Optical Properties of VO_2 between 0.25 and 5 eV

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The optical constants of VO_2 have been determined between 0.25 and 5 eV, both below and above the semiconductor–metal transition temperature $T_t = 340°K$. Reflectivity and transmission spectra have been measured on both single crystals and thin films. The reflectivity spectra of the bulk crystals were measured with $E \perp c$ axis in the tetragonal phase (or $\perp$ a axis in the monoclinic phase) and $E \parallel$ to these axes. While there are some differences in magnitude between the dielectric constants obtained from thin-film and single-crystal measurements, the structural features are in good agreement. Below T_t there are four prominent absorption peaks centered near photon energies of 0.85, 1.3, 2.8, and 3.6 eV. Above T_t metallic free carrier absorption is observed below 2.0 eV, but the same two absorption peaks near 3 and 4 eV are present. The energy location and polarization dependence of these two higher energy peaks can be related to similar absorption peaks in rutile, and are interpreted using the rutile band structure. The results are consistent with a picture in which filled bands arising primarily from oxygen $2p$ orbitals are separated by approximately 2.5 eV from partially filled bands arising primarily from vanadium $3d$ orbitals. Transitions from the filled $2p$ bands are responsible for the high-energy peaks in the optical absorption in both the high- and low-temperature phases. In the high-temperature metallic phase there is evidence that there is overlap among the $3d$ bands such that at least two bands are partially occupied by the extra d-electron per vanadium ion. In the low-temperature semiconductor phase a band gap of approximately 0.6 eV opens up within the $3d$ bands separating two filled bands from higher lying empty bands. The two absorption peaks at 0.85 and 1.3 eV are due to transitions from these two filled bands.

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Photoemission from VO_2*

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Photoemission quantum yield and energy distribution curves have been measured for VO_2 in the tetragonal (100°C) and monoclinic (25°C) phases over the photon energy range from 7 to 11.5 eV. The VO_2 studied was a polycrystalline film of several microns thickness formed by oxidizing vanadium. The experimental data, although distorted by strong energy-dependent inelastic scattering and by work-function variations due to the polycrystallinity, shows most of the major features expected on the basis of a simple model of VO_2 and supports the interpretation of optical data given by Barker *et al.*[1] In both the semiconductor and metallic phases, there is evidence of a high density-of-states band starting approximately 2.5 eV below the Fermi level. This band is believed to be due primarily to the oxygen $2p$ orbitals in VO_2. The photoelectric yield is considerably higher at 100°C than at 25°C consistent with the formation of a forbidden gap at temperatures below 67°C. This is accompanied by expected changes in the energy distribution curves particularly for these electrons photoexcited from states near the Fermi level.

Discussion of Barker's and Powell's Papers

J. FEINLEIB (Massachusetts Institute of Technology): I think Dr. Powell answered one of Dr. Barker's dilemmas and that is the absorption edge at 0.6 eV is not very sharp and that is probably because these are d-to-d transitions which are not allowed. You wouldn't expect a very sharp absorption edge until you got well up into the band. This is also true of V_2O_3.

A. S. BARKER: This might also be attributed to lattice interactions.

J. FEINLEIB: You mean not direct gap.

R. J. POWELL: No, a configurational coordinate argument might apply. You may get significant broadening effects from this. It has been suggested that this kind of lattice relaxation can produce Urbach-type absorption.

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[1] H. W. Verleur, A. S. Barker, and C. N. Berglund, Rev. Mod. Phys. **40**, 737 (1968), previous paper.