the chemical and physical mechanisms at work in the plasma-modified ALD process. The distribution of radical and excited species, mean ion energy, and electron energy distribution within the plasma depend greatly on the gas composition and pressure, even for the same nominal applied RF power. The concentration of reactive atomic hydrogen species in a plasma has been shown to vary with gas composition in a complex way such that a higher \(\text{H}_2\) flow sometimes actually yields lower amounts of energetic atomic \(\text{H}.38\) In addition to providing reactive species, the plasma may deliver localized surface heating through the exothermic recombination of atomic radicals as well as the physical impact of other energetic species (i.e., electronically excited states, low-energy ions, and fast neutrals).39 During the \(\text{H}_2\)-plasma pulse of the modified ALD process, the impingement of reactive and/or energetic species may alter the distribution of adsorbates and dangling bonds on the growth surface, possibly favoring the more thermodynamically favorable energy facets of crystals or modifying the number and types of sites available for reaction in the following ALD step (the second TEMAV pulse before reaction with water). The modification of the growth surface in this way could lead to changes in the incorporation of precursor that would impact the stoichiometry and morphology of the resulting film. Regardless of the mechanism, it is noteworthy that the effects due to the ALD hydrogen plasma treatment persist even after high-temperature anneals, which suggests it to be a robust means for controlling film properties.

Finally, as the variation in composition and morphology could account for the trends in the electronic behavior of \(\text{VO}_2\) films that we observe, one may ask whether there is a possible incorporation of hydroxyl groups or hydrogen doping as contributing factors due to the \(\text{H}_2\) plasma step. However, it is important to note that all samples, including those grown with additional \(\text{H}_2\) plasma steps, were annealed in nitrogen at 480 °C following growth to induce crystallization. As it has been previously shown that water and hydrogen desorb at 420 °C in similar metal oxides40 and dehydrogenation in \(\text{VO}_2\) occurs at 320 °C,41 there should be a negligible hydrogen content in the annealed crystalline \(\text{VO}_2\) films, suggesting that hydrogen doping is not responsible for the electronic behavior observed.

## CONCLUSIONS

In summary, a plasma-modified deposition method was developed to tune the electrical properties of ALD-grown and postannealed crystalline \(\text{VO}_2\) films. By inserting a plasma pulse with varying \(\text{H}_2\) gas flow rates between two TEMAV pulses during the ALD growth cycle, the temperature-dependent electrical properties of \(\text{VO}_2\) could be varied, with the IMT temperature increasing, the resistance ratio of insulator-to-metal phases decreasing, and the metal and insulator phase resistances increasing with increasing hydrogen flow rate. The variation in the electrical properties is suggested to arise from a combination of stoichiometric, morphological, and chemical effects introduced by the modified growth sequence. The plasma-modified ALD using hydrogen plasma exposure extends the versatility of ALD for vanadium oxide deposition and represents a method for tuning the film properties that are not currently accessible by conventional \(\text{VO}_2\) ALD.

## EXPERIMENTAL SECTION

Vanadium oxide films with thickness of approximately 40–60 nm were grown at 150 °C on Si(100) and quartz substrates in a commercial Beneq TFS-200 PEALD system. The precursors used were tetrakis(ethylmethylamino)vanadium(IV) (TEMAV, V(NEtMe)\(_4\), Air Liquide) and deionized \(\text{H}_2\text{O}\) for the vanadium and oxygen sources, respectively, with ultrahigh-purity argon used as the carrier gas. The vanadium precursor was evaporated at 60 °C from an open boat inside a hot cell (Beneq 500 cell) attached to the chamber. The exposure times for each dose of TEMAV and \(\text{H}_2\text{O}\) were 2 and 0.2 s, respectively. For the hydrogen-plasma-treated samples, the \(\text{H}_2\) plasma was dosed during the deposition using the following ALD sequence: TEMAV/\(\text{H}_2\) plasma/TEMAV/\(\text{H}_2\text{O}\). The \(\text{H}_2\) plasma exposure step consisted of a 3 s pulse of 13.56 MHz, 100 W RF power, in a closely spaced, capacitively coupled geometry, with the \(\text{H}_2\) gas flow, introduced from the plasma shower head, set variably to 30, 50, or 100 sccm. The Ar flow rate through the shower head was held constant at 400 sccm for all plasma runs. A grid installed between the plasma and the substrate intercepts most ions, ensuring primarily neutral species to reach the sample. For comparison, an untreated film was deposited by thermal ALD using the conventional ALD sequence of TEMAV/\(\text{H}_2\text{O}\). Films grown by the conventional thermal ALD sequence and the four-step plasma sequence all have similar growth rates of \(\sim0.2\ \text{Å/cyc.}\) Vanadium oxide films grown by ALD are generally reported to be amorphous in the as-deposited state, with no significant IMT behavior, and therefore require annealing to be converted to crystalline \(\text{VO}_2\).18–20 Previous studies have reported that postannealing in \(\text{N}_2\) or a \(\text{N}_2/\text{O}_2\) gas mixture with a low \(\text{O}_2\) partial pressure resulted in crystalline monoclinic \(\text{VO}_2\) for the temperature range of 450–500 °C.19,20 As a result, following deposition, all of the samples in this study were annealed at 480 °C for 1 h in a hot-wall chamber connected to a roughing pump under a constant flow of \(\sim8\) Torr of 99.5% \(\text{N}_2\) gas. Determined by calculations based on the total gas pressure and the gas purity, the \(\text{O}_2\) background pressure is \(\sim0.008\) Torr.

Temperature-dependent resistivity measurements on deposited films were made using a four-point probe system with a heated sample holder. The film thickness for each sample was verified by spectral ellipsometry. The film crystallinity was analyzed by Raman spectroscopy, using a 100 µW 488 nm laser, and the film composition was examined by XPS (Thermo Scientific, K-Alpha with an Al K\(\alpha\) source), and the surface morphology was investigated by tapping-mode AFM (Bruker).

## AUTHOR INFORMATION

**Corresponding Author**
*E-mail: prokes@nrl.navy.mil.*
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