Dielectric Constant and Dielectric Loss of TiO₂ (Rutile) at Low Frequencies*

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Measurements have been made of the complex capacitance $(C=C'-iC'')$ of undoped, high-resistance, single-crystal TiO₂ (rutile) in vacuum at 78, 195, 273, and 300°K as a function of frequency between 10^1 and 3×10^6 cps with a 0.1-volt ac signal. With the field in the c direction, one low-frequency loss peak is found at 200 cps. The capacitance C' and loss C'' of a 2-mm cube with the field in the c direction are characterized by $1/2\pi\tau = 200$ sec⁻¹, $\tan\delta_{200\ cps} = 0.7$, and a dielectric constant $(\epsilon')_{1\ Mc/sec}$ of 170, while $(\epsilon')_{20\ cps} = 30\ 000$. The loss and low-frequency capacitance of the crystal are directly proportional to the area of the electrodes and depend but slightly on the sample thickness, electrode materials and surface treatment. C' and C'' have been measured at 300°K as a function of the oxygen vacancy concentration in the crystal. C' and C'' have also been measured as a function of dc bias from 0 to 400 volts; $(C')_{20\ cps}$, $(C'')_{max}$ and τ are proportional to V^{-n} where n is between 0.3 and 0.8. The results of the experiments can be explained by an electron-deficient barrier layer whose thickness increases with increasing applied dc voltage. When the dc voltage in the c direction is changed, effects are observed whose time constants are of the order of hours or even days.

INTRODUCTION

THE dielectric constant of titanium dioxide (rutile) is of interest because it is large and anisotropic. Grant[1] quotes values for the static dielectric constant at room temperature of 173 with the electric field in the c direction and 89 perpendicular to the c direction, compared with the optical value of ~7. Recently Nicolini[2] has reported that the dielectric constant ϵ' of ceramic rutile at room temperature increased from a value of about 100 at 10^6 cps to a value of 10 000 for frequencies below $\sim10^2$ cps. Moore[3] has found similar low-frequency dielectric constants in both the a and the c directions of single-crystal rutile. Srivastava[4] measured a value of 760 for the dielectric constant at 100 cps in the c direction at 300°K; but this dielectric constant was a function of frequency, apparently increasing without limit as the frequency decreased. Van Keymeulen[5] did not find this effect in his measurements of the dielectric constant of single-crystal rutile.

A series of experiments designed to find the source of these amazing low-frequency dielectric constants seemed to be lacking. An investigation was therefore made of the capacitance (C') and loss (C'') of undoped, single-crystal rutile as a function of frequency $(10^1-3\times10^6$ cps) and temperature (78–300°K). The effects of various parameters such as the electrode metal, sample dimensions, surface treatment, bias voltage, and carrier (electron) concentration, were studied. A few measurements were also made of the two-terminal dc resistance of the samples.

The experimental results may be explained by an electron-deficient barrier layer at the electrode-crystal interface such as has been proposed to explain the action of contact rectifiers.[6] The experimental results cannot be explained by assuming that the crystal is ferroelectric.

THEORY

The exhaustion layer theory of rectification is due to Schottky.[6] When a metal and a semiconductor of different work functions are placed in contact, the difference in work function causes the formation of a double layer which reduces the potential at the surface of the semiconductor by an amount equal to the difference in work function, thus equalizing the Fermi levels. In the case of TiO₂, the double layer consists of positive ionized impurity centers in the semiconductor and electrons at the metal-TiO₂ interface. If the density of ionized donors in the exhaustion layer is assumed constant and equal to the total bulk donor density N, the thickness b of the layer for a given difference in work function ϕ and applied dc bias voltage V is given by

$$b = [\epsilon(\phi - V)/2\pi Ne]^{\frac{1}{2}}, \qquad (1)$$

where ϵ is the static dielectric constant of the semiconductor and e is the electronic charge. The conductivity of the barrier layer will be reduced by the removal of the electrons. This layer then has all the properties necessary for rectification. And as Breckenridge and Hosler[7] have shown, the Ti−TiO₂ contact does rectify.

Joffé[8] and Torrey and Whitmer[9] have pointed out that such a barrier layer should have a capacitance which could be used to measure its thickness. A simple

¹ F. A. Grant, Revs. Modern Phys. **31**, 646 (1959).
² L. Nicolini, Nature **170**, 938 (1952); Nuovo cimento **13**, 257 (1959).
³ C. H. Moore, Jr., Mining Trans. **184**, 194 (1949).
⁴ K. G. Srivastava, Laboratory for Insulation Research, Massachusetts Institute of Technology Technical Report 127, June, 1958 (unpublished).
⁵ J. Van Keymeulen, Naturwissenschaften **45**, 56 (1958).
⁶ W. Schottky, Z. Physik **118**, 539 (1942).
⁷ R. G. Breckenridge and W. R. Hosler, J. Research Natl. Bur. Standards **49**, 65 (1952).
⁸ A. F. Joffé, *The Physics of Crystals* (McGraw-Hill Book Company, New York, 1928).
⁹ H. C. Torrey and C. A. Whitmer, *Crystal Rectifiers* (McGraw-Hill Book Company, New York, 1948).
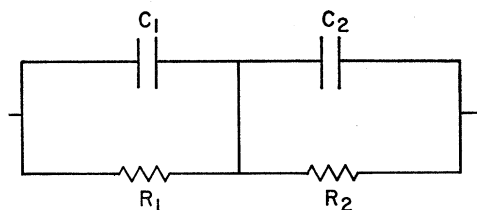
FIG. 1. Equivalent R-C circuit for discussing the complex capacitance of a crystal with a barrier layer.

$R-C$ circuit whose capacitance has the same frequency dependence as that of the crystal for small ac voltages is shown in Fig. 1. The capacitance and resistance of the barrier layer (C_1 and R_1) and the capacitance and resistance of the rest of the crystal (C_2 and R_2) are given in Gaussian units by

$$C_1 = \epsilon A/4\pi d,$$
$$C_2 = \epsilon A/4\pi(L-d),$$

and

$$R_2 = \rho(L-d)/A,$$

where A is the cross-sectional area of the crystal, L is the total crystal thickness, and ρ is the bulk resistivity. ϵ is assumed to be constant and equal to the static value of the dielectric constant of the crystal. Since the electrodes are symmetrical, there are two barrier layers in the crystal, one at each electrode. Thus, for zero bias, d in the equations above will be equal to twice the barrier layer thickness. However, under high dc bias, the resistance of the barrier layer at the negative electrode will be increased, and that at the positive electrode decreased. In this case, d will be equal to the thickness of the barrier layer at the negative electrode, the value for b calculated from Eq. (1) with V taken as a negative quantity.

Von Hippel[10] has shown that the complex capacitance ($C=C'-iC''$) of the circuit shown in Fig. 1 exhibits a Debye-type loss with an added term for the dc resistance:

$$\frac{C'-C_\infty'}{C_0'-C_\infty'} = \frac{1}{1+\omega^2\tau^2},\tag{2}$$

$$\frac{C''-1/\omega R_{dc}}{C_0'-C_\infty'} = \frac{\omega\tau}{1+\omega^2\tau^2}.\tag{3}$$

Here $R_{dc}=R_1+R_2$ is the dc resistance of the crystal and τ, C_0', and C_∞' are complicated functions of R_1, R_2, C_1, and C_2.[10] Now since Breckenridge and Hosler found that the Ti—TiO_2 contact is rectifying, the resistance of the barrier layer must be much greater than the bulk resistance. Using therefore the approximation $R_1 \gg R_2$,

the expressions for τ, C_0', and C_∞' become

$$C_\infty' = \epsilon A/4\pi L,\tag{4}$$

$$C_0' = \epsilon A/4\pi d,\tag{5}$$

and

$$\tau = \epsilon\rho L/4\pi d.\tag{6}$$

The bulk resistivity may be conveniently calculated from relations derived from these equations:

$$\frac{2(C''-1/\omega R_{dc})_{max}}{\tau} = \frac{A}{\rho L}\left(1-\frac{d}{L}\right),\tag{7}$$

and

$$\lim_{\omega\to\infty}(\omega C'') = \frac{A}{\rho L}\left(1-\frac{d}{L}\right).\tag{8}$$

EXPERIMENTAL

Sample Preparation

A boule of undoped rutile grown by the flame-fusion technique was obtained from the Linde Company. The boule was oriented by x-ray back reflection. Samples approximately $1\times2\times3$ mm were cut with a diamond saw. One of the directions in the sample corresponded to the c axis and the other two to a or 110 axes. The samples were polished gently by hand on No. 600 corundum paper to remove gross irregularities in the surface. The dimensions were then measured with a micrometer. A few samples were polished further, using 0.3-micron alumina on a paraffin lap as the final polish.

The orientation of the c axis of the samples was checked with polarized light, and was in all cases correct within $2°$. The samples were not perfect single crystals; they seemed highly strained and most contained two or three low-angle (~5 min) grain boundaries. The dielectric properties did not seem to be affected by the presence of these boundaries.

The crystals were washed with water, alcohol, and trichloroethylene. Treatments of the crystal with hot dilute or concentrated acids such as HNO_3 or H_2SO_4 did not alter the dielectric properties.

The carrier (electron) density in the crystals depends upon the concentration of oxygen vacancies; the number of vacancies can be increased by reduction of the crystal, or decreased by oxidation. The bulk resistivity of the crystals as cut is calculated in a later section to be about 3×10^6 ohm cm in the c direction. This can be decreased two orders of magnitude by heating the crystal to $1000°C$ in one atmosphere of oxygen and then decreasing the temperature as rapidly as possible. (Further reduction can be accomplished by heating in vacuum.) The resistivity can be increased one or two orders of magnitude by cooling the crystal slowly from $1000°C$ in 1 atm O_2.

Several different metal electrodes were tried. Indium and indium-gallium amalgam wet the crystal and were spread on in a thin uniform coat; in the case of indium,

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[10] A. R. von Hippel, in *Handbook of Physics*, edited by E. U. Condon and H. Odishaw, (McGraw-Hill Book Company, New York, 1958), pp. 4–121ff.

the crystal was warmed until the metal flowed easily. Silver and titanium were evaporated onto the crystal at a pressure of ∼1 micron Hg; the crystal was cleaned by glow discharge before the evaporation and a shutter was used so that the metal could be cleaned by partial evaporation before the crystal was coated. The evaporated electrodes were quite adherent. Silver paint was fired on by heating the crystal gently until the organic material in the paint had burned off. Electrodes were removed with warm dilute acids such as HNO_3. The application of the electrodes and their subsequent removal with acid had no effect on the surface or bulk resistivities or on the capacitance and loss of the crystal.

Apparatus

Measurements of capacitance were made by a substitution method with General Radio 716 and 716-CS capacitance bridges and a 722-DQ variable precision capacitor. The technique is described by von Hippel.[11] The ac signal strength was reduced until a further reduction in signal strength had no effect on the measured capacitance, usually about 0.1 volt. The dc bias voltage was supplied with batteries. Before measurements of capacitance under dc bias were made, the bias voltage was applied until the capacitance of the crystal did not change with time; this usually required about 20 minutes.

For the measurements, the sample with metal electrodes applied was held between the lightly spring-loaded plates of a shielded parallel plate capacitor. The plates were 0.8 cm in diameter; the plate spacing was adjusted by moving the upper plate which was mounted on a screw. The capacitor was connected through a stainless steel coaxial pipe about 18 in. long to a switching arrangement which made a coaxial connection to the bridge when the sample holder was in the circuit and grounded both holder terminals when the holder was out of the circuit. The part of the apparatus containing the sample, parallel plates and center conductor of the coaxial lead from the switch was evacuated to at most 20 microns Hg pressure. The total capacitance of the holder, coaxial connectors, and external capacitor was at least 136 μμf. The capacitance difference between the holder in and out of the circuit was about 40 μμf. C'' for the holder was no larger than 0.005 μμf. For a dielectric constant of 100, the capacitance of the samples was 2–10 μμf. Though capacitance differences could be measured to ±0.01 μμf, the absolute value of the sample capacitance could be determined to only ±0.05 μμf because of the errors involved in setting the plate spacing for the measurement of the capacitance of the sample holder. Because of the large dielectric constant of the material, this error was not serious in these experiments. The loss of the sample was measured to ±0.005 μμf or ±2%, whichever was the larger error.

[11] A. R. von Hippel, *Dielectric Materials and Applications* (John Wiley & Sons, New York, 1954).
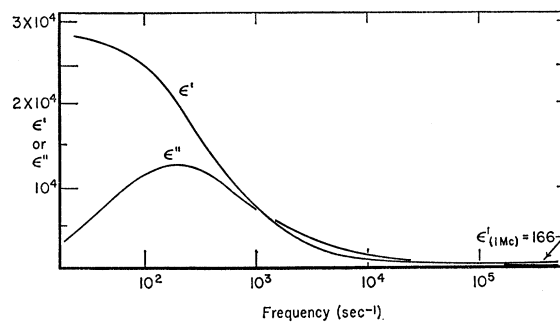

FIG. 2. Apparent dielectric constant and loss of single-crystal TiO₂ (rutile) in the c direction at 300°K. Sample dimensions 2×2×2 mm. Indium electrodes.

Two-terminal dc resistance was measured with a General Radio electrometer which read the current through its internal resistance in series with the sample and a voltage source. The sample holder was connected through coaxial pipe to a carefully shielded voltage supply (batteries) which made in turn a coaxial connection to the electrometer. The resistance of the leads and the sample holder with the sample removed was greater than the largest measurable resistance under all conditions of temperature and voltage used in these experiments.

RESULTS

The complex dielectric constant $(\epsilon = \epsilon' - i\epsilon'')$ of rutile when the electric field is in the c direction is strongly dependent on frequency. Figure 2 shows data for an as-cut, unpolished crystal with indium electrodes at 300°K. ϵ' at 10^6 cps is 166, in good agreement with the values of the static dielectric constant in the c direction quoted by Grant.[1] But the apparent value of ϵ' at low frequencies is about 30 000 and is fairly independent of frequency below 50 cps. At intermediate frequencies a loss peak is observed; ϵ'' rises to a maximum at 200 cps, at which frequency $\tan\delta = 0.7$. This is similar to the behavior of ceramic TiO₂ reported by Nicolini.[2]

With the field perpendicular to the c direction, ϵ' was 89 at all frequencies and ϵ'' was 3 or 4 orders of magnitude smaller than in the c direction. In Fig. 3 are shown data for ϵ'' as a function of frequency for two orientations (a and c) of an unpolished, very lightly reduced sample with indium electrodes. The curves marked 110 were measured in the 110 directions of another similarly treated crystal. Since in a direction perpendicular to c, ϵ' and ϵ'' do not depend on the crystal dimensions, the capacitance and dielectric loss in these directions is a normal bulk effect.

The complex capacitance in the c direction was measured as a function of frequency for two identically treated crystals of different dimensions. The values for ϵ'' and $\epsilon' - (\epsilon')_{1\,Mc/sec}$ calculated from the capacitance data are strongly dependent on the crystal dimensions, though $(\epsilon')_{1\,Mc/sec}$ is not. In Fig. 4, the ratios of the
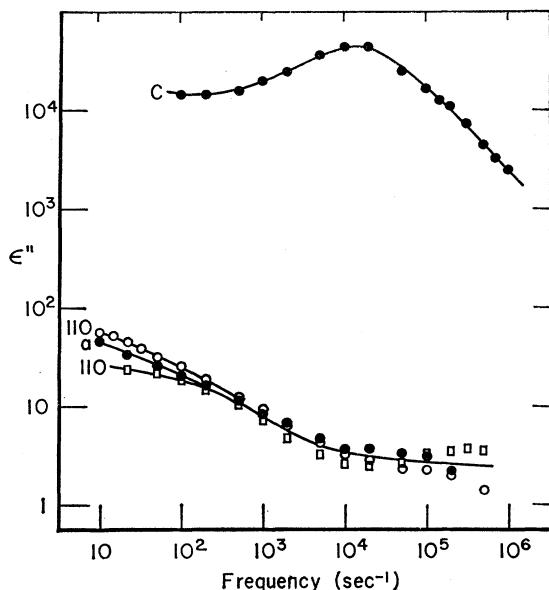
FIG. 3. Dielectric loss of single-crystal TiO_2 at 300°K as a
function of orientation. Indium electrodes.

measured losses C_1''/C_2'' and of the capacitance incre-
ments $[C'-(C')_{1\,Mc/sec}]_1/[C'-(C')_{1\,Mc/sec}]_2$ are shown
as a function of frequency. The frequency was normal-
ized by setting $\omega\tau$ equal to one when $C''-1/\omega R_{dc}$ was
a maximum. If this were a bulk effect, these ratios
would have been $(A_1/L_1)/(A_2/L_2)=5.7$ at all fre-
quencies, the upper horizontal line in Fig. 4. Instead
the points cluster about the lower line in the figure
which corresponds to A_1/A_2, the ratio of the areas of the
c faces of the two crystals. Therefore, the increase in
capacitance at low frequencies in the c direction must
be a surface effect and is best described as a capacitance
per unit area of c face rather than as a dielectric con-
stant. The points shown in Fig. 4 represent a collection
of data taken with different electrodes, principally
soldered In and evaporated Ti.
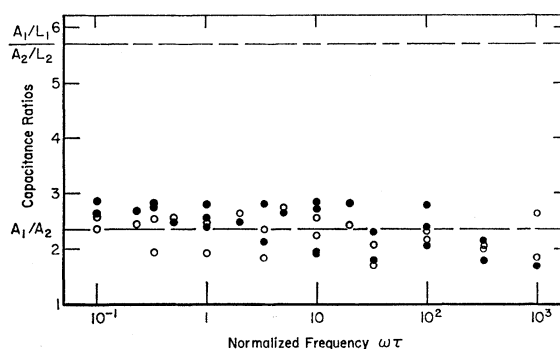
Measurements of $D-E$ curves for these crystals at

FIG. 4. Ratios of measured capacitances in the c direction at
300°K for two different size samples of single-crystal TiO_2. Indium
and titanium electrodes. $\bullet = C_1''/C_2''$; $\bigcirc = [C'-(C')_{1\,Mc/sec}]_1/$
$[C'-(C')_{1\,Mc/sec}]_2$.

60 cps and 500 volts ac showed hysteresis loops in the
c direction similar to those shown by Nicolini[2] for
ceramic TiO_2, and completely linear behavior in direc-
tions perpendicular to c.

The values for the dielectric constant and loss of the
crystal are not affected by changing the metals used for
electrodes—indium, indium-gallium amalgam, silver,
or titanium. Nor does the treatment of the surface seem
to be important. The largest change observed, the
result of highly polishing the surface under the electrode,
was a 30% increase in the low-frequency dielectric
constant in the c direction.

The effect of lowering the temperature is to lower
both the low-frequency capacitance and the relaxation
frequency. A change of a factor of about 5 in these
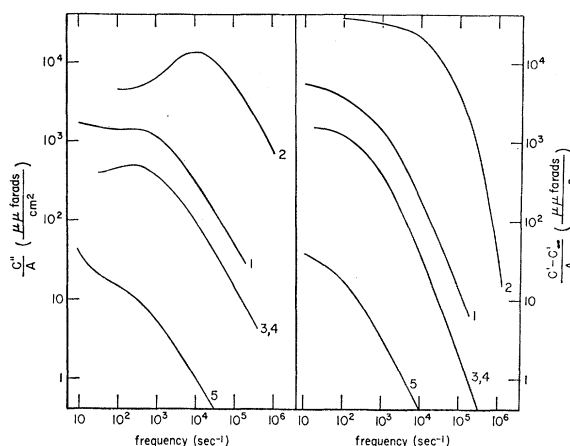quantities is seen when the temperature is changed
from 300°K to 78°K.

FIG. 5. Capacitance of single-crystal TiO_2 in the c direction at
300°K as a function of oxidation of the crystal. Indium electrodes.
Sequence of treatment of the crystal: No. 1, as cut from the boule;
No. 2, reduced slightly; No. 3, oxidized slightly; No. 4, heated
under conditions which should have neither oxidized nor reduced;
No. 5, oxidized further.

The low-frequency capacitance and the relaxation
frequency are changed by orders of magnitude when the
crystal is slightly oxidized or reduced. In Fig. 5, data
for the capacitance and dielectric loss of a crystal at
300°K are shown as a function of frequency for several
stages in the oxidation of a crystal. Curve No. 1 is the
measurement on the as-cut crystal. For No. 2, the
crystal was reduced slightly; for No. 3, oxidized slightly.
For No. 4, the crystal was then heated five days at
300°C in 1-atm air, a treatment which should have
neither oxidized nor reduced it, and as is seen in Fig. 5
the properties were the same as before. Number 5 was
measured after yet further oxidation. Oxidation of the
crystal causes a decrease in both the low-frequency
capacitance and the relaxation frequency.

The most striking result of the experiments is the
dependence of the capacitance and loss on dc bias
voltage. In Fig. 6 is shown a series of measurements

taken at 78°K in the c direction of an untreated sample with evaporated Ti electrodes. As the dc bias is increased, the capacitance and loss decrease at low frequencies but are not affected much at high frequencies, while the relaxation frequency is increased. Similar measurements were made at 195 and 273°K; the only difference was that the losses, capacitances and relaxation frequencies were all somewhat larger.

Whenever it was possible, the two-terminal dc resistance of the crystal was measured. The resistance at 78°K was greater than 10^{14} ohms, and thus could not be measured with the electrometer. At 273 and 300°K, continued application of the measuring voltage caused a decrease in the resistance of the sample. The resistance returned to its original value if the crystal was heated (e.g., $\frac{1}{2}$ hour, 1000°C, 1 atm O₂) or if it was allowed to stand for several weeks (e.g., 3 weeks, 300°K, 20 microns Hg pressure). At 195°K it was possible to measure the two-
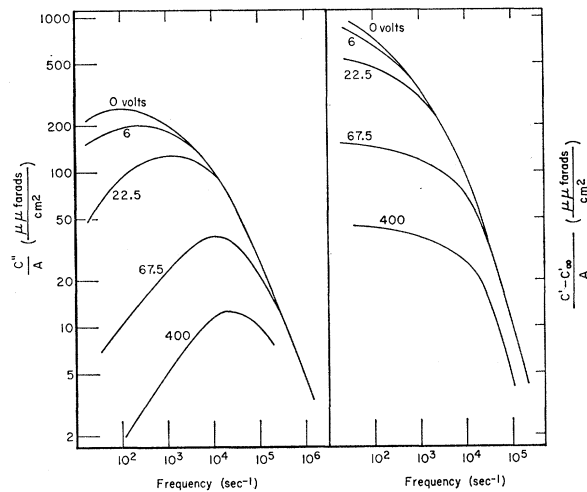

Fig. 6. Capacitance of single-crystal TiO₂ in the c direction at 78°K as a function of dc bias. Titanium electrodes.

terminal resistance as a function of voltage over several orders of magnitude in voltage. Expressed in terms of voltage and current, $I \propto V^{\frac{3}{2}}$ fit the data very well from $V=1.5$ to $V=400$ volts. For $V=9$ volts, the dc resistance of the sample whose capacitance is shown in Fig. 6 was 78°K, $\gtrsim 10^{14}$ ohms; 195°K, 10^{11} ohms; 273°K, 10^{9} ohms; 300°K, 5×10^{8} ohms.

When the dc voltage was removed from the sample, the sample generated a voltage of the same sign which required several minutes to decay, the decay time being about 1 hour at 195°K and faster at higher temperatures, an effect first observed for glass by Franklin[12] in 1748.

INTERPRETATION AND DISCUSSION

Ferroelectricity as an explanation for the high apparent dielectric constants is immediately ruled out

by two experimental results. The low-frequency capacitance in the c direction for identically treated crystals depends only on the cross-sectional area of the crystals. And this capacitance changes when the concentration of oxygen vacancies in the crystal is changed.

The general form of the dependence of dielectric constant and dielectric loss on frequency for an untreated crystal under zero bias, as in Fig. 2, is well explained by the barrier layer model. According to Eqs. (2) and (4), the capacitance at high frequencies should correspond to the static dielectric constant, as is observed. The capacitance at low frequencies [Eq. (5)], however, depends on the barrier layer thickness and will be much larger, as is also observed. Since the low-frequency capacitance does not depend on the sample thickness, this capacitance is better represented as a capacitance per unit area, $C_0'/A = \epsilon/4\pi d$, which agrees with our results shown in Fig. 4. As long as $d \ll L$, Eqs. (2), (3), (4), and (5) show that the ratios of C'' and of $C'-C_\infty'$ measured for crystals of different dimensions at corresponding normalized frequencies $\omega \tau$ should be equal to $(C_0'-C_\infty')_1/(C_0'-C_\infty')_2 \simeq A_1/A_2$ at all frequencies. This is also observed in the data in Fig. 4.

The model predicts, in Eqs. (2) and (3), that C' and C'' will show a Debye-type frequency dependence. The data in Fig. 2 have the general form of Eqs. (2) and (3); as C' changes from its high-frequency to its low-frequency value, $(C''-1/\omega R_{dc})$ goes through a maximum. (In this case, $1/\omega R_{dc}$ is negligible, even at the lowest frequencies.) But the data are not fit exactly by the equations. The loss peak is a little broader than is predicted and the peak occurs at a frequency below that at which $C'-C_\infty' = (1/2)(C_0'-C_\infty')$. These deviations from ideal behavior are not large enough, however, to cause significant difficulties in this analysis.

The model is most successful in explaining the dc bias dependence. As can be seen from Eq. (1), dc bias will cause an increase in the barrier layer thickness. Consequently, according to Eqs. (5) and (6), both τ and the low-frequency capacitance will decrease. However, Eqs. (7) and (8) show that as long as the barrier layer occupies a small fraction of the crystal, the high-frequency values of C'' and the value of $(C''-1/\omega R_{dc})_{max}/\tau$ should be constant. These predictions are borne out in the data shown in Fig. 6. The decrease in the capacitance at high frequencies for 400-volt bias occurs because $d=0.8L$, and hence the term $(1-d/L)$ in Eqs. (7) and (8) becomes appreciably less than one. Similar results are obtained at different temperatures and with other differently treated samples. The same kind of behavior has also been observed by Stucky[13] for the capacitance and loss of copper oxide rectifiers.

The thickness of the barrier layer for $|V| \gg \phi$ can be calculated from Eq. (5) as $d=\epsilon A/4\pi C_0'$. The static values of the dielectric constant ϵ were calculated from

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[12] J. T. Littleton and G. W. Morey, *Electrical Properties of Glass* (John Wiley & Sons, New York, 1933).

[13] J. N. Shive, *Semiconductor Devices* (D. Van Nostrand and Company, Princeton, New Jersey, 1959).
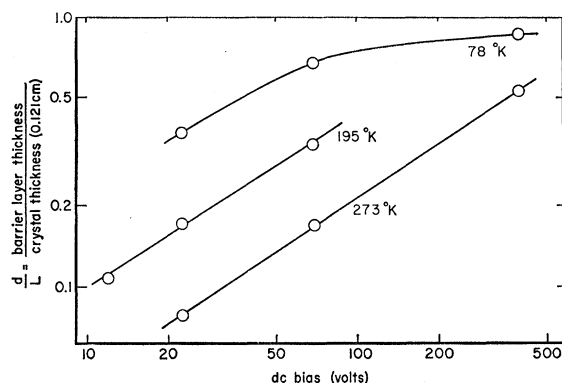
FIG. 7. Barrier layer thickness as a function of dc bias for $|V| \gg \phi$, calculated from data in Fig. 6 at 78°K and similar data taken at 195 and 273°K.

C_∞' at a particular temperature [Eq. (4)]. Calculated values for d are shown in Fig. 7 for the data in Fig. 6 at 78°K, and similar data taken at 195 and 273°K. From Eq. (1) it is predicted that d should vary as $V^{0.5}$ for $|V| \gg \phi$. The dependence in Fig. 7 is closer to $V^{0.65}$ at all three temperatures, except for dc bias above 60 volts at 78°K, where the layer thickness approaches the total thickness of the crystal. For other samples, exponents as low as 0.3 and as high as 0.8 have been observed.

The thickness of the barrier layer can be calculated from Eq. (1) as $d = (|V| \epsilon/2\pi Ne)^{\frac{1}{2}}$ for $|V| \gg \phi$. The bulk resistivity of the sample at a particular temperature was calculated from Eqs. (7) and (8). For the data shown in Fig. 6, ρ calculated from Eq. (7) is 6×10^6 ohm cm and, from Eq. (8), 3×10^6 ohm cm. This value is relatively independent of temperature between 78 and 300°K; this has also been observed by Breckenridge and Hosler[14] for the resistance of more highly reduced samples. From the calculated values of the bulk resistivity of these samples and the data of Breckenridge and Hosler[14] for the mobility of electrons in more reduced samples, the total density of donors N is calculated to be about $5 \times 10^{12}/\mathrm{cm}^3$. Taking, for example, the data in Fig. 6 for $V = 22.5$ volts: ϵ calculated from C_∞' is 240; the value calculated for d is 3.5×10^{-2} cm, in good agreement with the value 4.4×10^{-2} cm calculated from the height of the loss peak in Fig. 6.

Other parameters besides V in Eq. (1) for the barrier layer thickness can be varied, thus changing the low-frequency dielectric constant and the relaxation frequency. For example, if the concentration of donors N is varied by changing the concentration of oxygen vacancies by oxidation or reduction of the crystal, ρ will vary as $1/N$, and C_0' and $1/\tau$ will both vary as $\sqrt{N}$ [Eqs. (5) and (6)]. This sort of behavior is seen in Fig. 5 for the capacitance and loss as a function of oxidation of a crystal. The bulk resistivity calculated from Eqs. (7) and (8) shows that N decreases when the crystal is

oxidized, as was expected. And as N decreases, C_0' and $1/\tau$ decrease as $N^{0.54}$.

If the temperature is varied, the quantities in Eq. (1) which vary are ϵ and ϕ. Again for dc voltages very much larger than ϕ, the barrier layer thickness should vary as $\sqrt{\epsilon}$, i.e., it should increase about 20% as the temperature decreases from 273° to 78°K. As can be seen in Fig. 7, d does increase as the temperature decreases, but the increase is larger than 20%; for a given voltage it is closer to a factor of 3.

If the electrodes are changed, the quantity in Eq. (1) which is changed is ϕ, the difference in work function. In the measurements reported here, the changing of electrodes did not affect the results appreciably. But all of the metals tried as electrodes have work functions of about 4 ev. No experiments were performed with metals of quite different work functions.

The results of the experiments were also rather insensitive to the treatment of the surface of the samples. Since the behavior observed is not a "surface effect" in the usual sense, surface treatment would not be expected to change the capacitance and loss unless the density of donors in the vicinity of the surface were sufficiently altered to change d. This may be what happened when the samples were polished protractedly; in the damaged region of the crystal at the polished surfaces the donor density was increased and hence d was decreased and the low-frequency capacitance increased. As stated above, the magnitude of this effect was no greater than 30%.

From Eq. (3) it is seen that if R_{dc} is sufficiently small, there will be an increase in C'' at low frequencies with $C'' = 1/\omega R_{dc}$ with no corresponding change in C'. In the data in Fig. 3, this can be seen particularly for the losses in directions perpendicular to c. (It is also present in the measurements parallel to c in Figs. 3 and 5, but is not seen so easily until the loss peaks are subtracted out.) There was no corresponding increase in C' in any case. The values calculated for R_{dc} from the low-frequency losses agree within a factor of two with the two-terminal dc resistance measurements made on the samples with the electrometer.

One of the assumptions upon which this analysis is based is that the barrier layer resistance is much greater than the bulk resistance. The bulk resistivity calculated from the high-frequency losses is of the order of 10^6 ohm cm. In the absence of any leakage conductance of the sample, $R_{dc} = R_1 + R_2 \simeq R_1$. In the c direction, values for R_{dc} were at least two orders of magnitude larger than the values calculated from the bulk resistivity.

The resistance measurements suggest a possible explanation for the absence of losses in the a and 110 directions in Fig. 3. The resistance in directions perpendicular to c is about five times that parallel to c for $\rho_c \sim 0.1$–10 ohm cm.[14,15] For higher resistivities, the

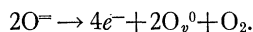[14] R. G. Breckenridge and W. R. Hosler, Phys. Rev. **91**, 793 (1953).

[15] L. E. Hollander, Jr., and P. L. Castro, Phys. Rev. **119**, 1882 (1960).

difference between the two directions becomes more pronounced, e.g., a factor of 100–1000 for $\rho_c \sim 10^3$ ohm cm.[15,16] Now as the bulk resistivity increases, the relaxation frequency decreases. The loss peak could thus be shifted to frequencies below the limit of 10 cps of these experiments. In Fig. 4, this has almost occurred in the c direction for $\rho_c \sim 10^8$ ohm cm. In addition, if the resistivity becomes high enough, the assumption $R_1 \gg R_2$ used in this analysis breaks down; and a more detailed analysis shows that for $R_1 \approx R_2$, the loss peak disappears, $C_0' = C_\infty'$, and $C'' = 1/\omega R_{dc}$, which is what is observed in the a and 110 directions in Fig. 3. Moore[3] has found large low-frequency dielectric constants in the a direction for lower resistivity material.

At 195°K, the measurement of the resistance of the crystal as a function of voltage gave $I \propto V^{1.5}$, just Child's law[17] for a space-charge-limited current.

The resistance at 78°K was too high to be measured. The resistances at 273 and 300°K were fairly ohmic and probably corresponded to the current leakage mentioned above.

The barrier layer model is too simple to cover the several long-time-constant effects which were observed. The two-terminal dc resistance of the crystals (and simultaneously the apparent barrier layer thickness) at 273 and 300°K decreased when the crystals were subjected to prolonged high dc bias. Koller and Pospíšil[18] correlate the decrease in resistance of ceramic TiO₂ capacitors under these conditions with the generation of color centers in the vicinity of the negative electrode. Bogoroditskii and Fridberg[19] attribute the decrease in resistance to the generation of oxygen vacancies at the positive electrode by the reaction

$$2O^= \rightarrow 4e^- + 2O_v{}^0 + O_2.$$

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[16] R. A. Parker (to be published).
[17] C. D. Child, Phys. Rev. **32**, 492 (1911).
[18] A. Koller and Z. Pospíšil, Czechoslov. J. Phys. **8**, 315 (1958).
[19] N. P. Bogoroditskii and I. D. Fridberg, Elec. Tech. (U.S.S.R.) **2**, 259 (1959).

In addition, the high fields across the barrier layer at the negative electrode might be sufficient to cause the accumulation of vacancies in the vicinity of that electrode. When the electrodes were removed from one of these crystals, the conductivity of the surfaces in the vicinity of the electrodes was increased by two orders of magnitude over the value for the same treatment for the crystal but omitting the dc bias. However, the process is too fast to be explained by the motion of vacancies, as judged from measurements of vacancy diffusion at 800-1000°C,[16] and is too slow for an electronic process.

Since this analysis is restricted to small voltage changes, it cannot be used to explain the time effects connected with large voltage changes which were observed, such as the generation of voltage by the crystal when the dc bias was removed and the hysteresis loops observed in the $D-E$ measurements.

CONCLUSIONS

Large apparent dielectric constants, of order 30 000, are observed in the c direction of undoped single-crystal rutile. The behavior of the capacitance and dielectric loss of undoped rutile as a function of frequency ($10^1-3\times10^6$ cps), temperature (78–300°K), dc bias (0–400 volts), and oxygen vacancy concentration can be explained by an electron-deficient barrier layer at the electrode-crystal interface. It is not necessary to postulate any increase in the dielectric constant above the usual "static" value. The experimental results cannot be explained as ferroelectric phenomena.

Several effects with very long time constants have been observed to occur on large changes in voltage; concerning these, the barrier layer model as developed here makes no predictions since it is specifically restricted to very small voltage changes. Further experimental work is necessary for these effects to be understood.