

LOW TEMPERATURE ELECTROREFLECTANCE OF TiO_2 *

K. Vos and H.J. Krusemeyer

Solid State Department, Physics Laboratory, University of Utrecht,
Sorbonnelaan 4, "De Uithof", Utrecht, The Netherlands

(Received 25 June 1974 by G.W. Rathenau)

Franz–Keldysh type electroreflectance finestructure has been observed on single crystals of TiO_2 between 3.0 and 3.7 eV at LNT. Critical points have been designated to two sets of oscillations which are dependent on the direction of polarization of the light and of the applied field.

THE ELECTRON energy bands of rutile have been investigated in various ways, mostly in connection with the *n*-type electrical transport properties. The nature of the lowest conduction band could not be unambiguously determined from these measurements, which could be fitted both to a model with a multiple band minimum at $k = 0$ ^{1,3} and to a single band multivalley model with energy minima in a *k*-direction perpendicular to [001].⁴ Optical absorption,⁵ electroreflectance⁶ (er) and electroabsorption² (ea) data favour the indirect gap model with a midpoint of 3.027 eV between the energies of the phonon emission and absorption process at 168 K and a bandgap in that neighbourhood. At room temperature the er³ as well as the unperturbed reflectance⁷ spectra are broad which makes it difficult to identify critical points and to determine their energy accurately. A two-photon absorption spectrum has been interpreted by an *s*-type exciton at 3.57 eV which belongs to a direct dipole-forbidden edge at 3.75 eV.⁸ Some information on the density of valence and conduction band states was obtained from photoemission⁹ and X-ray band spectra.¹⁰

In this letter we report for the first time on er spectra at LNT. These spectra reveal rich finestructures

of the Franz–Keldysh type, not present at room temperature, superimposed on a relatively broad background which has also been observed before.^{6,11} Slices with typical dimensions of $7 \times 7 \times 2 \text{ mm}^3$ were cut from X-ray oriented boules, purchased from the National Lead Company. Samples from undoped boules were reduced in a hydrocarbon free vacuum system at 700°C in the presence of pure carbon while samples from a nominally 500 ppm Nb-doped boule were used in the as-grown condition. High quality optical surfaces were obtained by etching the carefully ground surfaces in molten NaOH. For the surface barrier er measurements a semi-transparent gold layer of 60 Å was evaporated onto the crystal surface, giving rise to a Schottky type barrier. The field in the depletion layer was modulated by applying a voltage between the gold film and an ohmic indium contact soldered to the opposite side of the sample. Values of $\Delta R/R$ at fixed wavelength intervals were obtained by automated equipment and recorded on papertape. The er spectrum was obtained by averaging several scans in opposite directions, made with opposite phases of the lock-in reference signal, thus eliminating d.c. drift problems associated with the sample and the equipment. The sensitivity for 15 sec total integration time per selected wavelength position has been found to correspond to $\Delta R/R \approx 1 \times 10^{-6}$.

Er spectra measured at 84 K for three different directions of the perturbing field are shown in

* This work was performed as a part of the research programme of the Stichting voor Fundamenteel Onderzoek der Materie.

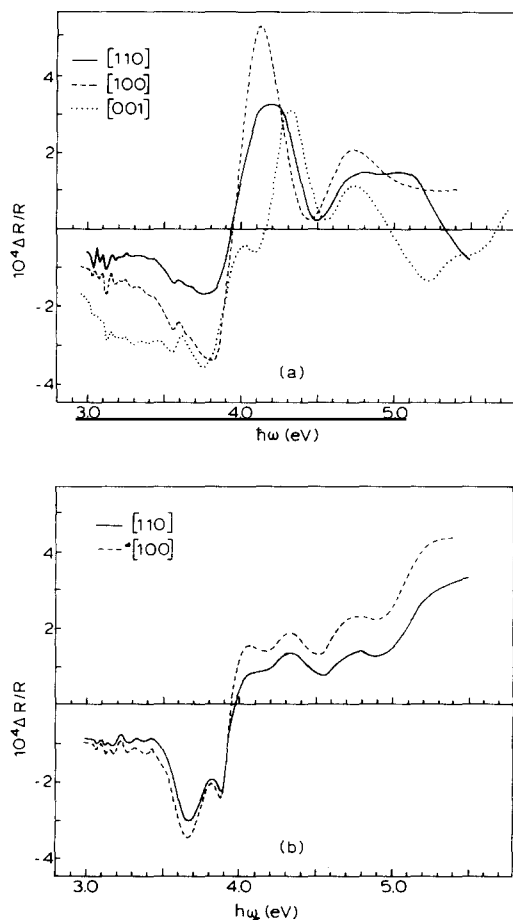


FIG. 1. Electrorreflectance of TiO_2 single crystals at 84 K for $E \perp c$ (a) and $E \parallel c$ (b). Surface parameters are listed in the table.

Figs. 1(a) and 1(b) for light polarized perpendicular ($\perp c$) respectively parallel ($\parallel c$) to the c -axis. No correction has been made for reflection losses at the front side of the gold layer. Some relevant sample and measurement conditions are listed below.

Table 1. Sample and measurement conditions

orientation	donor conc. cm^{-3}	mod. volt. V	max. surf. field V/cm
[110]	1.3×10^{18}	2.0	3.4×10^5
[100]	1.0×10^{18}	4.0	4.2×10^5
[001]	5.0×10^{18}	0.5	3.0×10^5

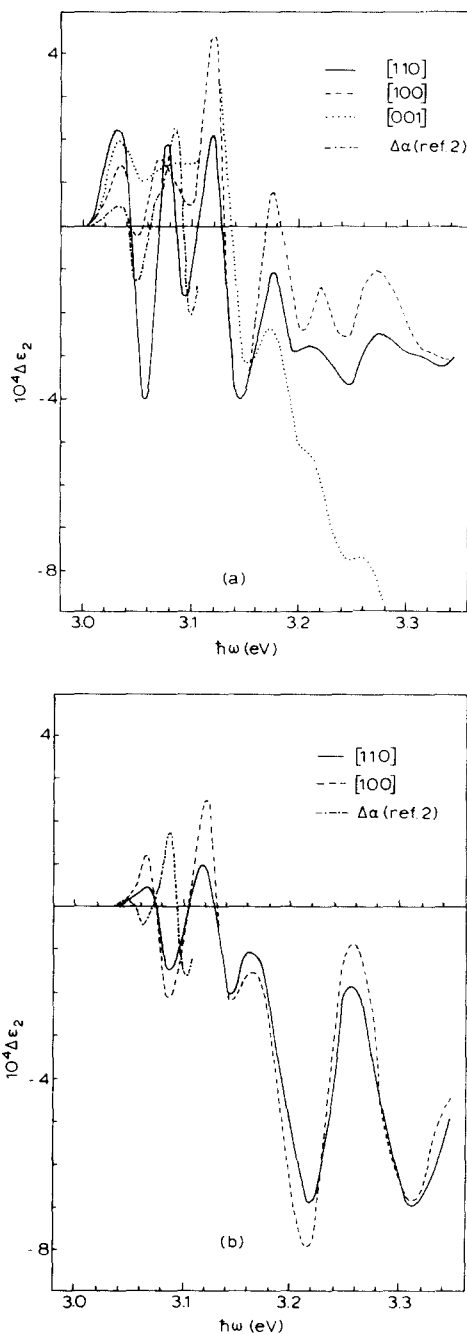


FIG. 2. Modulation of the imaginary part of the dielectric constant $\Delta\epsilon_2$ for $E \perp c$ (a) and $E \parallel c$ (b) computed from the er spectra of Fig. 1. The low field ea spectra from reference 2 (not to scale) are indicated by the dash-dotted curves.

The field in the depletion layer was square wave modulated from a value corresponding with a few tenths of a Volt bandbending to the maximum value indicated in Table 1. It was verified that the low energy structure is not due to a spurious signal caused by electroabsorption in the depletion layer of light transmitted through and reflected at the back surface of the crystal.

The newly observed finestructure, this is for $\hbar\omega \leq 3.7$ eV, reproduces very well for all field directions although the relative peak strength depends on the field orientation. Lowering the temperature from LNT to 25 K does not improve the spectra significantly but displaces them -7 ± 3 meV. In Fig. 2 the change of the imaginary part of the dielectric constant $\Delta\epsilon_2$, computed from the $\Delta R/R$ spectra of Fig. 1 by Kramers–Kronig transformation, is plotted for $E \perp c$ and $E \parallel c$ and the various applied field directions. The smoothly varying background and the oscillations superimposed on it are clearly of a different origin. The strength of the $E \perp c$ structure between 3.0 and 3.1 eV is strongly field orientation dependent with a maximum for [110] fields as can be seen in Figs. 1(a) and 2(a).

It was further found that the period of this structure for [110] fields increases when the field strength is gradually increased from 1×10^5 V/cm to 4×10^5 V/cm, showing up to four half oscillations. From the fact that this low energy structure occurs at the same energy for all field directions it is concluded that it originates from one critical point, while the differences in amplitude are caused by a selective sampling of the light for the different branches of the star of k^{12} and by variations in the reduced effective electron–hole mass for the different directions in k -space around the critical point. The finestructure for $E \parallel c$ is not very different for [110] and [100] fields as may be expected from symmetry arguments.¹² The structure centered at 3.13 eV is present for both directions of polarization, is rather insensitive to the field direction and has about the same amplitude as the lower energy structure. As $\Delta\alpha \approx (\omega/\hbar c) \Delta\epsilon_2$ in the low photon energy range of Fig. 2 a comparison is possible with the ea measurements for a [100] field of Arntz and Yacobi.² There is qualitative agreement if we identify our low energy structure with the LEP structure and our 3.13 eV

structure with the HEP structure. The LEP structure for $E \parallel c$ is however 17 meV and the HEP structure 33 meV lower in energy.

It was shown in reference 2 that the LEP structure is caused by indirect transitions involving different phonons for $E \perp c$ and $E \parallel c$, but with the same energy difference between the initial and the final electronic state. The energy difference between our $E \parallel c$ structure and the LEP structure of reference 2 indicates that the coincidence in energy they found for $E \perp c$ and $E \parallel c$ was accidental. An attempt to describe our low energy structure with the one-electron Franz–Keldysh theory for a M_0 indirect allowed edge yielded a gap for the phonon emission of 3.026 eV for $E \perp c$ and 3.059 eV for $E \parallel c$. Inclusion of electron–hole attraction might improve the fit and alter these figures slightly.

Arntz *et al.* pointed out that the HEP structure might be due to a direct forbidden transition or to an indirect transition involving degenerate phonons for $E \perp c$ and $E \parallel c$, but they preferred the first model. Neutron diffraction data for TiO_2 ,¹³ which have become available, show however that there are k -values, especially at the M and Z -point of the Brillouin zone, where degenerate phonons do exist. Therefore the second model cannot be ruled out *a priori*. Our 3.13 eV structure could be reasonably explained by the one-electron Franz–Keldysh theory for a M_0 indirect transition at 3.114 eV if a small shift was assumed of the critical point energy due to lattice polarization by the modulating field. This type of shift, which is the largest for [001] fields, is about 1 meV for a field of 4×10^5 V/cm in this direction. Its occurrence was to be expected as it plays a major role in the electro–optical behavior of some perovskites^{14,15} e.g. SrTiO_3 , having the same short range order as TiO_2 . Calculations of the effect by Brews¹⁶ show that the energy shift could be different for each critical point and could depend on the field orientation. This may account for the fact that the amount of the apparent shift associated with the 3.13 eV structure seems to vary with the direction of polarization of the light and the direction of the field. No attempt has been made yet to designate critical points to the finestructure between 3.2 and 3.7 eV.

Very recently Mack and Handler¹⁷ looked for but did not observe sharp finestructure in the *er* spectra at low temperature for SrTiO_3 . The *er* spectrum of this material shows a broad structure similar to that of TiO_2 .

REFERENCES

1. BECKER J.H. and HOSLER W.R., *Phys. Rev.* **137**, A1872 (1965).
2. ARNTZ F. and YACOBI Y., *Phys. Rev. Lett.* **17**, 857 (1966).
3. HASIGUTI R.R., YAGI E. and AONO M., *Nonmetallic Crystals* p. 137, Gordon & Breach, London (1970).
4. ACKET G.A. and VOLGER J., *Physica* **32**, 1680 (1966).
5. CRONMEYER D.C., *Phys. Rev.* **87**, 876 (1952).
6. FROVA A., BODDY P.J. and CHEN Y.S., *Phys. Rev.* **157**, 700 (1967).
7. CARDONA M. and HARBEKE G., *Phys. Rev.* **137**, A1467 (1965).
8. WAFF H.S. and PARK K., *Phys. Lett.* **32A**, 109 (1970).
9. DERBENWICK G.F., *Stanford Electronics Laboratories Technical Report*, No. 5220-2 (1970), unpublished.
10. FISCHER D.W., *Phys. Rev.* **B5**, 4219 (1972).
11. To be published.
12. BOTTKA N. and FISHER J.E., *Phys. Rev.* **B3**, 2514 (1971).
13. TRAYLOR J.G., SMITH H.G., NICKLOW R.M. and WILKINSON M.K., *Phys. Rev.* **B3**, 3457 (1971).
14. YACOBI Y. and NAVEH O., *Phys. Rev.* **B7**, 3991 (1973).
15. FROVA A. and BODDY P.J., *Phys. Rev.* **153**, 606 (1967).
16. BREWS J.R., *Phys. Rev. Lett.* **18**, 662 (1967).
17. MACK S.A. and HANDLER P., *Phys. Rev.* **B9**, 3415 (1974).

Elektroreflexion Feinstruktur von dem Franz-Keldysh Typ ist beobachtet an TiO_2 Einkristallen zwischen 3.0 und 3.7 eV bei flüssiger Stickstoff Temperatur. Kritische Punkte sind zuerkannt an zwei Gruppen von Oszillationen die abhängig sind von der Richtung der Lichtpolarisation und von dem angewandten Feld.