Optical properties of vanadium pentoxide determined from ellipsometry and band-structure calculations

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(Received 16 March 1990)

The optical constants of V_2O_5 single crystals along the three principal crystallographic axes were measured with use of spectroscopic ellipsometry. Theoretical optical constants of V_2O_5 were derived from band-structure calculations using the first-principles orthogonalized linear combination of atomic orbitals (OLCAO) method. The measured and calculated optical properties are presented and compared.

INTRODUCTION

The vanadium oxide system has gained most of its attention because of the metal-insulator transitions that occur in the lower oxides, VO, V_2O_3, and VO_2.[1–3] The most stable vanadium oxide with the highest oxygen concentration is V_2O_5, which exhibits highly anisotropic electronic and optical properties. Although V_2O_5 has been widely studied experimentally, the success in the theoretical interpretations of the experimental evidence has been limited.[4,5] V_2O_5 has an orthorhombic crystal structure with a rather complicated molecular building block, which may be one of the inherent problems with theoretically modeling and interpreting experimental data.

The optical properties of V_2O_5 single crystals have been investigated in an effort to gain a better understanding of the electronic band structure of this material.[6–13] It was shown that part of the band-edge absorption of V_2O_5 is due to direct forbidden transitions ($\mathbf{k}\neq\mathbf{0}$) predicting an energy gap near 2.3 eV.[6,7] Above the band edge, the optical properties exhibit sharp resonance structures with anisotropies as large as 4:1 in the *a* and *c* directions.[8–13]

Previous theoretical calculations of the electronic structure of V_2O_5 were done with a tight-binding-approximation method[4] and cluster calculations,[5] with the latter being in slightly better agreement with experimental optical data. The tight-binding calculations are currently the most comprehensive and were done by first calculating the band structure of the simpler rocksalt-structured VO (with its perfect octahedron). The calculations were then extended to the more complicated V_2O_5 with the addition of a $pd\pi$ interaction which was added to obtain good agreement with x-ray photoemission spectroscopy (XPS) data. The optical properties derived from the calculated band structure were compared with reflectivity data[13] and showed that the energy assignments of the fundamental band edge and other spectral features were in error by as much as 0.5 eV in the spectral range of 1–6 eV. The authors attributed the failing of the theory to the lack of self-consistency in the tight-binding method.

In light of recent success obtained in theoretical calculations of the optical properties of other oxide materials[14–18] using the first-principles orthogonalized linear combination of atomic orbitals (OLCAO) method, we have reexamined the optical properties of V_2O_5 with a combined experimental and theoretical approach. The optical properties of V_2O_5 single crystals were obtained for each crystallographic axis through a series of measurements using spectroscopic ellipsometry. The experimental results were compared with the theoretical optical spectra calculated from the wave functions derived from the OLACO band-structure calculations.

EXPERIMENTAL RESULTS

Single crystals of V_2O_5 were grown by the slow cooling of a vanadium pentoxide melt from 700 °C.[7] V_2O_5 powder (research grade, 99.999% pure) was packed into pellets and loaded into a conical-shaped platinum crucible. The pellets were melted at 700 °C in flowing oxygen and then slowly cooled at a rate of 1 °C/min at 400 °C. From 400 °C to room temperature the cooling rate was increases to 10 °C/min. The slow cooling yielded a large boule of material from which single crystals could be extracted. The crystals cleaved readily along the [010] direction. The cleavage generally yielded very thin (0.5 mm in the *b* direction) crystals with large, optically smooth *a*-*c* plane surfaces (10×5 mm^2). Due to the high surface quality of the cleaved faces, no polishing was needed to do the optical measurements.

The ellipsometer is a conventional null system that has been computer interfaced for sensitive data acquisition. The instrument has a high degree of accuracy in determining the ellipsometric angles Δ and ψ (0.01° for Δ and ψ) as compared to photometric techniques[19] due to the fine positioning of the polarization mounts. The additional sensitivity is based in the computer control which

allows accurate detection of null points using the method of "swings."[20]

Ellipsometry is capable of measuring both the amplitude and phase change without the need of a Kramers-Kronig (KK) analysis. Ellipsometry is less sensitive to the complications that are more commonly inherent in reflectivity studies, e.g., surface quality and the need for a large spectral range for accurate KK analysis.

There are limitations to conventional ellipsometry when it is used to study optically anisotropic materials since it cannot directly measure a large (larger than two) number of optical constants, e.g., V_2O_5 which has six optical constants, $n_a - ik_a$, $n_b - ik_b$, and $n_c - ik_c$. However, it has been shown that in some cases crystal symmetry can be exploited and used to do ellipsometric analyses of anisotropic materials.[21] By placing the crystal in the plane of incidence with the crystal axes in a specific orientation, the optical constants of materials with tetragonal or orthorhombic symmetry can be measured.[21] The analysis of orthorhombic crystals is made simpler when two crystal faces (any combination of *x-y*, *x-z*, and *y-z* faces) can be measured. However, in our case we only have one crystal plane (the *a-c* plane) with large enough dimensions to perform measurements. It is possible to extract the six optical constants from the single crystal[21] face by making four independent measurements with the sample and ellipsometer configured as shown in Table I. The optical constants of the material were then self-consistently calculated from the data using an iterative technique.[22] The *a*- and *c*-direction optical constants were calculated using the Newton-Raphson method and once these optical constants were determined the optical constants for the *b* direction could be calculated.

The imaginary part of the optical dielectric function and the real part of the refractive index for all three crystallographic directions, in the photon-energy range 1–4 eV are shown in Figs. 1 and 2, respectively. As can be seen there is a large anisotropy in all three crystallographic directions. These measurements are in good agreement with previous measurements of the V_2O_5 optical properties in both the *a* and *c* directions,[7–13] but these are the first detailed[23] measurements of the optical properties for the *b* direction. The spectral dependence of ϵ_2 is commonly analyzed because it is related to the optical transition matrix elements and usually gives a good gauge of the theory.

TABLE I. Experimental configuration of the ellipsometer used to determine the six optical constants of V_2O_5. All measurements were done on the (010) plane of the V_2O_5 single crystals. The sample orientation (the crystal axes *a* and *c*) relative to the plane of incidence and the light angle of incidence are indicated in the table.

Sample orientation relative to the plane of incidence	Angle of incidence
$a\perp, c\parallel$ $a\parallel, c\perp$	65°
$a\perp, c\parallel$ $a\parallel, c\perp$	75°

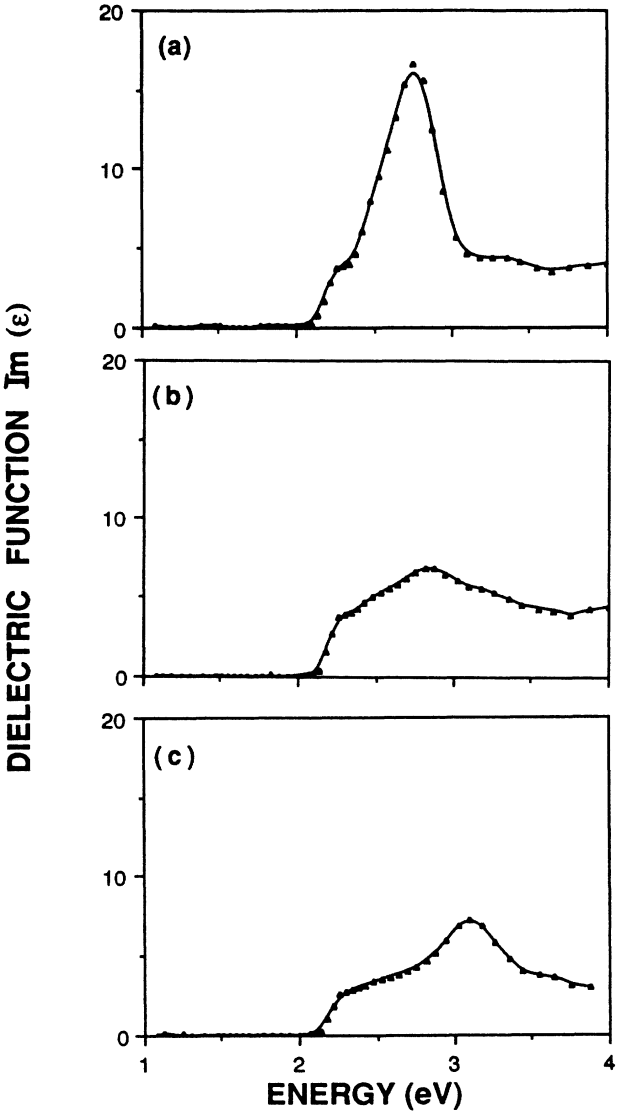

FIG. 1. The imaginary part of the optical dielectric function of V_2O_5 as determined by spectroscopic ellipsometry. The three crystallographic axes *a*, *b*, and *c* are indicated in the figure.

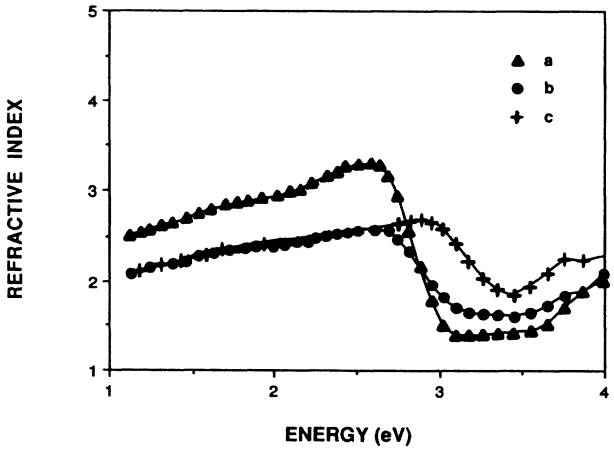

FIG. 2. The real part of the refractive index of V_2O_5 for the three crystallographic directions *a*, *b*, and *c* as indicated in the figure.

THEORETICAL RESULTS

The band structure and the optical properties of V_2O_5 are calculated by the first-principles OLCAO method. The OLCAO method has been demonstrated to be one of the more useful methods for calculating the electronic and optical properties of complex oxides.[14–18] In the present calculation for V_2O_5, we have used a full basis function which consists of the V 4*s*, 4*p*, 3*d*, 5*s*, 5*p*, and 4*d* and O 2*s*, 2*p*, 3*s*, and 3*p* atomic orbitals. With two formula units per cell for the V_2O_5 crystal, and with all the core orbitals eliminated by the orthogonalization process, the secular equation associated with this basis set for the determination of the energy bands $E(\mathbf{k})$ has a dimension of 152×152. The crystal potential is constructed according to the local-density approximation with correction for the correlation effect using the Wigner interpolation formula and is fitted to a set of atom-centered Gaussian functionals. We have attained an accuracy of 0.000 003 electron per valence electron in the unconstrained charge-density fit in the self-consistent iteration procedure, which is more than adequate for the band-structure studies. The energy eigenvalues and the wave functions are obtained at the 144 **k** points in $\frac{1}{8}$ of the Brillouin zone (BZ) of the orthorhombic cell. These 144 **k** points correspond to the corners of 450 tetrahedron microzones which are used in the BZ sum for the optical-absorption calculation. All the momentum-matrix elements for dipole transitions between the occupied valence band (VB) and the empty conduction band (CB) are evaluated exactly using the wave functions obtained at the same 144 *ab initio* **k** points.

The band structure of V_2O_5 along the lines of high symmetry is shown in Fig. 3. V_2O_5 is seen to be a semiconductor with an indirect band gap of about 2.0 eV. The top of the VB is at a point along the *RZ* direction while the bottom of the CB is at point Γ. The direct band gap at point Γ is 2.4 eV and the width of the VB is about 5.1 eV. The most conspicuous feature of this band structure is that the lowest CB consists of a pair of rather localized bands with a width of 0.75 eV. Inspection of eigenfunctions reveals that this pair of bands have V $3d_{xy}$ and V $3d_{yz}$ character with slight mixing from the O $2p_y$ orbitals. This pair of localized bands are separated from the higher CB by another energy gap of 0.6 eV. Therefore, we may view the electronic structure of V_2O_5 as a semiconductor with a large energy gap of 3.3 eV; but within this gap, there exist two localized bands. Once an electron is trapped in this CB, it is most likely that it will be confined in that band because of the large effective mass and the presence of another gap above it. The VB almost exclusively consists of the V 3*d* and the O 2*p* orbitals.

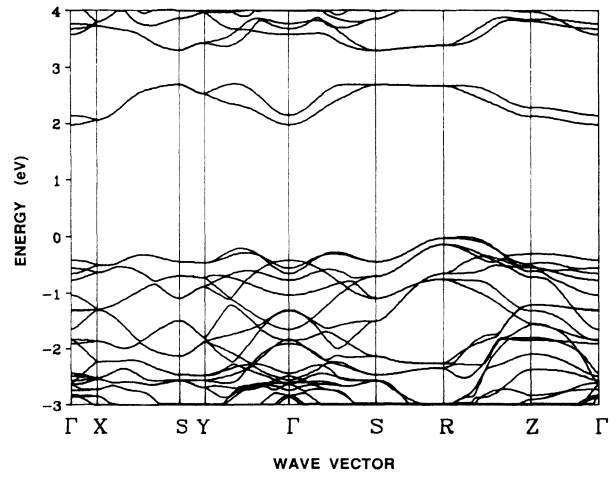

FIG. 3. The band structure of V_2O_5 determined by first-principles OLCAO calculations. The points labeled Γ, R, S, X, Y, Z are the high-symmetry points of the Brillouin zone.

The calculated imaginary parts of the frequency-dependent interband dielectric function up to a photon energy of 10 eV along the three crystallographic directions are shown in Fig. 4 along with the experimental data (solid circles) from Fig. 3. It is apparent that the calculated optical absorption in this crystal is highly anisotropic. We shall discuss the calculated result in comparison with the measured data for the photon energy only up to 4 eV. In the crystallographic **a** direction, a strong absorption at 2.8 eV is reproduced by the calculation which was in excellent agreement with the measured value at 2.75 eV. Also in agreement is the much reduced absorption in the 3.0–3.6-eV range. The only discrepancies in this direction seem to be in the intensity of the major peak and the presence of additional structures in the experimental data just below the major absorption peak (shoulders at 2.5 and 2.3 eV). In the **b** direction the calculation shows two strong and closely spaced absorption peaks at 2.7 and 2.6 eV, whereas the experimental spectrum shows a broad peak at 2.9 eV with a much reduced intensity. In the **c** direction, the experimental spectrum shows a peak of intermediate intensity at 3.10 eV, while the calculation shows much weaker absorption in this direction. Still, some structures at 2.7 and 3.2 eV in the theoretical spectra can be identified.

Within the energy range of 0–4 eV, the optical transitions originate from the top part of the VB to the pair of localized CB mentioned above. The strong directional anisotropy in the absorption curve is related to the orbital symmetry of these two localized bands. Obviously, the fact that these two bands have their wave functions mainly derived from the d_{xy} orbital of V and the p_y orbital of O explains the very low *z*-component absorption in the theoretical curve. However, it is also possible that a strong lattice vibrational effect may also mask some of the anisotropy in optical absorption. The calculated absorption curves show a sharp drop at about 3.4 eV and start to rise rapidly above 4 eV. The measured data from the ellipsometry is less accurate near 4.0 eV because of the detector sensitivity in this region. The existence of this absorption minimum is due to the second band gap between the lower pair of localized CB and the higher CB discussed above. Beyond 4 eV, there are very rich structures and anisotropies in the calculated curves. These high-energy structures appear to be consistent with

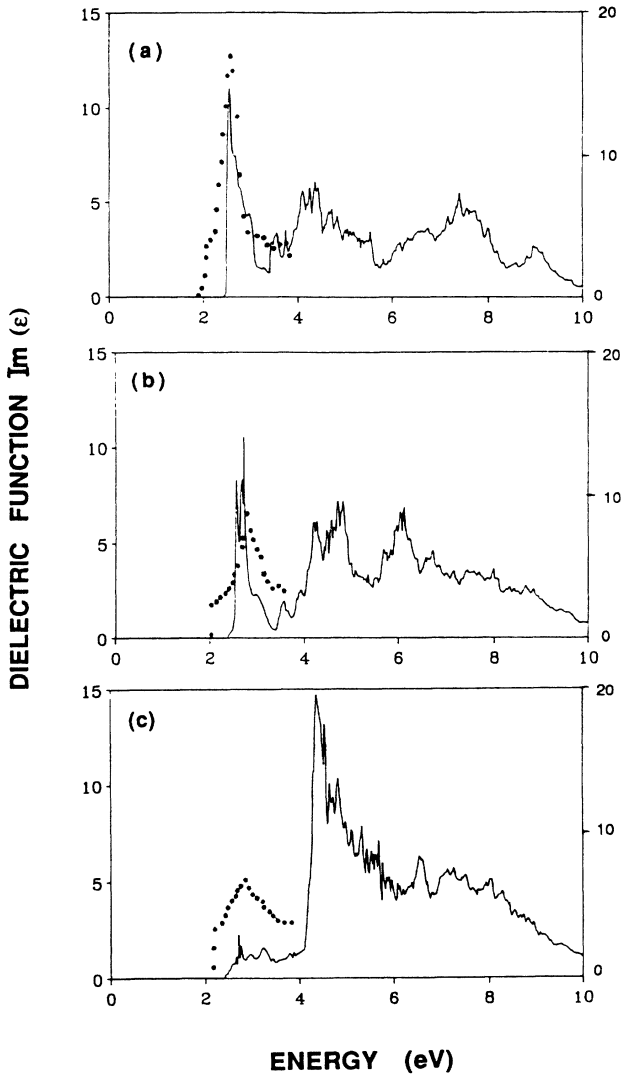

FIG. 4. The imaginary part of the optical dielectric function of V_2O_5 calculated from the wave functions determined by the band-structure calculation. The three crystallographic directions *a*, *b*, and *c* are indicated in the figure. The solid circles represent the data shown in Fig. 1. Note that the experimental data have a different ordinate scale which is shown to the right of the graph.

reflectivity measurements on V_2O_5 single crystals in this energy range.[5]

DISCUSSION

The band-structure calculations predict the presence of an indirect band gap for the closest bands which are separated by 1.9 eV. Previous band edge studies of V_2O_5 by Kenny *et al.*[7] and by Bodo and Hevesi[6] have clearly shown that the absorption edge has an Urbach-rule dependence and above 2.4 eV the absorption is due to transitions at $\mathbf{k}\neq 0$. Neither group has addressed the possibility of indirect transitions primarily in the energy range near 2.0 eV. We are currently investigating the absorption edge in our own V_2O_5 single crystals near 2.0 eV to test the possibility of indirect transitions.

The energy assignments of major spectral features from the theoretical calculations are in good agreement with our experimental spectra. This is admittedly surprising because the calculations [using local-density-functional theory (LDFT)] represent the 0-K, electronic ground state, whereas the experimental absorption spectra are a probe of the electronic excited states.

Although the energy assignments are good, there is some discrepancy in the intensity of the ϵ_2 values particularly in the *b* and *c* directions. Some of the following problems inherent in our measurements and data analysis may contribute to these differences. For example, it was necessary for us to use a large slit width on our monochromator in order to obtain sufficient light intensity for accurate null measurements. This led to a spectral resolution of 0.2 eV, which is significant since the calculated values of ϵ_2 did not include instrumental broadening. Also, the ellipsometric analysis of anisotropic materials can lead to errors when the anisotropy is large. Graves[21] has stated that the analysis of an orthorhombic crystal using the single-face method can produce errors in the analysis when the optical anisotropy is greater than 5:1. Our data and that of Mokerov *et al.*[13] show that the anisotropy in ϵ_2 along the *a* and *c* directions are as large as 4:1 in a narrow region near 3.0 eV, but the rest of the spectrum was of the order 2:1 or less. A large anisotropy may contribute some error in our analysis of the data near 3.0 eV, but should be negligible over the rest of the spectrum. We find that the experimental values of ϵ_2 in this report are in good agreement with that of Mokerov *et al.* for the *a* and *c* directions.

It is also possible that the discrepancy between the calculated and measured intensity of ϵ_2 may be attributed to the optical-property calculations. In principal the calculated ϵ_2 curve should include a lifetime-broadening effect which would reduce the intensities of the sharper structures in the spectrum. It is conceivable that this broadening effect may be anisotropic since the effective-mass components of the electrons (and holes) are so highly anisotropic. We also suggest that the intensity discrepancies between the theoretical and experimental absorption may be attributed to the LDFT, which may be less valid for highly anisotropic crystals involving highly localized bands (because it is pushing the limits of the electron correlation theory which assumes a slowly varying charge density). Our preliminary results obtained from the calculated and measured optical properties of VO_2 single crystals (monoclinic and tetragonal) show better agreement between theory and experiment[24] possibly due to the less anisotropic nature of VO_2.

ACKNOWLEDGMENTS

The work at the University of Missouri–Kansas City is supported by U.S. Department of Energy (DOE) Grant No. DE-FG02-84-ER45170. The work at Argonne National Laboratory is supported by DOE (Division of Materials Science of the Office of Basic Energy Sciences) Contract No. W-31-109-ENG-38. The authors would also like to thank John Downey for his assistance in the preparation of the single crystals. A special thanks is due to Stephen Marshall for his assistance with the ellipsometry-analysis computer software.

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[1]B. W. King and L. L. Suber, J. Am. Ceram. Soc. **39**, 306 (1955).
[2]F. J. Morin, Phys. Rev. Lett. **3**, 34 (1959).
[3]G. J. Hyland, J. Phys. C **1**, 189 (1968).
[4]W. Lambrecht, B. Djafari-Rouhani, M. Lannoo, and J. Vennik, J. Phys. C **13**, 2485 (1980); W. Lambrecht, B. Djafari-Rouhani, M. Lannoo, P. Clauws, L. Fiermans, and J. Vennik, *ibid.* **13**, 2503 (1980).
[5]N. I. Lazukova, V. A. Gubanov, and V. G. Mokerov, Int. J. Quantum Chem. **12**, 915 (1977).
[6]Z. Bodo and I. Hevesi, Phys. Status Solidi **20**, K45 (1967).
[7]N. Kenney, C. R. Kannewurf, and D. H. Whitmore, J. Phys. Chem. Solids **2**, 1237 (1966).
[8]R. T. Jacobsen and M. Kerker, J. Opt. Soc. Am. **57**, 751 (1967).
[9]V. G. Mokerov and A. V. Kakov, Fiz. Tverd. Tela (Leningrad) **11**, 197 (1969) [Sov. Phys.—Solid State **11**, 150 (1969)].
[10]V. G. Mokerov and B. L. Sigalov, Fiz. Tverd. Tela (Leningrad) **14**, 3405 (1972) [Sov. Phys.—Solid State **14**, 2875 (1973)].
[11]P. Clauws and J. Vennik, Phys. Status Solidi B **66**, 553 (1974).
[12]P. Clauws and J. Vennik, Phys. Status Solidi B **69**, 491 (1975).
[13]V. G. Mokerov, V. L. Makarov, V. B. Tulvinskii, and A. R. Begishev, Opt. Spectrosc. **40**, 58 (1976).
[14]G.-L. Zhao, Y. Xu, W. Y.Ching, and K. W. Wong, Phys. Rev. B **36**, 7203 (1987).
[15]W. Y. Ching and B. N. Harmon, Phys. Rev. B **34**, 5305 (1986).
[16]G. L. Zhao, W. Y. Ching, and K. W. Wong, J. Opt. Soc. Am. **6**, 505 (1989).
[17]W. Y. Ching, Y.-N. Xu, and K. W. Wong, Phys. Rev. B **40**, 7684 (1989).
[18]Y.-N. Xu and W. Y. Ching, Phys. Rev. B **41**, 5471 (1990).
[19]R. M. A. Azzam and N. M. Bashara, *Ellipsometry and Polarized Light* (North-Holland, New York, 1977).
[20]U. Merkt, Appl. Opt. **20**, 307 (1981).
[21]R. H. W. Graves, J. Opt. Soc. Am. **59**, 1225 (1969).
[22]J. M. McCormick and M. G. Salvadori, *Numerical Methods in FORTRAN* (Prentice-Hall, New Jersey, 1965).
[23]The data in Ref. 8 were measured at a limited number of wavelengths.
[24]J. C. Parker, D. J. Lam, Y.-N. Xu, and W. Y. Ching (unpublished).