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Optical Properties of Semiconducting VO_2 Films*

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The reflectivity of a thick sputtered film of VO_2 has been measured in the energy range 0.5–11.0 eV at room temperature. The complex dielectric constant (ϵ_1, ϵ_2) and the complex index of refraction (n,k) have been obtained from the reflectivity measurements using the Kramers-Kronig relations. We have also measured the transverse electroabsorption spectrum of a thin sputtered film of VO_2 at liquid-nitrogen temperature. Comparison of the electroabsorption spectrum with theoretical predictions identifies the edge at 2.011 eV as corresponding to a direct transition at an M_0 edge. In spite of the lack of a band-structure calculation for VO_2, the singularities in ϵ_2 at 0.6, 1.04, 1.32, 1.82, 2.64, 3.6, 5.89, and 9.6 eV are assigned to specific interband transitions.

I. INTRODUCTION

Transition-metal oxides which show a phase transition from a semiconducting to a metallic state have been the subject of considerable interest.[1,2] Of all these materials VO_2 is the most interesting in terms of applications.[3,4] The transition in VO_2, which is a first-order semiconductor-to-metal transition, occurs at 68 °C. This transition is accompanied by a lattice distortion from a low-temperature monoclinic to a high-temperature tetragonal structure. The origin of this transition has been the subject of considerable controversy.[1,5–7] The electrical and optical properties of VO_2 have been studied extensively.[8–11] However, in most cases the stoichiometry, chemical purity, and freedom from defects of the measured VO_2 have not been high, at least by the standards of semiconductor technology, and this fact has produced a very large dispersion in the published data.

The electronic contribution to the optical properties of VO_2 has been studied by Verleur *et al.*[10] and by Borisov *et al.*[12] The temperature and pressure dependence of the energy gap has been measured by Ladd and Paul,[13] and photoemission measurements have been performed by Powell *et al.*[14] These measurements indicate that in the low-temperature phase VO_2 has an energy gap between 0.6 and 1.0 eV due to the crystal-field splitting of the uppermost partially filled vanadium 3*d* conduction band. Optical transitions at energies higher than 2.5 eV have been assigned to interband transitions between an oxygen 2*p* valence band and the lowest empty vanadium 3*d* conduction band.

Standard optical measurements, such as reflection and absorption, do not provide very high resolution for solids whose optical spectra show very large structureless backgrounds. Several modulation techniques have been developed in the last few years. By measuring the derivative of the optical spectrum with respect to some parameter, these techniques eliminate the background and enhance the structure to allow very precise determination of the energies of the transitions. These methods have proved to be useful in determining the energy of the interband transitions in semiconductors, in-

sulators, and even metals.[15,16] We have applied the electroabsorption technique[17] to VO_2 films in the energy range 0.5–6.0 eV.

The analysis of the modulated spectrum requires a reasonably good knowledge of the optical constants of the unperturbed material. Values for the real and imaginary parts of the dielectric constant (ϵ_1 and ϵ_2) have been published previously.[10,12] However, there are large differences between the values reported. Also in some cases the measurements have been performed on films which have not been completely characterized so as to make meaningful comparisons impossible. To obtain values for ϵ_1 and ϵ_2, we performed measurements of the reflectivity of VO_2 films in the energy range 0.5–11.0 eV.

II. EXPERIMENTAL TECHNIQUES

We shall describe in Sec. II A the techniques of sample preparation and in Secs. II B and II C the optical and electronic equipment used in these measurements.

A. Sample Preparation

The VO_2 films used in this work were prepared by reactive sputtering of vanadium onto polished sapphire substrates in an argon-oxygen atmosphere[18] under carefully controlled conditions. Electron diffraction studies show that the films used in the measurements were composed of stoichiometric polycrystalline VO_2 with a grain size of approximately 600 Å. Films 8000 and 2100 Å thick were used for reflection and electroabsorption measurements, respectively. The ratio of the conductivities above and below the metal-semiconductor transition temperature for both films was better than 1000 : 1. The electrical characteristics of this material are described in the conductivity (σ) vs reciprocal temperature (T^{-1}) plot for the 2100-Å film as shown in Fig. 1. The thin film was coated with two parallel nichrome-gold electrodes with a spacing of 0.5 mm. The sample was mounted with silicone grease on the cold finger of an optical cryostat cooled by liquid nitrogen.[19] The gap between the parallel electrodes was aligned with the 0.5×6.0-mm slit on the cold finger. When cooled to liquid-nitrogen temperature, the sample resistance measured across the electrodes was 10^9 Ω. A transverse electric field could then be applied to the sample without causing Joule heating.

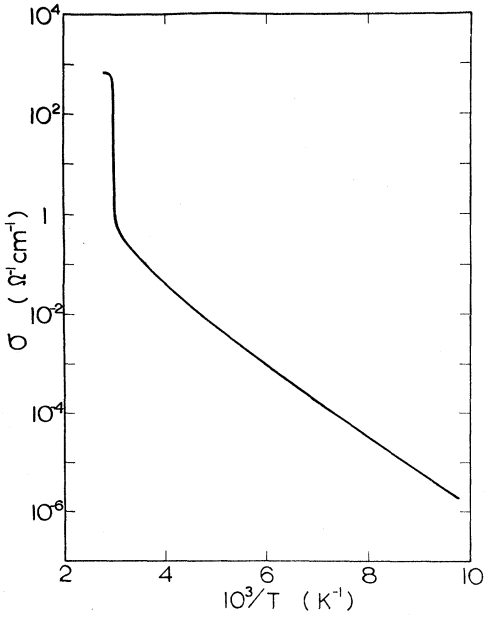

FIG. 1. Electrical conductivity of a 2100-Å-thick sputtered VO_2 film as a function of $1/T$.

B. Optical Equipment

The optical equipment used in the reflection and electroabsorption measurements is very similar. The light sources used were a 650-W quartz-iodine tungsten-filament lamp in the visible and infrared region, a 150-W xenon arc in the ultraviolet region, and a hydrogen discharge in the vacuum-ultraviolet region. The dispersing element was a $\frac{3}{4}$-m Spex model No. 1702 monochromator with suitable gratings. The detectors used were an EMI 9635Q photomultiplier in the visible and ultraviolet, an RCA 7102 in the near infrared and a PbS photoconducting cell in the infrared. A spectral resolution of 10 Å was used in the ultraviolet, correspondingly smaller resolutions in the visible and infrared.

C. Electronic Equipment

We used ac techniques throughout the measurements. The light was mechanically chopped at 89 Hz and synchronously detected with a Brookdeal system 40 lock-in amplifier. The reflectance measurements were performed point by point by taking the sample in and out of the beam. In the electroabsorption measurements two ac signals have to be detected simultaneously. These are (i) the signal at 89 Hz proportional to the product of the incident light on the sample times the transmissivity of the sample and (ii) the signal at the frequency of the modulating field, 200 Hz in our measurements, proportional to the product of the incident light times the electric-field-induced changes in the transmissivity. Both signals were detected using Brookdeal system 40 lock-in amplifiers, divided electronically and plotted on an x-t recorder as a function of the wavelength of the light. The ac modulating field was applied to the sample using a Kepco OPS2000 operational power supply, capable of delivering up to a 3000-V peak, driven by a square-wave generator. A dc bias was

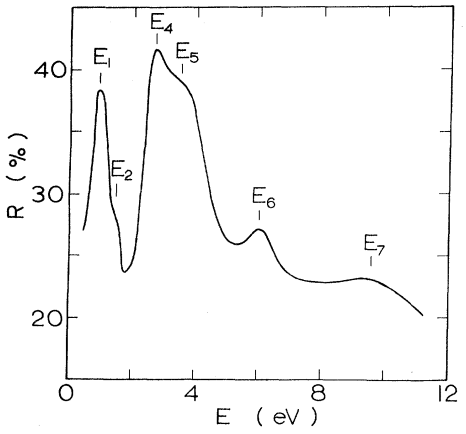

FIG. 2. Reflectivity spectrum of a VO_2 film at room temperature.

superimposed in order to modulate between zero and the maximum field.

III. EXPERIMENTAL RESULTS

Figure 2 shows the room temperature reflectivity of an 8000 Å thick sputtered VO_2 film. Because of the thickness of the film no measurements were performed at energies lower than 0.5 eV. The general shape of the reflectivity spectrum is very similar to published results,[10] the main difference being the relative strength of the 1 eV peak to that of the 3 eV. In the reflectivity spectrum we can identify two main peaks, one at 1.04 eV labeled E_1 in Fig. 2, and a second one, which is really a doublet, labeled E_4, E_5 at 2.64 and 3.56 eV, respectively. There is also some structure at higher energies; peaks E_6 and E_7 are at 6.0 and 9.6 eV, respectively. Figure 3 shows the transverse electroabsorption spectrum of a 2100-Å-thick sputtered VO_2 film. This measurement was performed at 80 K with an applied field ($\vec{E}$) of 5×10^4 V/cm. The samples had to be precooled before applying the field because of Joule heating at room temperature. The field dependence of the strength of the electroabsorption signal was measured for fields between 10^4 and 5×10^4 V/cm. The strength of the signal was found to be proportional to the $\frac{4}{5}$ power of the electric field. In spite of having performed measurements between 0.5 and 6.0 eV, we have only found the signal shown in Fig. 3. Our system has a sensitivity of one part in a million in its most sensitive region, i.e., from 2 to 3 eV. The sensitivity drops by at most a factor of five outside this range. No polarization effects were observed.

IV. DATA ANALYSIS

The use of the Kramers-Kronig relations in the analysis of the reflectance data has been discussed in previous papers.[20, 21] These relations are usually used in the following form:

$$\Theta(E_0)=\frac{E_0}{\pi}\int_0^\infty \frac{\ln R(E)-\ln R(E_0)}{E^2-E_0^2}\,dE \qquad (1)$$

to compute $\Theta(E)$, which is related to the optical constants by

$$\tan\Theta=-2k/(n^2-k^2-1)\ . \qquad (2)$$

The Kramers-Kronig relations involve an integral over all energies; however, we have performed measurements only between 0.5 and 11.0 eV. We have extrapolated our results to $E=0$ by using the values of the real part of the dielectric constant in the infrared in the absence of carriers.[9] To obtain the values of the reflectivity at energies higher than 11 eV, we have used the following asymptotic expression for the reflectivity for $E>11$ eV:

$$R(E)=qE^{-p}\ , \qquad (3)$$

where q and p are parameters to be determined. We have determined p by making $\Theta(E)$ go to zero at energies lower than the energy gap, a value of $p=2.2$ was found to give the best results. The parameter q was determined by making the reflectivity at high energies match the last measured value. The small value obtained for p is an indication that the reflectivity measurements have not been performed up to sufficiently high energies.

The results obtained for the real and imaginary parts of the dielectric constant are shown in Fig. 4. These results show a striking resemblance to those of Verleur *et al.*[10] for single crystals with light polarized parallel to the a_m axis. Apart from the peaks that have been identified in the reflectivity

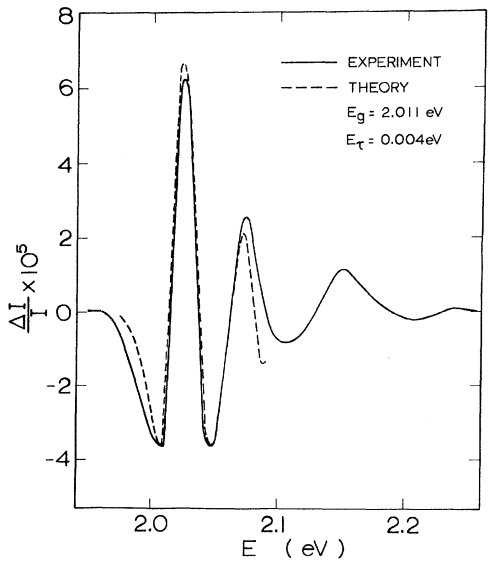

FIG. 3. Electroabsorption spectrum of a VO_2 film at 80 K, $\vec{E}=5\times10^4$ V/cm.

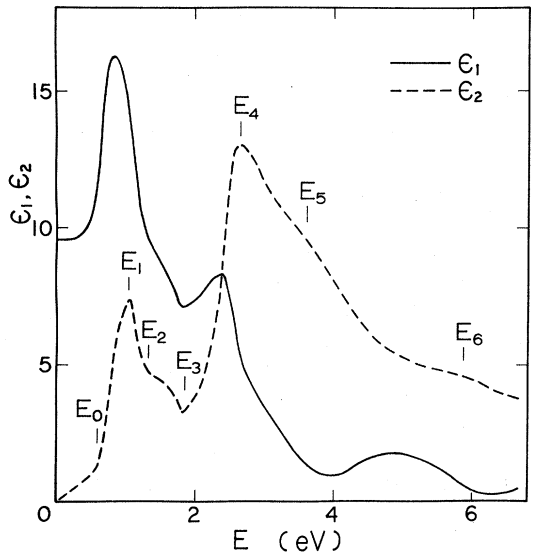

FIG. 4. Real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric constant of VO_2 at room temperature.

two new thresholds E_0 and E_3 at 0.6 and 1.82 eV can be resolved. The E_0 threshold corresponds to a definite change in the slope of $R(E)$ and is not related to the extrapolation used for $E < 0.5$ eV. The results for the index of refraction (n) and the extinction coefficient (k) are shown in Fig. 5, and those for the absorption coefficient (α) are shown in Fig. 6.

The effects of an electric field on the optical properties of semiconductors have been studied extensively. In particular, the electric-field-induced changes in the real and imaginary parts of the dielectric constant in the proximity of an interband edge have been the subject of several papers.[22–24]

The simplest method of calculating the effect of the electric field on allowed interband transitions around a Van Hove singularity of type M_0, M_1, M_2, or M_3 involves the assumption of parabolic bands around the singularity and the use of the effective-mass approximation. The electric field $\vec{E}$ is introduced as a perturbation to the unperturbed effective-mass Hamiltonian H_0:

$$H = H_0 - e\vec{E}\cdot\vec{r} \,. \tag{4}$$

To obtain the field-induced changes in the dielectric constant, we have to calculate only the interband matrix elements of the momentum operator, using as wave functions the eigenfunctions of H. It is possible to show that the changes in the real and imaginary parts of the dielectric constant can be expressed as functions of two universal electro-optic functions F and G.[24]

In the electroabsorption measurements we do not measure directly the changes in ϵ_1 or ϵ_2 but a combination of them. In the range in which we have a nonzero signal and for the thickness of the sample used, the transmissivity of the sample can be written

$$I = I_0(1-R)^2 e^{-\alpha d} \,, \tag{5}$$

where I_0 is the incident light, R the reflectivity and d the thickness of the sample. The relative change in the transmissivity can be written

$$\frac{\Delta I}{I} = -\frac{2\Delta R}{1-R} - d\Delta\alpha \,. \tag{6}$$

Taking into account the relationship of R and α to ϵ_1 and ϵ_2, it is possible to write (6) as

$$\Delta I/I = \alpha_1(\epsilon_1, \epsilon_2, E)\,\Delta\epsilon_1 + \alpha_2(\epsilon_1, \epsilon_2, E)\,\Delta\epsilon_2 \,, \tag{7}$$

with

$$\alpha_1 = -\frac{1}{n^2+k^2}\left(\frac{n^2-3k^2-1}{n^2+k^2+2n+1} - \frac{dEk}{\hbar c}\right) \,,$$
$$\alpha_2 = -\frac{1}{n^2+k^2}\left(\frac{(3n^2-k^2-1)k}{(n^2+k^2+2n+1)n} + \frac{dEn}{\hbar c}\right) \,. \tag{8}$$

The functions α_1 and α_2 can be computed using the values of ϵ_1 and ϵ_2 from Fig. 4. We have found that α_2 is practically independent of the energy and equal to -0.76; α_1 however varies between 0.12 and 0.20 in the energy range 1.96–2.20 eV. These values together with the theoretical values obtained for $\Delta\epsilon_1$ and $\Delta\epsilon_2$[24] were used to obtain the best fit to the experimental results. We found that broadening has to be introduced in order to obtain a good fit. Figure 3 shows the fit obtained for an M_0 edge with a broadening parameter (E_τ) of 0.004 eV and an

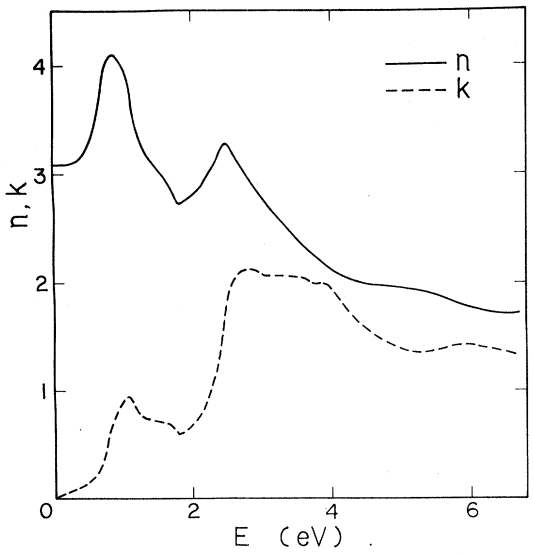

FIG. 5. Real (n) and imaginary (k) parts of the index of refraction of VO_2 at room temperature.

energy gap (E_g) of 2.011 eV.

V. DISCUSSION

Fine structure in the interband ϵ_2 spectrum is often obscured because ϵ_2 has been derived from an integral transform such as Eq. (1). In attempting to recognize structure, we should examine the experimental data, in our case R. However, in quoting edge energies to be compared with theory, we should refer to ϵ_2 as derived from the Kramers-Kronig relations.

We shall analyze the structure above and below 1.8 eV separately. (i) $E < 1.8$ eV. In agreement with previous authors,[10,12] we assign the E_0, E_1, and E_2 structure to transitions between the highest $3d$ vanadium valence band and the lowest crystal-field-split $3d$ conduction band. The large values of the absorption coefficient (10^5 cm^{-1} for $E = 1$ eV) are an indication of strong hybridization of the $3d$ vanadium bands with the $2p$ oxygen bands. There is no definite threshold in the absorption coefficient; α increases smoothly from 10^3 cm^{-1} at 0.2 eV to 10^5 cm^{-1} at 1 eV. This behavior can be explained as a combination of several effects: partially forbidden transitions, indirect transitions, and probably most important, sample imperfections (deviations from stoichiometry, impurities, etc.). Taking these facts into account, we assign the E_0 threshold at 0.6 eV to the band gap and the E_1 and E_2 peaks to transitions between the same bands at other points in the Brillouin zone.

(ii) $E > 1.8$ eV. The onset of the $2p$-$3d$ transitions has been described as lying somewhere between 2[12] and 2.5 eV.[10,12] Based mainly in our electroabsorption measurements, we assign the E_3 threshold to an M_0-type transition between the highest $2p$ oxygen band and the lowest $3d$ conduction band. The structure around 2.5 eV in the reflectivity spectrum of VO_2 has usually been compared to that of TiO_2 (rutile)[10]; however, we feel that it resembles more the results obtained for $BaTiO_3$ at room temperature.[25] The crystallographic structure of tetragonal VO_2, TiO_2, and $BaTiO_3$ are quite similar in the sense that the titanium and vanadium atoms are situated in an oxygen environment of octahedral coordination. The reflectivity spectrum of $BaTiO_3$ consists of an E_0 threshold at 3.2 eV and a doublet A_1, A_2 at 3.91 and 4.85 eV, respectively. This structure is not only very similar to our results for VO_2, but the splitting of the doublet and the separation of the doublet from the E_0 edge are virtually the same as that of the E_3 threshold and E_4, E_5 doublet. The structure of the optical spectrum of $BaTiO_3$ has been interpreted based on a band-structure calculation for $SrTiO_3$.[26] Following this interpretation, we assign the E_3 threshold to a transition at $\vec{K} = 0$. The A_1, A_2 doublet has been assigned to transitions between the split p valence bands and the conduction band at $\vec{K} = (1, 0, 0)$.[25] In the case of VO_2 the tetragonal field has already split the $2p$ oxygen bands at $\vec{K} = 0$ so is not possible to say at which point in the Brillouin zone these transitions occur.

It is very difficult to assign the high-energy structure to specific interband transitions. However, considering the width of the $2p$ bands, the E_6 peak probably corresponds to a transition between the $2p$ bands and a higher-lying d band. The E_7 peak can be assigned to a $3d$-$4p$ transition.

We shall now discuss the E_3 threshold in somewhat more detail by considering the electroabsorption results. The position of the edge, 2.011 eV in the electroabsorption spectrum, agrees well with a value of 1.82 eV in ϵ_2 if we take into account the temperature dependence of the energy gap. As stated in Sec. IV, we have tried various possibilities to explain the measured line shape of the electroabsorption spectrum. The best fit obtained is shown in Fig. 3. The theoretical curve was calculated using Eq. (7) with the values of $\Delta\epsilon_1$ and $\Delta\epsilon_2$ obtained for an M_0 edge.[24] In order to obtain a good fit of the relative strength of the peaks, broadening had to be introduced. We have used a broadening parameter (E_7) of 0.004 eV, which is reasonable at 80 K. Another parameter that had to be introduced is the optical interband mass (m_0^*). Taking into account the known value of the applied electric field, m_0^* was found to be $0.12m_e$. This value is lower than the reported values of $m_c^* = 0.5m_e$,[6] $0.8m_e$,[12] and $4m_e$[9] for the conduction electrons obtained from plasma-frequency mea-

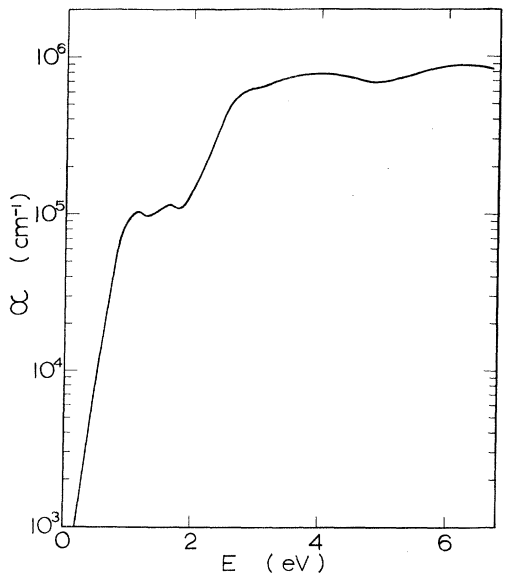

FIG. 6. Absorption coefficient (α) of VO_2 at room temperature.

surements and the estimate of from $2m_e$ to $7m_e$ obtained from transport measurements.[8] However, considering that the $2p$ valence band is broader than the $3d$ conduction band, the value obtained for m_0^* is very reasonable.

The field dependence of the strength of the electroabsorption signal was found to be

$$\Delta I/I \propto \vec{E}^{4/5} . \quad (9)$$

This value compares well with theoretical predictions for the intermediate field regime at which our measurements were performed and the broadening parameter used.[24]

The fact that no signal was observed for the E_0-E_2 structure can be explained by taking into account the relative weakness of the electroabsorption signal for forbidden transitions.[16] It is more difficult to explain why we have not seen any structure due to the E_4, E_5 doublet. One possibility could be phonon emission broadening of this structure. Since the E_4, E_5 transitions are most probably of M_1 or M_2 type, they are more sensitive to phonon broadening at low temperatures than an M_0-type edge.

VI. CONCLUSIONS

In conclusion we can say that we have unambiguously identified the threshold of the $2p$-$3d$ optical transitions in VO_2. We have also obtained the first estimate of the optical interband mass for this transition. Based on a comparison with the optical spectra of $BaTiO_3$ we have been able to assign the observed structure in ϵ_2 to appropriate interband transitions. We have also obtained reliable data for the dielectric constant (ϵ_1, ϵ_2) and the index of refraction (n, k) for energies up to 11 eV.

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