Optical properties of Mg-doped VO2: Absorption measurements and hybrid functional calculations

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(Received 28 September 2012; accepted 22 October 2012; published online 13 November 2012)

Mg-doped VO2 thin films with thermochromic properties were made by reactive DC magnetron co-sputtering onto heated substrates, and spectral absorption was recorded at room temperature in the 0.5 < hω < 3.5 eV energy range. Clear evidence was found for a widening of the main band gap from 1.67 to 2.32 eV as the Mg/(V + Mg) atomic ratio went from zero to 0.19, thereby significantly lowering the luminous absorption. This technologically important effect could be reconciled with spin-polarized density functional theory calculations using the Heyd-Scuseria-Ernzerhof [Heyd et al., J. Chem. Phys. 118, 8207 (2003); ibid. 124, 219906 (2006)] hybrid functional. Specifically, the calculated luminous absorbance decreased when the Mg/(V + Mg) ratio was increased from 0.125 to 0.250. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4766167]

This letter reports experimental and theoretical data on Mg-doped VO2 thin films. The main constituent (VO2) is a well known thermochromic material capable of reversible transition between a solar-transparent, semiconducting, and monoclinic state below a “critical” temperature τc of ~68 °C and a near-infrared reflecting, metallic-like and tetragonal state above τc.1,2 The associated modulation of solar energy transmittance makes VO2-based thin films a very promising candidate for window coatings for energy efficient buildings.3–6 The dopant (Mg) serves to widen the main band gap of VO2 and boosts luminous transmittance,7 which otherwise tends to be undesirably low and constitutes a major obstacle for practical implementation of thermochromic fenestration.6 Mg doping also decreases τc and brings it closer to room temperature.7 We present spectral measurements of optical absorption in the 0.5 < hω < 3.5 eV range of photon energy and find that these data can be reconciled with hybrid functional calculations.

Mg-doped VO2 thin films were made by reactive DC magnetron sputtering from 5-cm-diameter targets of V (99.5%) and Mg (99.9%) onto glass and carbon plates concurrently. The substrates were put on a rotating holder located 13 cm below the targets and were kept at ~450 °C during depositions. The deposition chamber was evacuated to 6.3 × 10⁻⁷ mbar before the substrates were heated. 80 ml/min of Ar and 5 ml/min of O2 (both 99.997%) were then introduced via mass-flow-controlled inlets. A total pressure of ~0.2 mTorr was maintained during film fabrication, and sputter powers were 172 W and 40–40 W for the V and Mg targets, respectively. Films were grown at ~0.056 nm/s to thicknesses d of 56 to 67 nm. We recorded d on a Bruker DektakXT profilometer, and supporting data were found by modeling of optical measurements. Elemental compositions were obtained from Rutherford backscattering spectrometry (RBS) applied to films on carbon. Mg contents were inferred from simulations based on the SIMNRA program,8 which executes iterative least-square fits to experimental spectra. Mg/(V + Mg) ≡ z atomic ratios lay in the 0 ≤ z < 0.19 interval.

Spectral normal transmittance T and near-normal reflectance R were recorded in the 0.5 < hω < 3.5 eV range for the semiconducting phase of the films, deposited onto glass, by use of a single-beam spectrophotometer for absolute measurements.9 The glass is transparent, and the absorption coefficient a was obtained from Beer-Lambert’s Law, i.e., a = ln[T/(1 – R)]. Optical band gaps (denoted Eg) were determined—using standard procedures10—from (zhω)m ≡ A(hω – Eg), where A is a constant. The exponent m depends on the nature of the optical transition and is 1/z, 1/z, 2, and 2/z for indirect-allowed, indirect-forbidden, direct-allowed, and direct-forbidden optical transitions, respectively. Linear extrapolation of (zhω)m vs hω near the band gap gave Eg as the intercept with the z = 0 axis.

Figure 1(a) shows (zhω)m vs hω for films with different Mg contents and presuming indirect-allowed transitions. Extrapolations yield two band gaps for pure VO2, Eg1 and Eg2, at 1.67 eV and ~0.5 eV, respectively, which are in line with well established data.11 It is essential to note that Eg1 shifts towards higher energy for increasing doping levels, specifically from 1.67 eV to 2.32 eV as z goes from zero to 0.190. For z = 0.116, which corresponds to about one of eight V atoms substituted by Mg, one finds Eg1 ≈ 1.95 eV. The strong displacement of Eg1 leads to significantly decreased luminous absorbance in thin films, as inferred from the bell-shaped shaded region in Fig. 1 illustrating the relative luminous efficiency of the eye.12 The observation of two band gaps can be rationalized from Goodenough’s seminal work on the electronic structure...
Monoclinic M1 phase of VO₂ were studied using the density functional theory (DFT) plane wave basis-set code package VASP. Core electrons were treated with the projector augmented wave (PAW) method. We used the Perdew-Burke-Ernzerhof (PBE) version of the generalized gradient approximation functional and the Heyd-Scuseria-Ernzerhof (HSE) hybrid functional and performed spin-polarized calculations. The energy cut-off for basis-set expansion was put at 500 eV, and the Gaussian broadening width for electronic smearing was 0.05 eV. Geometries were relaxed until residual atomic forces were < 0.1 eV/nm, at which point the total energies were calculated to a convergence threshold of 10⁻⁵ eV per cell for both functionals.

The crystallographic unit cell for the M1 phase comprises four V and eight O atoms and was used in calculations for pure VO₂. To simulate 25% doping, one V atom was replaced by Mg in this cell, while 12.5% doping was simulated by creation of a 2 × 1 × 1 supercell wherein one V atom was replaced by Mg. Gamma-centered 2 × 2 × 2 (for the supercell) and 4 × 6 × 6 (for the unit cell) were used. The crystal structure—i.e., cell parameters and atomic positions—was relaxed in each case. For pure VO₂, this procedure yielded lattice parameters agreeing with experimental data to within 0%–3% for different cell axes, always exceeding experimental values. Mg concentrations below 12.5% would require a supercell at least twice as large, which was deemed too demanding for HSE functional calculations.

The electronic and optical properties of the Mg-doped monoclinic M1 phase of VO₂ were studied using the density functional theory (DFT) plane wave basis-set code package VASP.

FIG. 1. (a) Experimental and (b) calculated (shaded) vs photon energy hω, where x is absorption coefficient, for Mg-doped VO₂ with the shown Mg/(V + Mg) atomic ratios. The shaded bell-shaped region signifies relative luminous efficiency of the eye (Ref. 12).

Electronic and optical properties of the Mg-doped monoclinic M1 phase of VO₂ were studied using the density functional theory (DFT) plane wave basis-set code package VASP. The crystallographic unit cell for the M1 phase comprises four V and eight O atoms and was used in calculations for pure VO₂. To simulate 25% doping, one V atom was replaced by Mg in this cell, while 12.5% doping was simulated by creation of a 2 × 1 × 1 supercell wherein one V atom was replaced by Mg. Gamma-centered 2 × 2 × 2 (for the supercell) and 4 × 6 × 6 (for the unit cell) were used. The crystal structure—i.e., cell parameters and atomic positions—was relaxed in each case. For pure VO₂, this procedure yielded lattice parameters agreeing with experimental data to within 0%–3% for different cell axes, always exceeding experimental values. Mg concentrations below 12.5% would require a supercell at least twice as large, which was deemed too demanding for HSE functional calculations.

The dielectric function ε(ω) = ε₁(ω) + iε₂(ω) fully describes the optical properties of a medium at all photon energies. The dielectric function for interband transitions was calculated in the momentum representation, which requires matrix elements between occupied and unoccupied eigenstates. The imaginary part of the dielectric function can be derived from

FIG. 2. Schematic band structure for monoclinic, semiconducting VO₂ according to Goodenough (Ref. 13). E_F denotes Fermi level.

\[ \varepsilon_2(\omega) = \frac{4\pi^2e^4}{\Omega} \lim_{\lambda \to 0} \frac{1}{2\varepsilon_{ck}} \sum_{c,k} \int_{\Omega} \delta(\varepsilon_{ck} - \varepsilon_{ck} - \omega) \times \langle \mathbf{u}_{ck+e_{ck}} | \mathbf{u}_{ck} \rangle \langle \mathbf{u}_{ck+e_{ck}} | \mathbf{u}_{ck} \rangle^*, \]

where \( e \) is elementary charge, \( \Omega \) is volume of the Brillouin zone, indices \( c \) and \( v \) refer to conduction and valence band states, respectively, \( w_k \) is weight of the \( k \)-point vector, \( \varepsilon_{ck} \) and \( \varepsilon_{ck} \) are energy levels, \( n_k, n_{ck} + e_{ck} \), and \( n_k, n_{ck} + e_{ck} \) are cell periodic parts of the wavefunction at a given \( k \)-point, and \( \varepsilon_1 \) and \( \varepsilon_2 \) are components of the unit vector. A Kramers–Kroning transformation was used to get the real part \( \varepsilon_1 \) from \( \varepsilon_2 \) by

\[ \varepsilon_1(\omega) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon_2(\omega') \omega'}{\omega'^2 - \omega^2 + i\eta} d\omega', \]

where \( P \) signifies the principal value and the integral is evaluated in the limit where \( \eta \) approaches zero. The absorption coefficient was then derived from

\[ \alpha(\omega) = 2(\omega/e) \left[ \left[ \varepsilon_2^2(\omega) + \varepsilon_1^2(\omega) \right]^{1/2} - \varepsilon_1(\omega) \right]/2 \right]^{1/2}. \]

We first consider pure VO₂ whose electronic band structure was recently studied with the HSE functional; the
electronic and optical properties have also been calculated by several other methods. Our results are almost identical to those of Eyert. Specifically, we find an indirect band gap of 1.38 eV corresponding to the difference between the maximum and the minimum of the bands in $k$-space. Figure 1(b) shows calculated spectral absorption coefficients for VO$_2$ as well as the doped systems. A comparison with the experimental data in Fig. 1(a) for $z = 0.116$ and $z = 0.190$—which are the compositions closest to those of the calculations—shows clear qualitative correspondence with theory.

The match between experimental and calculated spectral absorption is better for the Mg-doped samples than for pure VO$_2$, and one may ask why this is so. We speculate that a possible answer could be that electron correlation effects in VO$_2$ are reduced as a consequence of the Mg doping, thus allowing a more accurate description of electronic structure with DFT-based methods. Substitution of some V by Mg clearly influences the structure and leads to rearrangement of ionic positions, notably those of V. Thus, our calculations predict that the alternating V–V distances (0.315 and 0.252 nm, etc.) for pure VO$_2$ along the $a$ direction ( rutile $c$ axis) change for $z = 0.125$ and, moreover, become pair-wise similar (0.316 and 0.302 nm; 0.264 and 0.261 nm, etc.), as indicated in Fig. 3. It is interesting to note that even this modest Mg content affects the structure throughout the supercell. For $z = 0.25$, the V–V distances along the $a$ direction become 0.302 and 0.290 nm. We are not aware of any experimental attempts to determine the structural modifications invoked in VO$_2$ by Mg doping.

We also studied the electronic properties of Mg-doped VO$_2$, and Fig. 4 shows density of states for $z = 0.125$ and $z = 0.25$. The overall agreement with Goodenough’s band scheme, illustrated in Fig. 2, is apparent. The band gaps $E_{g1}$ and $E_{g2}$, calculated from the eigenvalues, are noted in the figure. Specifically, our $E_{g1}$ and $E_{g2}$ values are 2.07 and 0.72 eV for $z = 0.125$ and 2.12 and 1.01 eV for $z = 0.25$, respectively. Band structure calculations give clear evidence of indirect band gaps for $z = 0.25$ and pure VO$_2$.

Summarizing, we investigated the optical properties of Mg-doped VO$_2$ films experimentally and computationally.


