Atomic Layer Deposition of Vanadium Dioxide and a Temperature-dependent Optical Model

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Abstract

Vanadium dioxide is a material that has a reversible metal-insulator phase change near 68 °C. To grow VO₂ on a wide variety of substrates, with wafer-scale uniformity and angstrom level control of thickness, the method of atomic-layer deposition was chosen. This ALD process enables high-quality, low-temperature (<150 °C) growth of ultrathin films (100-1000 Å) of VO₂. For this demonstration, the VO₂ films were grown on sapphire substrates. This low temperature growth technique produces mostly amorphous VO₂ films. A subsequent anneal in an ultrahigh vacuum chamber with a pressure of 7x10⁻⁴ Pa of ultra-high purity (99.999%) oxygen produced oriented, polycrystalline VO₂ films. The crystallinity, phase, and strain of the VO₂ were determined by Raman spectroscopy and X-ray diffraction, while the stoichiometry and impurity levels were determined by X-ray photoelectron spectroscopy, and finally the morphology was determined by atomic force microscopy. These data demonstrate the high-quality of the films grown by this technique. A model was created to fit to the data for VO₂ in its metallic and insulating phases in the near infrared spectral region. The permittivity and refractive index of the ALD VO₂ agreed well with the other fabrication methods in its insulating phase, but showed a difference in its metallic state. Finally, the analysis of the films' optical properties enabled the creation of a wavelength- and temperature-dependent model of the complex optical refractive index for developing VO₂ as a tunable refractive index material.

Video Article

Introduction

Vanadium dioxide undergoes a crystalline phase transition near 68 °C. This produces a structural crystal change from monoclinic to tetragonal. The origin of this transition remains controversial¹, however recent research is helping develop an understanding of the processes that produce this transition²,³,⁴. Irrespective of the origin, the phase transition changes the optical properties of VO₂ from an insulator (transmitting light) at room temperature to a more metallic material (reflecting and absorbing light) above the transition temperature².

A variety of methods have been used to fabricate VO₂ in the past (sputtering, physical vapor deposition, chemical vapor deposition, molecular beam epitaxy, solution, etc.)⁵. The properties of VO₂ largely depend on the technology used to fabricate the films⁶, which has produced significant variability between different growth techniques and subsequent anneal and led to varying crystallinity and film properties. This work investigates the optical properties of atomic layer deposited (ALD) grown films, however, the approach is applicable to modeling all types of VO₂ films.

Recently, groups are constructing optical devices by incorporating thin films of VO₂ onto optical substrates. As a rapidly growing new deposition method, ALD can assist in fabricating these optical devices and has several advantages over alternative techniques, such as large-area uniformity, angstrom level thickness control, and conformal film coverage⁷,⁸,⁹. ALD is the preferred technique for applications requiring a self-limiting layer-by-layer deposition approach, fabrication on a wide variety of substrate materials (e.g., for heterogeneous integration), or conformal coating of 3D structures¹⁰. Finally, the conformal coating of 3D structures of ALD process is particularly useful in optical applications.

For the experiments in this paper, ultrathin, amorphous ALD films were grown on double-side-polished, c-plane sapphire substrates at low temperatures and annealed in an oxygen environment to produce high-quality crystalline films. Using the experimental measurements, a model is created for temperature and wavelength dependent optical changes in VO₂ to enable its use as a tunable refractive index material¹¹.

Protocol

Caution: Consult all relevant material safety data sheets (MSDS) before use, and follow all appropriate safety practices and procedures. The atomic layer deposition growth of vanadium dioxide uses an ALD reactor. The precursors used for the ALD growth are tetrakis(ethylmethylamido)vanadium(IV) (TEMAV) and ozone (generated from ultra-high purity, UHP, 99.999% oxygen gas at 0.3 slm flow and 5 psi backing pressure). In addition, UHP (99.999%) nitrogen gas is used for purging the reactor chamber. For the subsequent vacuum
2. Annealing

NOTE: VO₂ films grown by the ALD technique in step 1 produce amorphous VO₂. To create oriented polycrystalline VO₂ films, the samples are annealed in a custom ultra-high vacuum annealing chamber with a six-way cross. To keep the annealing chamber clean, a load lock is created to insert and remove samples. A 3" diameter oxygen resistant heater is composed of a custom platinum wire heater. This heater provides radiative heating of an oxidized Inconel sled, to which the samples are mounted. The sled has high emissivity for good heat transfer from the heater to the samples.

1. Clean a c-Al₂O₃ (sapphire) substrate as follows: Solvent clean the substrate in acetone at 40 °C in sonicator for 5 min, then transfer it directly (no rinse) to 2-propanol at 40 °C and sonicate for 5 min. Rinse the substrate in running deionized water for 2 min, and dry it with nitrogen gas.
2. Ensure that ALD reactor chamber is at 150 °C and vent the ALD reactor with nitrogen gas.
3. Load cleaned sapphire substrate into the reactor, close the reactor, and pump to <17 Pa vacuum. Wait at least 300 s to ensure that the sample reaches 150 °C.
4. Prepare the ALD chamber by flowing 20 sccm UHP nitrogen into the chamber (the base pressure should not exceed 36 Pa), and then pulse oxygen for 15 saturated cycles, where one cycle is a 0.05-s pulse followed by a 15 s purge.
5. To grow vanadium dioxide, pulse TEMAV for 0.03 s followed by a 30 s purge, then pulse ozone for 0.075 s followed by a 30 s purge. Repeat this pulse and purge cycle until desired growth is reached.
   NOTE: This process is nearly linear with a growth rate of 0.7-0.9 Å per cycle.
6. Remove the sample from the ALD reactor by first venting the ALD reactor chamber with UHP nitrogen gas. Place the sample on a metal plate (heat sink) to cool to room temperature. Close the ALD reactor and pump to <17 Pa vacuum. The sample now contains an amorphous vanadium oxide film on sapphire substrate.
   Caution: Remove the sample carefully, since the sample is heated to 150 °C.

3. Characterization

1. Examine the sample using Raman spectroscopy with a 532-nm laser excitation source.
   1. Load the sample into a microscope and bring it into focus. Verify the sample focus of the camera image in the software. Set the scan Laser Power to 4 mW, Exposure Time to 0.125 s. Number of Scans to 10, and preview size to 40 μm.
   2. Click Live Spectrum to observe Raman spectrum. Optimize focus, laser power, exposure time, and number of scans to maximize signal to noise ratio. Click Save spectrum to save the data.
   3. Open Spectrum in OMNIC. Click the "Find Pks" button to identify peaks. Determine crystallinity, phase (VO₂ vs. VO, V₂O₃, V₂O₅, etc.), and strain by comparing peaks to reference data for vanadium oxides, etc.
   NOTE: Narrow peaks indicate high crystalline quality, while hardening of Raman phonon modes 193, 222, and 612 cm⁻¹ and strain by comparing peaks to reference data for vanadium oxides.
2. Determine orientation, crystallinity, and phase by X-ray diffraction (XRD).
   NOTE: The appearance of peaks in the XRD spectra indicates the nature of the crystalline structure, specifically the crystal structure and orientation. The pattern of peaks in the XRD data is used to calculate the orientation of the sample as well as the phase of the material using the Inorganic Crystal Structure Database (ICSD) cards for different planes of VO₂. The pattern of peaks is compared to reference data for different vanadium oxide phases.
comparison of experimental peaks to the standard database was performed in this work. A single VO₂ peak at 39.9 degrees verifies the VO₂ crystal quality and demonstrates the monoclinic (020) orientation.

3. Determine stoichiometry and impurity levels by X-ray photoelectron spectroscopy (XPS).

1. Load the sample onto the sample holder. Open software and click vent load lock. Insert sample holder into load lock, and click pump down. Wait until pressure <4x10⁻⁵ Pa. Click the transfer button to move the sample holder into the chamber. Verify the chamber pressure is <7x10⁻⁶ Pa.

2. Input parameters into the experiment tree. Turn on X-ray gun with 400 µm spot size and then turn on flood gun. Add a point for survey measurement, and then add points for high resolution scans of precursor elements (C and N) as well as the film elements (V and O). For each measurement, add pass energy (200 eV for survey and 20 eV for high-resolution scans) and number of scans (2 or more for survey and 15 for high resolution).

3. Place crosshairs for point measurement at the desired location on the sample. Click and highlight the experiment tree title and then click “Experimental Run” on the menu bar to execute all measurement scans.

4. Execute the survey ID procedure to identify and analyze the elements in the film. Select Manual Peak Add followed by Peak Fit buttons to analyze bonding in high-resolution data scans. Determine stoichiometry by taking the ratio of the integrated peak intensities according to the XPS Handbook.

5. When finished, shutdown the guns, then click the transfer button to move the sample holder into the load lock. Once the sample is in the load lock, click vent load lock and unload the sample.

NOTE: This identifies the presence of all elements in survey, thereby identifying impurities. XPS peaks at specific binding energies show the valences of vanadium oxides, as shown in Figure 1. For example, these results show two representative XPS measurements obtained by deep profiling with a cluster ion gun etching the as-deposited sample. The XPS measurement of the surface shows a peak at ~518 eV demonstrating the presence of V₂O₅, while the XPS measurement of the etched sample (in the film's bulk) shows a peak at ~516 eV demonstrating the presence of VO₂. The full-width-at-half-max indicates the bonding uniformity of the vanadium in the films (in other words, the phase purity). In addition, the analysis of the other energy peaks enables identification of contaminants (≥1 %).

4. Determine morphology by using atomic force microscopy (AFM).

1. Turn on the computer and AFM electronics. Start the Nanoscope program and select Tapping Mode, then select load Experiment. Initialize Stage.

2. Follow the experimental order on the left side of the screen and click Setup Menu. Use focus controls to focus optics on the cantilever. Align the laser on the probe by clicking Optimize Laser Position. Click Autobalance detector button, and then click the Autotune cantilever.

3. Load sample and turn on vacuum.

4. Click Navigate button and use the trackball to place the sample under the head. Click Tip Reflection and lower the head to the sample surface using Trackball, while holding the focus button down until the tip is in focus. Click the Sample button and close the AFM hood.

5. Click the Check Parameter Menu. Ensure the scan size is <1 µm and set the samples line to 512. Click the Engage Menu button. Wait 20 s.

6. Set the Scan size for 3 µm and move the scan speed at 3.92 Hz. Optimize the image, if necessary, by changing parameters: drive amplitude, amplitude set point, integral and proportional gains.

7. Capture the desired image by clicking the Frame Down button followed by the Capture Button. Following the scan, click the Withdraw button.

8. Double click on the desired image to open it in analysis software. To determine morphology, click the Flatten button and then click the Autotune button.

9. Click the Navigate Menu and click the Sample Load Position. Turn off the vacuum and unload the sample.

NOTE: For consistency from sample to sample, keep the same AFM scan parameters.

5. Determine optical transmittance and reflectance.

1. Use a tunable optical source and measure optical transmittance and reflectance at (or near) normal incidence in the near-infrared region. Calibrate the system without sample for 100% transmittance and with a gold mirror for near 100% reflectance.

2. Load the VO₂ sample onto the temperature controlled stage. Stabilize the sample at the desired temperature. Measure transmittance and reflectance over the desired spectral range, for example, throughout the near infrared region.

NOTE: For optimal results, the temperature should be varied at least 20 °C above and below the transition temperature of VO₂ (usually, 68 °C).

4. Modelling Optical Constants (Permittivity and Refractive Index)

1. Model the complex dielectric permittivity, ε, as a function of photon energy, E, using the following equation (where ε₀ is the high frequency permittivity followed by the sum of n oscillators where Aₙ is the oscillator amplitude, Eₙ the oscillator energy, and Bₙ the oscillator damping):

   \[ \varepsilon(E) = \varepsilon_{\infty} + \sum_{n} A_n \left( \frac{E_n^2 - E^2}{E_n^2 - i \varepsilon E B_n} \right) \]

   NOTE: Custom Matlab programs analyzed and modelled the data.

2. Enter known parameters for sapphire substrate in step 4.1, and use these to calculate the dielectric permittivity as a function of optical wavelength. Then calculate the refractive index \( n = \sqrt{\varepsilon} \), and use that, along with the VO₂ thickness, substrate thickness, refractive index (from step 4.3), optical wavelength, optical polarization, and angle of incidence as inputs to the transfer to obtain the reflectance and transmittance of the VO₂ coated substrate.
Employ an optimization technique (such as Nelder Mead\(^{15}\)) to update the VO\(_2\) input parameters and reduce the error between the measured and calculated results, thereby optimizing the parameters for the VO\(_2\).

5. Perform steps 4.2 to 4.4 at several temperatures spanning the insulating and metallic states of vanadium dioxide (temperatures from 30 to 90 °C). Model the temperature dependence of the refractive index of VO\(_2\) as follows:

\[
\varepsilon_{VO_2}(T) = f(T) \times \varepsilon_{\text{ins}} + (1 - f(T)) \times \varepsilon_{\text{metal}}
\]

where \(\varepsilon_{VO_2}(T)\) is the refractive index of VO\(_2\) as a function of temperature, \(\varepsilon_{\text{ins}}\) and \(\varepsilon_{\text{metal}}\) are the dielectric permittivity of the insulating and metallic phases, and \(f(T)\) is a temperature-dependent function governing the distribution of insulating and metallic optical properties.

Use a Fermi-Dirac-like function for \(f(T)\) to govern the transition between insulating and metallic state, similar to effective-medium approximations\(^{17,18,19}\), given by:

\[
f(T) = \frac{1}{\exp\left(\frac{T - T_c}{W}\right) + 1}
\]

where \(T_c\) is the transition temperature and \(W\) controls the width of the transition.

6. Employ an optimization technique to update the parameters (\(W\) and \(T_c\)) in the equation for \(f(T)\) to reduce the error between the measured and calculated results, thereby optimizing the transition temperature and width. This results in a temperature and wavelength dependent model for the dielectric permittivity and refractive index of VO\(_2\).

Representative Results

To identify the quality of the ALD grown vanadium oxide, X-ray photoelectron spectroscopy (XPS) was performed on the as-deposited, primarily amorphous VO\(_2\) films (Figure 1) as well as annealed crystalline VO\(_2\) films (not shown). X-ray diffraction (XRD) was performed on the annealed VO\(_2\) films (Figure 2). In addition, to help quantify the vertical profile of the chemistry within the film, depth profiling was performed with a cluster ion source to minimize preferential etching of cation/anion species. Two representative traces are shown in Figure 1, one at the surface and one in the bulk. The depth profile and subsequent XPS measurements show that the top 1-nm of the as-deposited film is not VO\(_2\) due to excess environmental (adventitious) oxygen and carbon, but after a more controlled annealing procedure in low-pressure oxygen even the surface stabilizes to VO\(_2\). X-ray diffraction measurements were performed with a Cu K-alpha X-ray energy source and show, in Figure 2, a single VO\(_2\) peak at 39.9°. The signature of this peak verifies the quality of the ALD-grown VO\(_2\) as well as that the (020) crystal orientation aligns with the sapphire substrate’s peak.

To analyze the crystallinity, phase, and strain, Raman spectroscopy was performed using a 532-nm laser for excitation. Figure 3 shows a Raman spectrum of the VO\(_2\) film and shows narrow peaks which indicate high crystalline quality. In addition, the increased energy in the vanadium-vanadium low-frequency phonons (193 and 222 cm\(^{-1}\)) and the 612 cm\(^{-1}\) mode, as well as the decreased energy of the 389 cm\(^{-1}\) mode, suggest tensile strain in these films\(^{12,13}\).

The morphology was observed by atomic force microscopy (AFM). Figure 4 shows crystal grain sizes on the order of 20-40 nm and a root-mean-square (RMS) roughness of 1.4 nm for as-deposited films (Figure 4A) and an RMS roughness of 2.6 nm for annealed films (Figure 4B).

Optical transmittance and reflectance data were obtained using a white light source with a scanning monochromator and a photodetector, which provided coverage in the visible and near infrared region. Figure 5 shows the temperature dependence of the film as it transitions from an insulator to a metal, demonstrating a transition temperature of 61 °C. Analyzing the experimental data enables the modeling of the temperature and wavelength dependent permittivity of the VO\(_2\) as it transitions from insulator to metal. Figure 5 shows how the model accurately predicts the optical behavior when using the parameters in Table 1.
Figure 1: Representative XPS measurements of 35-nm thick VO$_2$ on c-Al$_2$O$_3$. XPS shows that the bulk of the film is VO$_2$ while the surface, which contains C and O contaminants, is shifted more towards V$_2$O$_5$. Stoichiometry suggests VO$_2$. Please click here to view a larger version of this figure.

Figure 2: XRD measurements of 35-nm thick VO$_2$ on c-Al$_2$O$_3$. This XRD measurement shows a single VO$_2$ peak at 39.9° that independently verifies the crystal quality and demonstrates the monoclinic (020) orientation is aligned with the underlying sapphire peak. Please click here to view a larger version of this figure.
Figure 3: Raman spectra of VO$_2$ on c-Al$_2$O$_3$. This Raman spectrum has narrow peaks, indicating high crystalline quality, and shows a slight tensile strain. Please click here to view a larger version of this figure.

Figure 4: Morphology of VO$_2$ on c-Al$_2$O$_3$. The AFM images show uniform, continuous films with grain sizes on the order of 20-40 nm and RMS roughnesses of (A) 1.4 nm for the as-grown film and (B) 2.6 nm for the annealed film. Please click here to view a larger version of this figure.
Figure 5: Near-infrared optical transmittance and reflectance of 35-nm thick VO$_2$ on c-Al$_2$O$_3$. The temperature-dependent behavior of the optical transmittance and reflectance of vanadium dioxide film are show at 40, 60, 70, and 90 °C. The open circles in the plot are the measured transmittance, reflectance, and calculated absorptance of the VO$_2$ on sapphire structure at various temperatures, while the solid lines are the predicted values from the two-dimensional temperature- and wavelength-dependent model of VO$_2$. Please click here to view a larger version of this figure.
The growth methods described here provide reproducible results with regards to uniformity, chemistry, structure, and morphology. The vanadium precursor is critical to producing the correct stoichiometry of as-deposited ALD films. This particular precursor promotes the +4 vanadium valence state, unlike many of the others listed in the literature that promote the more common +5 valence state. Additionally, this particular precursor has a fairly low vapor pressure and requires heating to provide a sufficient dose to saturate under the conditions given. Since this precursor starts to degrade around 175 °C, this sets an upper temperature limit to both heating of the precursor and ALD growth. Another critical aspect to achieving correct stoichiometry is the ozone concentration (~125 mg/L here) during dosing. Often the concentration of ozone produced by a generator under particular conditions degrades or drifts over time. If this happens, the ozone pulse and purge durations will have to be adjusted to maintain stoichiometry, morphology, and wafer uniformity. What is described here is how to grow ALD VO$_2$ on c-plane sapphire substrates, which includes in-situ ozone pre-treatment. The steps prior to growth for cleaning and nucleation are dependent on the substrate; however, the process described here works for most substrates (inert, oxides, metals, etc.) To determine the best termination cleaning and preparation for VO$_2$ growth, one should consider reactivity between species termination and the vanadium precursor while minimizing any native oxide on the substrate. Finally, this process has been demonstrated on high aspect ratio substrates (up to ~100) but for extreme cases, one should consider an exposure or static ALD method to enhance conformity further.

Table 1: Representative model parameters for VO$_2$. These parameters are representative of those used in an oscillator model to estimate the permittivity of VO$_2$ in its metallic and insulating phases.

| Phase | $\varepsilon_\infty$ | $E_n$ | $A_n$ | $B_n$ |
|-------|---------------------|-------|-------|-------|
| Insulator | 3.4 | 3.8 | 33 | 1.4 |
| Metal | 4.5 | 3.2 | 13 | 1.1 |

The ability to achieve high quality, crystalline ALD VO$_2$ films is quite dependent on the post-deposition annealing parameters. The most critical aspect is the pressure, specifically the partial pressure of oxygen. High oxygen pressures lead to faceting and grain growth, eventually causing nanowire formation, as well as results in the V$_2$O$_3$ phase. If the oxygen pressure is too low, oxygen is annealed out of the films resulting in V$_2$O$_3$ phase. Thus, to maintain the correct phase and minimize film roughness, the oxygen pressure should be maintained in the range of $1\times10^{-4}$ to $7\times10^{-5}$ Pa. Similarly, the temperature is critical to both being able to crystallize the film, maintain stoichiometry, and minimize roughening of the film. While the temperature of the VO$_2$ film is difficult to measure, empirical findings suggest that crystallization requires stage temperatures greater than 500 °C. At higher temperatures, it is harder to maintain the correct stoichiometry and phase and produce pinhole free films. There is also a trade-off between temperature and anneal time, specifically higher temperatures can reduce the anneal time. Additionally, the anneal duration is directly tied to the thickness of the film. Thicker films require longer times to achieve maximum crystallization. Thus, the oxygen pressure, anneal temperature, and anneal time described in the methods above were optimized to produce high quality VO$_2$ films that exhibit the largest change in optical properties at a nearly ideal transition temperature. Finally, the ramping and cooling rates during the oxygen anneal have an effect on roughness and morphology; the slower these are, the smoother the films.

ALD deposition and subsequent anneal of VO$_2$ produces oriented polycrystalline films with large area uniformity. ALD offers conformally grown films on three-dimensional nanoscale morphologies of almost any substrate. This enables VO$_2$ integration into novel applications, and is especially well suited for optical devices.

Following growth and optical measurements, a model is created which provides a good fit to the data for both the transmittance and reflectance of VO$_2$ in its metallic and insulating phases in the near infrared spectral region ($R^2 = 0.96-0.99$). The reflectance of the infrared insulating phase is the most challenging process in creating this model. Additional oscillator terms were added, but this increased model complexity, only marginally improve the fit in this region. It should be noted that in this model, the superposition of Lorentz oscillators is a common optical model and do not necessarily correspond to specific electronic transitions. Initially, the models included a Drude term, however, after mathematical optimization, the Drude term was essentially eliminated. For this reason, several minimization techniques were examined. However, these different techniques converged upon similar solutions that did not involve a Drude term. The absence of a Drude term in the ALD VO$_2$ could be due to a number of factors, such as 1) doped-semiconductor-like resistivity, or 2) a plasma frequency shift to lower energies and/or large collision rate (damping term), in agreement with the metallic properties of these films.

In the insulating phase, T<60 °C, the permittivity and refractive index of the ALD VO$_2$ agree well with the other fabrication methods (sputtered$^{4,20,23}$ and pulsed-laser deposition$^{22,23}$). In the metallic state, T>70 °C, these ALD films exhibit lower loss than the VO$_2$ fabricated by other methods. It is important to note that while different fabrication methods produce somewhat different values for the permittivity and refractive index of VO$_2$, all films show similar trends.

The model in this paper of the temperature and wavelength dependence of the optical permittivity and refractive index agrees well with the experimentally measured data. This model’s ability to produce a good quality fit to the measured optical data demonstrates it can reliably predict the optical properties of VO$_2$ as the phase changes from an insulator to a metal. Using these models, the optical properties of VO$_2$ can be predictably tuned by temperature, thickness, and wavelength to design optical systems that achieve static and dynamic goals. These models
enable the design and development of optical systems using VO₂ in passive and active systems by modifying the film’s thickness as well as temperature.

Disclosures

The authors have nothing to disclose.

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