Thermochromic Phase Transitions in VO₂-based Thin Films for Energy-Saving Applications

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The thermochromic transition in vanadium dioxide (VO₂) has potential application as a smart energy-saving window coating, but the temperature of the transition must be depressed from 68 °C to Earth ambient temperatures by the incorporation of transition metal impurities. In this paper, we describe a high throughput combinatorial experiment to characterize the V₁₋ₓMₓO₂ phase space, in which M is another metal, for thermochromic transitions. Thin film combinatorial libraries were prepared by pulsed laser deposition on hot silicon substrates, and the M impurities were found to substitute into the VO₂ crystalline lattice on the V-site. For M = Ta, Nb, and W, the thermochromic transition temperature was depressed with increasing M concentration. Doping with multiple M atoms is also easily accomplished by combinatorial synthesis and was found to have unexpected effects on the thermochromic transition.

Introduction

Materials that contribute to more sustainable technologies are in high demand, and the highest impact can be made in the structures that are most ubiquitous. If widely implemented, thermochromic ‘smart’ building windows have the potential to save energy by making advantageous use of solar radiation and thereby reducing the energy load on heating, ventilation, and air conditioning (HVAC) systems (1, 2). Exploiting a crystalline phase transition in VO₂, these window coatings shift from infrared transparent on cold days when solar heating is desirable to infrared reflective as the ambient temperature increases. In pure VO₂, this transition occurs at 68 °C, but the incorporation of 1 % to 5 % cation impurities can depress the transition temperature to Earth ambient temperatures (1, 2).

To efficiently screen the vast compositional space of transition metal impurities in VO₂, we employed a combinatorial materials technique for both material synthesis and characterization. In addition to increasing experimental throughput by parallel material synthesis, these techniques can eliminate uncertainties associated with sample-to-sample or measurement-to-measurement variations (3, 4).

Experimental Methods

Combinatorial thin film libraries of continuously varying composition were prepared by pulsed laser deposition (PLD) from two or more unary metal oxide targets, e.g. V₂O₅ and Ta₂O₅. Taking advantage of the spatial non-uniformity of deposition rates from each
target, we produced library samples of composition $V_{1-x}M_xO_2$ where $M$ is a metal other than $V$ and $x$ is the fractional atomic substitution of $M$ for $V$. In this study, across a single library wafer, $x$ varied from $<0.01$ to $0.5$.

During deposition, the laser was pulsed at 10 Hz with 200 mJ pulses. The laser alternated among the targets, delivering 80 to 150 pulses to the $V_2O_5$ target and then 4 to 30 pulses to the other target(s), until a maximum film thickness of at least 150 nm was deposited. Recipes were chosen to give the desired range of film composition and thickness. Substrates were 76.2 mm diameter silicon wafers taken from the box without further cleaning prior to use. They were radiatively heated in vacuum to 500 °C prior to deposition. During deposition, the atmosphere was 0.67 Pa molecular oxygen.

The relative ratios of transition metals in this oxide thin film were determined by x-ray photoelectron spectroscopy (XPS). XPS\(^1\) was carried out on an Axis Ultra DLD spectrophotometer (Chestnut Ridge, NY) for all films measured. For the $V_{1-x}Ta_xO_2$ film, non-monochromated Mg Kα X-rays operating at 150 W were employed, while for all other films, monochromatic Al Kα X-rays operating at 150 W were employed. Spectra that are presented were collected at 40 eV pass energy via a hybrid lens, slot aperture and a hemispherical analyzer. Sample slices of up to 76.2 mm in length were analyzed at a time on an automated stage preprogramed to acquire spectra at evenly spaced intervals. Spectra were collected from the transition metal-oxide films for the O (1s), C (1s) and all employed transition metal elemental (e.g., V (2p), Ta (4d), Nb (3d), etc.) regions. Data analysis took place using Casa XPS (Teignmouth, UK). All presented spectra were energy referenced to the C (1s) peak maximum position at 284.5 eV representative of adventitious carbon and satellite subtracted. All acquired spectral regions were fit with a Shirley background with the exception of the Ta (4d) which was fit with a linear background.

A special high-throughput spectroscopic reflectance measurement apparatus has been constructed for screening these libraries for thermochromic transitions (5). A thermoelectric heater/chiller with a 90 mm plate maintained the library sample at a uniform temperature between 10 °C and 85 °C, while near infrared (NIR) reflectance measurements were made at many library locations, and hence many unique compositions. The heater/chiller temperature was then stabilized at a new setpoint, and the reflectances were measured again. In this way, a dataset of NIR reflectance as a function of temperature and film composition was built up and analyzed to identify thermochromic transition temperatures for each location on the library.

### Results and Discussion

#### Film Composition

In these combinatorial libraries, the film composition varied continuously with location on the film. Figure 1 is a digital photograph of the $V_{1-x}Ta_xO_2$ combinatorial library thin film. The spatial variation in deposition rate is evident by the different interference fringes that appear in the photo. The region of the highest deposition rate of

\(^1\) Certain commercial equipment, instruments, or materials are identified in this document. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the products identified are necessarily the best available for the purposes.
Ta oxide was 48 mm from the region receiving the highest deposition rate of vanadium oxide.

![Figure 1](image1.png)

Figure 1. A photograph of the V$_{1-x}$Ta$_x$O$_2$ combinatorial library thin film, 76.2 mm in diameter. Vanadium oxide deposition was centered at the top of the photograph, while Ta oxide deposition was centered in the bottom right of the film. The XPS analysis locations in Fig. 2 were spaced along the dashed arrow.

In Figure 2 we show XPS spectra at various locations from a region of high V content to the region of high Ta content along the photograph’s dotted orange arrow. The spectra in Fig. 2 demonstrate qualitatively that film composition changed dramatically over the 55 mm investigated. As the analysis location was moved across the library film, the area of the Ta (4d) peak increased significantly from almost imperceptible. Correspondingly, the V(2p) peak at 517 eV decreased in area but remained significant.

![Figure 2](image2.png)

Figure 2. Selected XP spectra at various locations on a V$_{1-x}$Ta$_x$O$_2$ combinatorial thin film library. As can be observed from the spectra, the Ta surface concentration decreases as the analysis location is shifted from the Ta-rich oxide film to the V-rich oxide film. As the Ta (4d) peak decreased, the V (2p) peak correspondingly increased. O (1s) was also visible at all analysis locations.
Thermochromic Behavior

We now consider the effect of the film composition on the insulator to metal crystalline and electronic transition. Because of our interest in smart thermochromic window applications, we characterize the transition by the changes in NIR reflectance.

For each composition represented on the $V_{1-x}Ta_xO_2$ sample library, the NIR reflectance switched from a low reflectance state to a high reflectance state, a consequence of the crystalline phase transition that occurred. In Fig. 3 transitions, indicated by measuring the reflectance at 1.7 $\mu$m as a function of temperature, are shown for four different library positions (film compositions). The library positions in the legend are the same scale as given in Fig. 2, and so the concentration of Ta impurities increased from the 59 mm position to the 24 mm.

Each reflectance transition is reversible with a hysteresis of $< 10 \, ^\circ C$, i.e., the material returned to its low reflectance state as it was cooled back to 20 $^\circ C$. As the Ta impurity content increased, the transition temperature decreased. However, for those films with greater Ta content, the character (shape) of the thermochromic transition has changed, with the transition occurring more gradually over a greater temperature range. Further, the difference between the reflectance at high and low temperatures has also decreased.

![Figure 3. The near infrared reflectance at 1.7 $\mu$m as a function of temperature at different positions on a $V_{1-x}Ta_xO_2$ combinatorial thin film library. In regions of the film with greater Ta content, the transition occurred at lower temperatures and over a wider range of temperatures.](image)

The trend seen in Fig. 3 was observed for several different impurity atoms in this study and in other studies (6-8), with a depression in transition temperature occurring at low impurity concentrations. At increasing impurity concentrations, the thermochromic transition itself can be suppressed, with little to no change in reflectance over the 10 $^\circ C$ to
85 °C temperature range. For other impurities, such as Hf, there was no depression of the thermochromic transition temperature over the investigated concentration range.

Figure 4 is a plot of NIR reflectance as a function of temperature for a variety of impurity atoms. These hysteresis curves were taken from five different combinatorial thin film libraries. The films differed in both thickness and impurity concentration, and without this information, no conclusions can be drawn about the efficacy of the different impurities. However, the curves are presented here to demonstrate the diversity of effects from different impurities. The transitions in VO₂ with Nb or W impurities appeared similar to those from the V₁₋ₓTaₓO₂ combinatorial library (Fig. 3), and the V₁₋ₓHfₓO₂ had a similar transition shape but with negligible depression in transition temperature from the VO₂ transition at 68 °C. Simultaneous doping with W and Nb decreased the reflectance of the high temperature state, though the impurities may have been too concentrated in this library (similar to the 24 mm position in the V₁₋ₓTaₓO₂ film in Fig. 3). Co-doping with W and Hf, in contrast, appeared to result in ‘double transition’ with possible transitions occurring at both 35 °C and 57 °C.

Figure 4. The NIR reflectance (1.7 μm) as a function of temperature for combinatorial thin film libraries of composition V₁₋ₓMₓO₂ with different M, as listed in the legend.

Figure 5 shows depression of transition temperatures in VO₂ due to the incorporation of Nb impurities. All of the film compositions represented on Fig. 5 came from a single V₁₋ₓNbₓO₂ thin film library and were measured simultaneously. Nb impurities were found to effect a temperature depression that is linear with Nb content (given as a percent of the total transition metal atoms) at 3.5 °C/cation percent, with 95 % confidence bounds of 3.1 °C/cation percent to 3.9 °C/cation percent. We found that the more electronegative impurities, e.g. W, Nb, and Ta, similarly depressed the VO₂ transition temperature while Hf incorporation had little to no effect.
Figure 5. The transition temperature for the thermochromic transition in $V_{1-x}Nb_xO_2$ combinatorial thin film library as a function of $x$, the Nb content. The transition temperature was depressed linearly at 3.5 °C/atomic percent.

Finally, we characterized the nature of the impurity incorporation into the VO$_2$ film. Because the thermochromic transition is an indicator of the metal-insulator crystallographic transition in VO$_2$, the crystal phase structure of the film at room temperature was expected to be monoclinic VO$_2$, the low temperature electrically insulating phase. Figure 6 presents the symmetric x-ray diffraction scans taken from two different regions of the $V_{1-x}Nb_xO_2$ combinatorial library. The two regions differ in their Nb content, $x = 0.6$ % and $x = 16$ %. Peak locations expected from both the monoclinic VO$_2$ phase and the tetragonal (rutile-type) VO$_2$ phase are also indicated. The prominent diffraction peak at both film compositions was the (011) peak at $2\theta = 28^\circ$. Because this peak is characteristic of both crystalline VO$_2$ phases and the phases differ only by peak shifting and the presence of low intensity peaks, the phases cannot be easily distinguished by their x-ray diffraction scans.

Figure 6. Room temperature x-ray diffraction scans of two compositions on a $V_{1-x}Nb_xO_2$ combinatorial thin film library, with $x = 0.6$ % Nb (upper, blue) and $x = 16$ % Nb (lower, gold). The locations of peaks expected from diffraction from tetragonal (green circles) or monoclinic (black triangles).
The (011) peak was shifted to a lower 2θ value (higher d spacing) in the film with 16 % Nb, consistent with substitution of the larger Nb atoms on the V site. Across the full combinatorial library, the d spacing of the (011) planes increased linearly with Nb impurity concentration, indicating the impurity is predominantly substitutional on the cation V site. This peak shifting in the direction of the tetragonal phase interferes with the ability to distinguish the crystalline transition to tetragonal at high Nb content.

Conclusions

The thermochromic phase transition in VO₂-based materials has potential application as a smart building window coating, if the transition temperature can be depressed to Earth ambient temperatures. We report a combinatorial materials experiment for surveying the phase space of prospective impurities for thermochromic transitions. Combinatorial libraries of the type V₁₋ₓMₓO₂ were prepared with a continuous gradient in M concentration. At low concentrations the impurity atoms were incorporated as substitutional on the cation V site. Thermochromism in thin film libraries was evaluated from NIR reflectance measurements at various temperatures and film compositions in a custom-built high throughput measurement system. For M = Ta, Nb, or W, the transition temperature was depressed with increasing impurity concentration. Doping with Hf, however, did not affect the transition. Co-doping with multiple impurities may produce synergistic or additive effects, but more study is needed.

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