V$_{1-x}$W$_x$O$_2$ thermochromic films for device applications

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Abstract
V$_{1-x}$W$_x$O$_2$ is known to be a reliable thermochromic material for multiple practical applications due to its insulator to metal transition temperature controlled by W doping. In this paper, we present electrical and optical properties of V$_{1-x}$W$_x$O$_2$ thin films synthesized by PLD technique. In this respect, the electrical resistance, the refractive index ($n$), and extinction coefficient ($k$) as a function of temperature from 25 to 80 °C and wavelength ranging from 500 to 3000 nm were obtained using conventional 4-probe resistance and ellipsometry methods. The direct and indirect bandgap values at different doping levels and temperatures have been calculated using $n$ and $k$ versus energy data and compared with thermally activated bandgap from electrical resistance. A decrease in direct and indirect bandgaps with temperature and wavelength was observed with doping and temperature. Comparison between thermal and optical bandgap demonstrates that activated thermal bandgap is only comparable with the lowest optical indirect bandgap.

Introduction
Vanadium dioxide VO$_2$/V$_{1-x}$W$_x$O$_2$ is one of the thermochromatic chemical compounds. Pure VO$_2$ undergoes a first-order phase transition from insulator with monoclinic structure, to metallic with tetragonal structure, around 68 °C [1]. The stimulation for the phase transition could occur thermally, electrically, optically, or under strain. V$_{1-x}$W$_x$O$_2$ is characterized by a transmittance that is strongly and reversibly temperature-dependent. However, the optical properties of electrochromic materials are controlled by electronic or ionic charges in the material as the phase transition occurs. The origin of insulator to metal phase transition is a matter of controversy, either due to charge transfer [2], Mott transition [3], or structural Peierls transition [4].

Various synthesis methods have provided different characteristic values for VO$_2$, including sputtering, sol–gel synthesis, atomic layer deposition, chemical vapor deposition, and pulsed laser deposition (PLD) [5]. The main factors that influence the processing methods are thickness, meta-morphology, impurity, microstructure, and oxygen concentration. The microstructure of the film, including grain size in the polycrystalline film, plays an important role in the sharpness of transition from the insulator to the metallic state. The insulator to metal transition temperature ($T_c$) depends on the oxygen concentration and the V/O ratio. The doping concentration M adjusts the $T_c$ in the V$_{1-x}$M$_x$O$_2$ system, where M is a divalent metal [5]. Specifically, a small amount of tungsten (W) reduces the $T_c$ at the expense of reduction on resistances at room temperature [7].

The optical properties of some transition metal oxides are known to be changed reversibly in connection with the phase transition from metallic to semiconductor in the films [5], which is attractive for smart window applications [6–8]. V$_{1-x}$M$_x$O$_2$ is the most attractive phase change material because the transition temperature is about 68 °C in the VO$_2$ and lower for V$_{1-x}$M$_x$O$_2$ films as determined in the visible and near-IR region [5]. The main challenge with the synthesis of V$_{1-x}$M$_x$O$_2$ is the purity, due to closely related phases. Vanadium dioxides (VO$_2$) are strongly correlated d1 electron systems and are known to have several polymorphs, which include VO$_2$(A), semiconductor perovskite VO$_2$(B), semimetal perovskite VO$_2$(M1) monoclinic, and VO$_2$(R) rutile structure. While the chemical formula is the same, they have different complex crystal structures. Among the above-mentioned VO$_2$ polymorphs, the rutile VO$_2$(R) and the monoclinic VO$_2$(M1) have been the most widely studied...
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phases due primarily to their metal-to-insulator transition (MIT) temperature (68 °C) close to room temperature. Since this phase transition is accompanied by a huge change in resistivity by more than three orders of magnitude, VO$_2$(R) and VO$_2$(M$_1$) have attracted electronic and optical applications [8]. There are limited data available in the optical characterization of polymorphous phases in the literature. The infrared optical measurements demonstrate low loss in the semi-transparent state, and higher loss is drastically reflective above the transition temperature where it is in a metallic state. In general, the loss depends on 2p electron transfer to the 3d level in the visual electromagnetic region around 400 nm, and in the near-infrared region, caused by the charge motion in electromagnetic waves [5].

In practice, the characteristics of the extinction coefficient ($k$), index of refraction ($n$), and other electromagnetic properties largely depend upon the synthesis technique. We have reported on the synthesis, transport, and optical properties of V$_{1-x}$M$_x$O$_2$ thin films in reference [5]. In this paper, we report on the optical properties of V$_{1-x}$M$_x$O$_2$ doped with W, using direct and indirect bandgap data obtained at various temperatures and doping levels. The influence of temperature and doping on direct and indirect electron transition is reported. Moreover, mechanisms of hysteresis in wavelength, resistance, and extinction loss are discussed.

**Experimental**

To synthesize various V$_{1-x}$W$_x$O$_2$ thin films, a Pioneer 240 large-area PLD System (Neocera) was utilized. The separation distance between the target and substrate was 50 mm, and a KrF excimer laser ($\lambda = 248$ nm) was used to ablate the target material [5]. The film thickness was approximately 180 nm on C-cut sapphire wafers. Two different methods were used for W doping: either by using 0.5 mm-diameter W-wires attached to the surface of the vanadium disk with various separation distances to control W percentage in the film structures or by incorporating W into the target [5]. The V$_{1-x}$W$_x$O$_2$ films were characterized using conventional four-probe electrical resistivity measurements [5]. A spectroscopic ellipsometry (J.A. Woollam V-VASE UV–VIS-NIR) is used for determining the complex refractive index of the V$_{1-x}$W$_x$O$_2$ films. The details of experimental measurement procedures have been published elsewhere [5].

**Results and discussions**

Figure 1 demonstrates the thermal and frequency hysteresis effects in both doped and undoped VO$_2$ films. The hysteresis in the films is due to two different effects: one due to crystal structure changing from monoclinic to tetragonal and the other due to correlated change from ordered to disordered phase. The plots in Fig. 1 show the complex refractive index of a 180 nm undoped ($x = 0$) VO$_2$ thin film (Fig. 1a) and resistance vs. temperature measurements for a 180 nm 0.34 at% W-doped VO$_2$ film (Fig. 1b) on sapphire substrate.

The bandgap of materials depends on two factors: (a) intrinsic factors including crystallographic structure, crystal field splitting, and hybridization O2p and V3d bands; (b) extrinsic factors include temperature, oxygen concentration, impurity, and doping or external electromagnetic field. The bandgap could be thermal bandgap or optical. The thermally activated bandgap can be obtained for the insulating region using Eq. 1.

![Fig. 1](image-url)  
**Fig. 1** a Refractive index vs wavelength for undoped VO$_2$ thin film. b Resistance vs temperature measurements obtained on 0.34 at% W-doped VO$_2$ thin film.
where $R_0$, $E_a$, and $K$ are pre-exponential factors, activation energy, and Boltzmann constant, respectively [5].

Figure 2 shows that the thermally activated bandgap decreases with temperature and doping with the exception of around transition temperature where the bandgap in the doped sample increases with temperature. Tauc’s approach is used to calculate the optical bandgap using energy-dependent absorption coefficient as [9]

$$ (\alpha E) = A(h\nu - E_g)^\gamma $$

where $h$ is the Plank constant, $\alpha$ is the absorption coefficient, and $E_g$ is the bandgap energy. The $\gamma$ factor depends on the nature of the electron transition and is equal to 1/2 or 2 for the direct and indirect transition bandgaps, respectively. The $A$ in the equation is the tangential constant that can be derived from measurement.

The attenuation coefficient, $\alpha$, is calculated using the relationship $4\pi k/\lambda_0$, where $\lambda_0$ is the wavelength of light in free space. The indirect and direct bandgaps of undoped and doped VO$_2$ thin films were determined from the attenuation coefficient plots; note, the indirect bandgap is associated with the splitting of the vanadium 3d states.

Figure 3 shows the plots of $(E \alpha)^{1/2}$ vs photon energy $E$, allowing the indirect bandgap approximated by linear extrapolation of the data onto the x-axis. The indirect bandgap at room temperature is ~0.35 eV for the undoped VO$_2$ and 0.22 eV for the 0.34 at% W-doped VO$_2$. After a sharp increase, there is a relatively flat band between 1 and 1.5 eV range, followed by a sharp increase above 1.5 eV. The flat band could be a result of inhomogeneity in the film consisting of both tetragonal and monoclinic forms resulting in multiband absorption. The rapid increase above 2 eV is attributed to a direct interband: O2p to V3d transition [10].

As shown in Fig. 4, the direct bandgap for the VO$_2$ thin films was determined from plots of $(\alpha E)^2$ vs $E$. It demonstrates the typical bandgap measurement by drawing the tangent on the steepest slope and interception of the slope with x-axis in eV. Identification of bandgap in multiphases with different crystal and polymorphous structure films is not straightforward due to overlapping of impure phases. The three bandgap values of $E_1$, $E_2$, and $E_3$ for direct and indirect bandgap are calculated and tabulated in Table 1 comparing both doped and undoped at room and elevated temperature. There is no obvious correlation between the values of $E_1$, $E_2$, and $E_3$, for direct and corresponding indirect doped and undoped films. However, there is a trend of decreasing direct and indirect bandgap with increasing temperature, which agrees with the general concept of the bandgap. Moreover, W doping increases the bandgap substantially at around 3 eV, but decreases at lower eV particularly close to zero.

Fig. 2 Thermally activated bandgap for doped and undoped VO$_2$ thin films

Fig. 3 a The indirect and direct bandgap determination for the undoped and 0.34 at% W-doped VO$_2$ thin films at room temperature and 80 °C. b Direct bandgap calculation graph [5]
The interesting feature of Fig. 4 is the disappearance of the bandgap values to zero eV at 80 °C, due to the change of crystal structure from monoclinic at room temperature to tetragonal at elevated temperature.

### Summary and conclusions

Thin films of $V_{1-x}W_xO_2$ synthesized using a large-area PLD system were characterized in this study. The electrical resistivity ratio of the undoped VO$_2$ between the insulating and the metallic states was in the order of $10^4$. The direct and indirect bandgaps at different doping levels and temperatures show $E_2$ values of 1.8 to 1.9 eV at room temperature for doped and undoped films for direct bandgap, and the $E_1$ edge value is around 0.5 eV. At a higher temperature beyond 80 °C, the film becomes tetragonal and metallic, with $E_2$ becoming zero. The effective bandgap is approximately 2.25 eV and 2.4 eV for the insulating state of the undoped and the 0.34 at% W-doped VO$_2$ thin films, respectively. The direct and indirect bandgaps decrease as temperature increases, and there is an irregular change in bandgap due to changing doping levels. Moreover, a comparison between optical and thermal bandgap demonstrates that there is no direct correlation between the two sets of data, except at lower indirect bandgap and thermally activated bandgap energy.

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