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Studies of the Surface of Rutile Single Crystals by Means of Electrical Conductivity

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The surface properties of rutile single crystals were studied by the measurement of the d.c. electrical conductivity. Upon successive thermal treatments *in vacuo* from 25 to 550 °C, the electrical conductivity on the (110) plane increased remarkable, while the activation energy decreased. The addition of oxygen decreased the conductivity according to the oxidation temperature, whereas the reduction by hydrogen above 300 °C increased the conductivity greatly. The number of carriers was also determined from the measurement of the Hall effect. These results, by reference to those of the photoconductivity, were interpreted in terms of the change in the energy band structure near the surface associated with the defect centers on the surface.

It is well known that titanium dioxide, though it is an insulator in the stoichiometric composition, becames an *n*-type semiconductor as a result of the removal of oxygen atoms when treated at a high temperature *in vacuo* or in a reducing gas, such as hydrogen or carbon monoxide.¹⁾ The reduction process may bring about a remarkable change in the structure and properties of the surface and also in the bulk, since oxygen atoms are removed from the surface and also from the bulk through the surface region. A number of studies of reduced titanium dioxide have been made by means of measurements of the electrical conductivities,²⁾ photoelectronic properties,³⁻⁵⁾ dielectric properties,⁶⁾ and diffusion of foreign atoms⁷,⁸⁾ in order to clarify the electronic structure in the bulk, but few have taken into account the properties of the surface.⁹,¹⁰⁾ So far, the heat of immersion in water and the adsorption of water vapor on the surface were examined for the powder specimen with an anatase modification; it has been found that these phenomena are considerably affected by a departure from the stoichiometric composition.¹⁰⁾ The purpose of the present study is to examine the surface of a single crystal with a rutile modification by the measurement of the electrical conductivity along with the photoconductivity.

The crystal structure of rutile is tetragonal; a titanium ion is located in the center of eight oxygen ions, and an oxygen ion is surrounded by three titanium ions on the (110) plane, which is a cleavage plane. The bond length between a titanium ion and an oxygen ion is longer by 0.044 Å in the (110) direction than in the other two directions.¹¹⁾ In this study, the electrical conductivity was measured mostly along the c-axis on the (110) plane. Since the value of the conductivity differs to some extent from one specimen to another, the conductivity was measured for a definite specimen treated successively in the following manner: outgassing from room temperature to an elevated temperature, oxidation with oxygen, and then reduction with hydrogen. As a result, it was clarified that the surface

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conductivity varied remarkably with the treatment. Further, the surface properties of a rutile single crystal were examined by means of measurements of the Hall effect and the photoconductivity.

Experimental

Material. A single crystal of rutile grown by the Verneuil method was obtained from the Nakazumi Crystal Co., Ltd. According to the spectroscopic analysis, its purity was above 99.99%; the main impurity was sodium, the amount of which was less than 0.005%.[12] The (110) plane was obtained by cleaving the crystal at a high temperature and was polished smoothly with α-corundum 0.1∼0.2 μ in diameter. The dimensions of the crystal were $10\times10\times2\ \text{mm}^3$. The specimen was treated with a chromic acid mixture, washed thoroughly with distilled water, and then dried at room temperature.

Electrode. As an electrode for the measurement of the electrical conductivity, gold was evaporated onto the (110) plane held at 100 °C. Various types of electrodes as is illustrated in Fig. 1 were used. As to Type I in the figure, all sides of the crystal were coated with evaporated SiO film in order to bring these surfaces to an insulator. Types II and III have guard-ring electrodes mounted to surround the surface in two ways. When the guard ring is grounded, the current which flows only in the bulk can be obtained since the surface current is intercepted by the guard ring, while both currents can be obtained when the guard ring is not grounded. Type IV, which was used for the measurement of the Hall effect, was formed by means of an ultrasonic cutter. The conductivity was measured parallel to the c-axis except for the case of Type III. Besides gold, several electrode materials such as In, Ti, and Ag, were evaporated on the surface of Type I in order to examine the contact between rutile and gold; further, the voltage-current character was examined at 25 °C under several treatments.

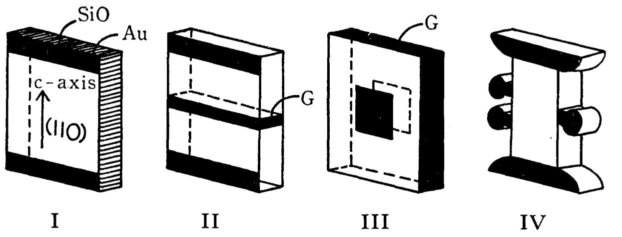

Fig. 1. Schematic drawing of four types of electrodes on the (110) planes of rutile single crystals.

Treatments. A rutile single crystal connected with electrodes was placed in a quartz cell; in this the crystal was thermally treated as will be described below. Both the dark conductivity and the photoconductivity were measured below room temperature in the same cell after each treatment. The treatment of the sample was as follows: evacuation was carried out at 10^{-5} Torr at temperatures from 25 to 300 °C for 3 hr and above 400 °C for 1 hr, oxygen was added at temperatures varying between 25 and 500 °C for several minutes under a pressure of 20∼50 Torr, followed by evacuation at 25 °C, and then hydrogen was added under the same conditions as in the case of oxygen, followed by evacuation at the temperature at which the hydrogen has been introduced. A liquid-nitrogen trap was used to protect the specimen from contamination by organic substances.[10]

Measurements. The electrical conductivity was measured at temperatures between −196 and 25 °C after helium gas had been introduced into the cell at 25 °C. A dry cell of about 1.5 V was used as the electric source. The electric current was measured with an Ohkura Electric Co. Model Am 5001 high-impedance microvoltammeter. The Hall e.m.f. was obtained in a three-electrode system under a magnetic field of about 4600 gauss. The photoconductivity was measured at −196 and 25 °C in the wavelength range between 350 and 600 mμ by using a tungsten lamp as the light source and interference filters. The intensity of the illuminating light was calibrated by means of a chemical actinometer using potassium ferrioxalate[13] and Rhodamine B.[14] The absorption spectrum was measured at −133 °C. and at room temperature over the wavelength range from 0.22 to 2.5 μ.

Results and Discussion

Contact between Rutile and Gold. When a metal and a semiconductor are brought into contact, a contact potential is formed by the difference between the work functions of these two materials. It was found that the electrical conductivity for the same specimen showed almost the same value regardless of the kind of electrode materials, such as In, Ti, Ag, and Au. The relationship between the electric current and the applied voltage indicated the Ohm law, as is shown in Fig. 2. From the above results, the Schottky barrier, which is generally seen in Si, GaAs, *etc.*[15], may not be formed in this contact. The measurement by the four-contact method, however, indicated a slight contact resistance at a low temperature when the specimen was evacuated above 300 °C.

According to the value of the electron affinity of rutile reported recently,[16] it is probable that the accumulation layer is formed near the surface by the contact with gold,[17] as is illustrated in Fig. 3, where the Fermi level of rutile is located below the conduction band, judging from the *n*-type semiconductor. The

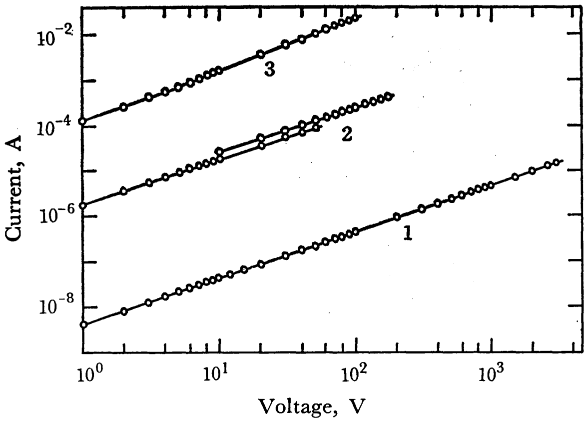

Fig. 2. Voltage-current characteristics for the contact between gold and rutile treated *in vacuo* at several temperatures; (1) 25 °C, (2) 300 °C, and (3) 500 °C.

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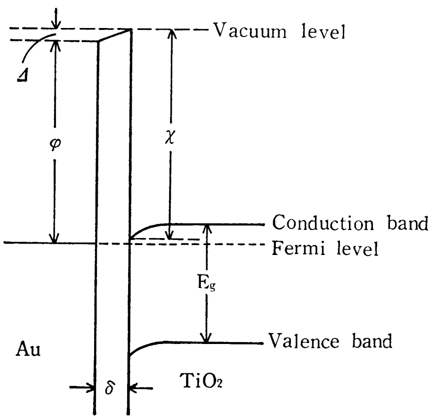

Fig. 3. Energy level diagram for gold and rutile in electrical equilibrium.

E_g: Band gap of rutile, 3.03 eV.
φ: Work function of gold, 5.32±0.1 eV.
χ: Electron affinity of rutile, 5.56 eV.
Δ: Potential across interfacial layer.
δ: Thickness of interfacial layer.

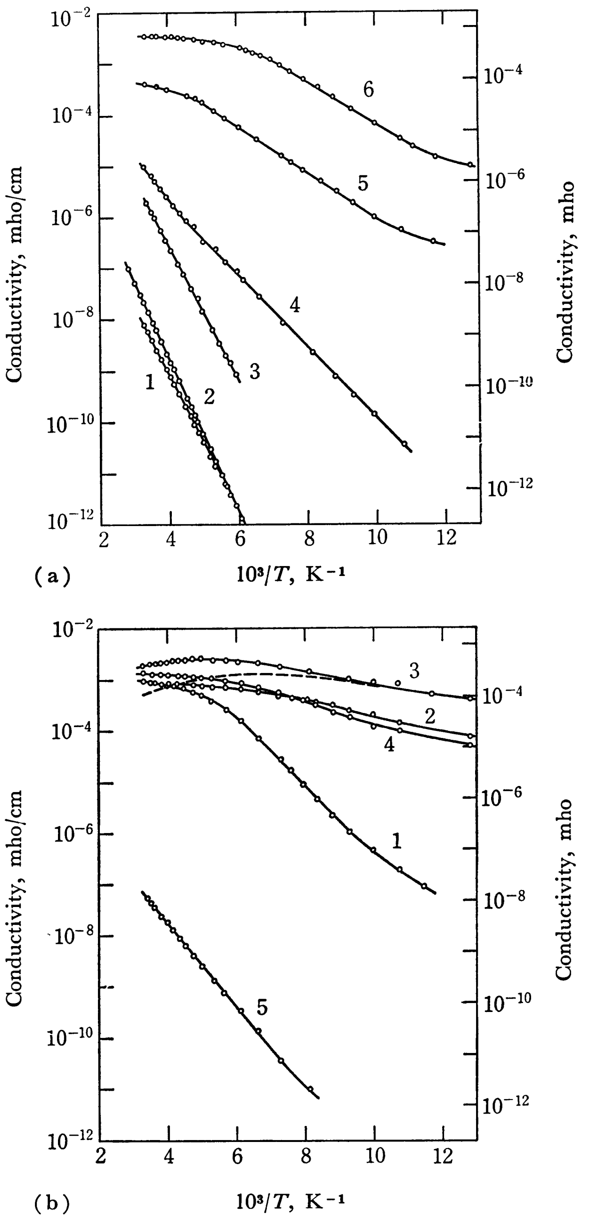

Fig. 4. Electrical conductivity of rutile treated under various conditions as a function of reciprocal absolute temperature.

(a) Successive evacuation at the following temperatures: (1) 25 °C, (2) 100 °C, (3) 200 °C, (4) 300 °C, (5) 400 °C, and (6) 550 °C.

(b) Successive introduction of oxygen or hydrogen as follows: (1) hydrogen, at 500 °C for 2 min after oxidation at 500 °C, (2) hydrogen, at 500 °C for 5 min, (3) hydrogen, at 500 °C for 5 min, (4) oxygen, at 25 °C for 2 min, and (5) oxygen, at 500 °C for 2 min.

energy level of the surface which is treated under various conditions may differ from that in the bulk because of the presence of impurities, lattice defects, and adsorbed gases, though the former may be identical with the latter if the surface is in an idealized state.

Changes in the Electrical Conductivity with Various Treatments. The changes in the electrical conductivity of the rutile treated successively at temperatures from 25 to 550 °C *in vacuo* are shown in Fig. 4(a) as a function of the reciprocal absolute temperature. The value of conductivity, σ, is expressed by the unit of mho/cm and also by that of mho; the latter unit is introduced on the basis of two-dimensional conductivity. It is clear from the figure that the conductivity increased remarkably with the outgassing temperature. A linear relation between log σ and $1/T$ was obtained over a considerably wide temperature range. The electrical conductivity can be expressed as $\sigma=\sigma_0 \exp(-\varepsilon/kT)$; ε is the activation energy for the electrical conductivity and is nearly equal to $E_d/2$ in this temperature range, where E_d is the donor level measured from the bottom of the conduction band, as will be discussed later. When the outgassing temperature increased from 25 to 550 °C, the conductivity at 25 °C, $\sigma_{25^\circ C}$, increased by 10^5, while ε decreased from 0.25 to 0.10 eV. The oxidation at 500 °C lowered the value of $\sigma_{25^\circ C}$ as low as below 10^{-13}. Not even evacuation at 500 °C restored the conductivity above 10^{-13}, but the introduction of hydrogen above 300 °C did. The reduction with hydrogen at 500 °C increased the conductivity remarkably and changed the sign of the temperature coefficient at around −25 °C, as can be seen in Fig. 4(b). On the other hand, when oxygen was added at a high temperature, σ decreased and ε increased. Moreover, when hydrogen was added at a high temperature after the oxidation, σ increased and ε decreased. This behavior observed by means of the reduction and oxidation cycle were reversible on the same sample, illustrating "Meyer's rule" that the larger the concentration of electrons, the lower the the activation energy becames.[18] The addition of oxygen at room temperature after the reduction also decreased the conductivity, which is represented by Curve 4 in Fig. 4(b). The decrement of the conductivity by the adsorption of oxygen is indicated by the dotted line in the figure. These results may indicate

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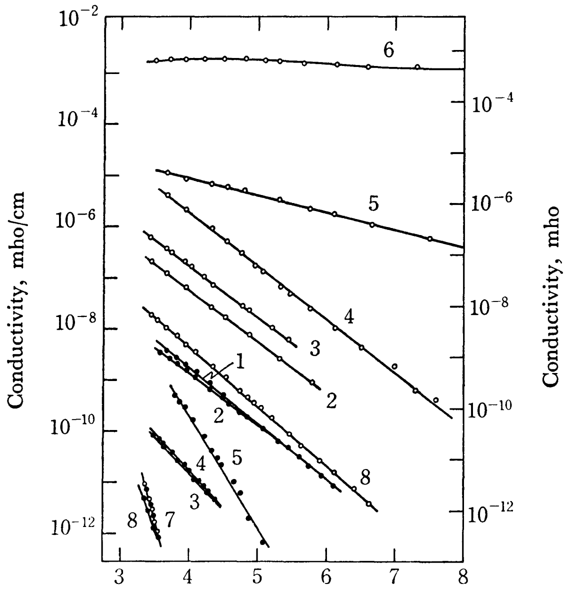

Fig. 5. Electrical conductivity of rutile with a guard ring treated under various conditions as a function of reciprocal absolute temperature. Successive treatments *in vacuo* and introduction of oxygen or hydrogen for 2 min at the following temperatures: (1) 25 °C, (2) 100 °C, (3) 200 °C, (4) 300 °C, (5) 500 °C, (6) hydrogen, 500 °C, after oxidation at 500 °C, (7) oxygen, 500 °C, and (8) hydrogen, 300 °C. In Figs. 5 and 6, open circle indicates that a guard ring was not grounded and closed one shows that it was grounded.

the effect of the adsorbed oxygen on the conductivity and the existence of the surface conductivity of the reduced rutile.

Contribution of Bulk Conductivity. The conductivity for the sample with a guard ring may clarify the problem of whether the remarkable variations in the electrical conductivity with pretreatments, as described above, occur predominantly on the surface region or in the bulk. The results for Type II presented in Fig. 1 are shown in Fig. 5. The closed circle given in the figure means that the guard ring was grounded, representing a bulk conductivity. The conductivity values obtained for the bulk were extremely small, though they differed to some extent according to the treatment. The conductivity with the guard ring not grounded shows a tendency similar to that in the case of Type I. The effect of the bulk on the conductivity seems negligibly small in the temperature range examined except for the case of the oxidation at high temperatures; the oxidation at high temperature makes the surface contribution extremely small.

The results of the conductivity in the case of Type III are shown in Fig. 6. When the specimen was evacuated at 100 and 200 °C, the bulk conductance became lower than 10^{-13} A/V. The bulk conductance increased after evacuation above 300 °C and increased significantly at 650 °C, though it is much smaller than the contribution of the surface. The oxidation at 500 °C after evacuation at 650 °C reduced the conductance extremely, as in the cases of Types I and II. Figure 6(b) demonstrates the dependence of the conductance on the reduced state of rutile, which was treated by the reduction with hydrogen at temperatures between 200 and 500 °C. After the oxidation at 500 °C, outgassing at a high temperature did not recover the conductance, but the reduction by hydrogen did.

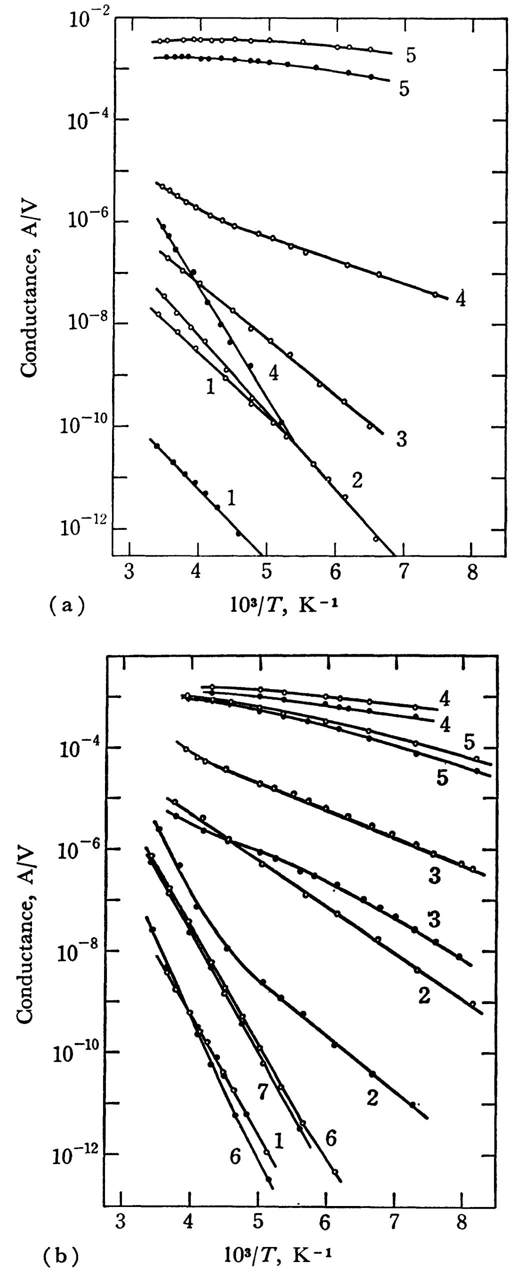

Fig. 6. Electric conductance of rutile with a guard ring under various treatments as a function of reciprocal absolute temperature.

(a) Successive evacuation at the following temperatures: (1) 25 °C, (2) 100 °C, (3) 200 °C, (4) 300 °C, and (5) 650 °C, (b) Successive introduction of oxygen or hydrogen for 2 min at the following temperatures: (1) hydrogen, 200 °C. after oxidation at 500 °C, (2) hydrogen, 300 °C, (3) hydrogen, 400 °C, (4) hydrogen, 500 °C, (5) oxygen, 100 °C, (6) oxygen, 400 °C, and (7) evacuation at 500 °C.

Surface State of Rutile. An idealized model of the (110) plane of rutile is illustrated in Fig. 7. The following three kinds of oxygen ions are present on the surface: A, above the titanium ion, B, between the titanium ions, and C, on the same plane as the

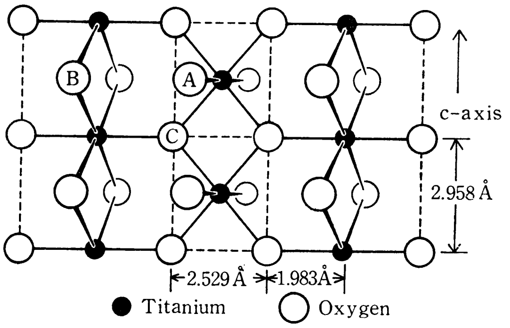

Fig. 7. Atomic model for the (110) plane of the surface of rutile.

titanium ions on the surface. Some of these oxygen ions can be excluded from the surface by virtue of the law of electric neutrality. The removal of the A oxygen is most probable because it is situated remotest from the plane composed of titanium ions. In general, the real surface of titanium dioxide is covered with hydroxyl groups which combine with titanium ions.[19] When titanium dioxide is evacuated at a high temperature, an oxo-structure similar to B in the figure is formed as a result of the condensation of these hydroxyl groups. As the surface oxo-structures thus produced are distorted,[10] these sites are considered to act as donors.

On the other hand, defect centers such as oxygen vacancies rather than interstitial titanium ions are produced by the removal of oxygen atoms when rutile is kept at high temperatures below 700 °C *in vacuo*[20] or in hydrogen.[21,22] The removal of one oxygen atom produces two electrons which reside in the oxygen vacancy or neighboring titanium ions of the lattice and which also serve as donors. Since the surface conductivity increased as the reduction proceeded, oxygen atoms, for example, B and C in the figure, may be removed from the surface. From the viewpoint of the band structure, the crystal imperfections on the surface create the energy level within the forbidden gap. This level is generally called the "surface state". When the donors in the surface state, such as the oxygen vacancy and Ti^{3+}, release the electrons to the conduction band at a moderate temperature, the surface is positively charged; the electrostatic potential for electrons bends down near the surface, in analogy with the scheme shown in Fig. 3. Therefore, as the accumulation layer is formed, the probability of the transition of the electron from the donor level to the conduction band becomes large and the concentration of the carrier electrons in the conduction band near the surface region may increase.

When oxygen molecules are admitted to the specimen at a high temperature after reduction, some are incorporated in the crystal lattice as O^{2-}, while the others adsorb as O^- and O_2^- on the surface. The incorporated oxygen may not be the defect center, but the anion radicals may form the surface state by drawing electrons from the conduction band and the donor level. As the surface is charged negatively, the surface potential bends upward to near the surface, resulting in the formation of the depletion layer.

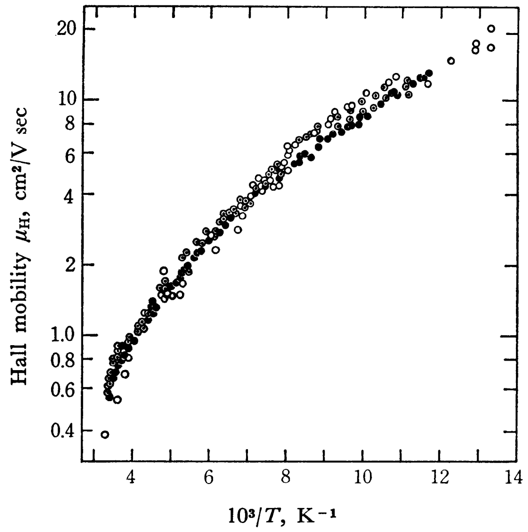

Fig. 8. Hall mobility of rutile treated under several conditions as a function of reciprocal absolute temperature. Treatments; ○: evacuation at 500 °C, ●: reduction by hydrogen at 450 °C for 2 min, and ⊙: reduction by hydrogen at 500 °C for 7 hr. The electrical conductivities at 25 °C, $\sigma_{25\,°\mathrm{C}}$, of the specimens treated above are 1.6×10^{-3}, 3.5×10^{-3}, and 1.5×10^{-1} mho/cm, respectively.

Hall Mobility. The Hall e.m.f. was measured at temperatures between −196 and 25 °C for a specimen reduced under several conditions. The Hall mobility, μ_H, is given as the product of the Hall coefficient and the conductivity. The results are shown in Fig. 8. The value changed over the range from 0.4 to 20 cm²/V s, and the following relation was obtained in this temperature range: $\mu_H \propto T^{-5/2}$. In general, when carrier electrons in a semiconductor are scattered by the thermal vibration of the crystal lattice, the mobility can be expressed as follows: $\mu \propto T^{-3/2} \cdot m^{*(-5/2)}$, where m^* is the effective mass of an electron.[23] Since the oxygen ion in rutile is considerably polarizable,[24] lattice scattering by the optical mode of vibration as well as by the acoustical mode must be taken into account in a manner similar to that in the case of the mobility of hole carriers in Si or Ge.[25] The estimated value of m^* has been reported to be 10∼30 m,[26] where m is the mass of a free electron. Yahia has suggested that the large effective mass at room temperature is due to a small polaron mass.[27] The low mobility may arise from the large effective mass. It should be noted that the mobility is not influenced even by the reduction with hydrogen for a long time, though the reduction may produce the defect centers

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Table 1. Donor level, donor concentration, and Fermi level of rutile

Treatment (°C)	E_{d_b} (eV)	E_{d_s} (eV)	n_s a)		ζ_b b)		ζ_s b)	
			230 °C (cm^{-2})	400 °C (cm^{-2})	−196 °C (eV)	25 °C (eV)	−196 °C (eV)	25 °C (eV)
25	0.66	0.67	2×10^{12}	8×10^{13}	0.38—0.29	0.54—0.59	0.33—0.35	0.36—0.41
100	0.68	0.70	5×10^{12}	4×10^{13}	0.39—0.40	0.56—0.40	0.35—0.36	0.38—0.41
200	0.58	0.59	4×10^{13}	3×10^{14}	0.33—0.34	0.48—0.51	0.29—0.34	0.30—0.33
300	0.34	0.35	2.5×10^{14}	8×10^{14}	0.21	0.35—0.37	0.17	0.17—0.18
400	0.21	0.21	1.2×10^{15}	1.8×10^{15}	0.14	0.27—0.28	0.10	0.09—0.10
500	0.19	0.20	1.1×10^{16}	1.4×10^{16}	0.13	0.24	0.08	0.06
H_2(500)	0.07	0.07	9×10^{15}	1.2×10^{16}	0.07	0.18	0.02	0.00
O_2(500)	0.35	0.38	4×10^{12}	1.4×10^{13}	0.24	0.42—0.43	0.20	0.24

a) n_b is larger by 5 times than n_s.

b) Fermi levels ζ_b and ζ_s are estimated respectively from the following relations:

$$\zeta_b = \frac{1}{2}E_{d_b} - \frac{1}{2}kT\log\frac{2N_d}{N_0(T)(m^*/m)^{3/2}} \text{ and } \zeta_s = \frac{1}{2}E_{d_s} - \frac{1}{2}kT\log\frac{N_d}{4(m^*/m)[N_0(T)/2]^{2/3}}.$$

in bulk to a considerable extent. This implies that the mobility of the carrier electron in rutile is not affected by the lattice defect on the surface or in the bulk. Therefore, this may be due to a small mean free path of the carrier electrons compared with the scattering cross-section of such lattice defects as oxygen vacancies. When the mobility, μ, is known, the concentration of carrier electrons, n, can be estimated from the relation: $\sigma = en\mu$, where e is the electronic charge. When the Hall mobility is presumed to be equal to the true mobility and also to be independent of the treatments, it is revealed that the variation in the conductivity with the treatments *in vacuo* at temperatures between room temperature and 300 °C is caused mainly by the variation in the concentration of carriers, and that the reversion of the temperature coefficient of the conductivity for the case of the reduction by hydrogen as indicated in Fig. 4(b) is to be ascribed to a decrease in the mobility with an increase in the temperature. If the donor level is composed of a single level, the two-dimensional concentration of carrier electrons, n_s, and the three-dimensional one, n_b, in the temperature range studied can be given, respectively, by:

$$n_s = (m^*/m)^{1/2}N_{d_s}{}^{1/2}[N_0(T)/2]^{1/3}\exp(-E_{d_s}/2kT),$$

$$n_b = (m^*/m)^{3/4}[N_{d_b}N_0(T)/2]^{1/2}\exp(-E_{d_b}/2kT),$$

where:

$$N_0(T) = 2(2\pi mkT/h^2)^{3/2};$$

N_{d_s} and N_{d_b} are the two-dimensional and three-dimensional concentrations of donors respectively, and E_{d_s} and E_{d_b} are the two-dimensional and three-dimensional donor levels respectively. The values of N_{d_s} and E_{d_s} are obtained from the intercept and the slope of the relation between $n_s/T^{1/2}$ and $1/T$ respectively, and N_{d_b} and E_{d_b}, from those between $n_b/T^{3/4}$ and $1/T$. However, the donor concentration obtained from the intercept is overestimated, as has been revealed in ZnO.28) As the donor centers were not completely exhausted at room temperature, the concentrations of the donor at 230 °C and 400 °C were estimated by the extrapolation of the relation between n and $1/T$ to these two temperatures, because an intrinsic conductivity of rutile occurred above 600 °C.3a) The results are listed in Table 1. From the crystal structure of rutile, the number of titanium ions was calculated to be 3.2×10^{22}/cm^3. On the assumption that all the oxygen atoms were removed from the surface of the (110) plane, the amount of the released electrons was calculated to be 4.36×10^{15}/cm^2. It is clear from the table that the electrical conduction for the specimen evacuated at 500 °C occurs not only on the top layer of the surface, but also considerably beneath the surface. The table also contains the Fermi levels, whose values were calculated by estimating m^* to be 25 m.

Photoconductivity. The typical spectral responses of the photoconductivity of the rutile measured at room temperature and −196 °C are shown in Fig. 9. The maxima in the photoconductivity curves occurred at

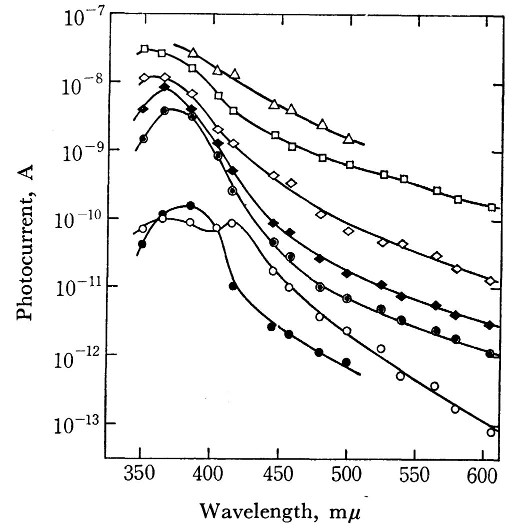

Fig. 9. Spectral responses of photoconductivity of rutile treated under several conditions at 25 and −196 °C. Treatment; ⊙: evacuation at 300 °C, −196 °C, ◇: evacuation at 400 °C, 25 °C, ◆: evacuation at 400 °C, −196 °C, □: evacuation at 500 °C, 25 °C, △: reduction by hydrogen at 500 °C for 2 min, 25°C, ○: oxidation at 500 °C for 2 min, 25 °C, and ●: oxidation at 500 °C for 2 min, −196 °C.

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the wavelengths between 350 and 400 mμ, which are near the fundamental absorption edge, as may be seen in Fig. 11. The photoconductivity increased as the out-gassing temperature rose from 300 to 500 °C. In particular, the photoconductivity in the wavelength region longer than the absorption edge increased when the rutile was reduced by hydrogen. This finding suggests that the large number of donors near the conduction band contribute to the photocurrent at the long wavelength. The rather sharper peak in the curve at −196 °C than that at room temperature may come from the more distinct band width of the forbidden gap, since most of the electrons are present in donor centers rather than in a conduction band at a low temperature. When the rutile was oxidized at 500 °C, a new maximum appeared at 415 mμ in the photoconductivity spectra at room temperature. This peak has also been observed for highly-oxidized rutile.[5,29] It may be presumed from the results of the conductivity measurements that donor levels are hardly present below the conduction band at the surface because of the formation of the depletion layer near the surface because of the presence of O^- or O_2^-. Therefore, this peak may be attributable to excitation from a level, such as O_2^- or O^-, near the valence band on the surface to the conduction band.

It is clear from Fig. 9 that the photocurrent of the rutile increases with an increase in the conductivity, *i.e.*, the dark current. The relationship between the photocurrent at 405 mμ and the dark current at room temperature is shown in Fig. 10. This implies that the population of electrons in the donor level on the surface may increase, since the accumulation layer becomes remarkable with a rise in the Fermi level on the surface. The photocurrents of both the specimen treated with hydrogen and that treated with oxygen decayed slowly when the illuminating light was cut off; This may be due to the existence of traps in the specimen treated with hydrogen and to the photodesorption of the adsorbed oxygen molecules from the specimen treated with oxygen.

Absorption Spectra. The absorption spectra of the rutile did not change upon the thermal treatment *in vacuo*, as is shown in Fig. 11. This finding is similar to that of Cronemeyer.[3a] The absorption edge shifted from 420 to 410 mμ as the temperature decreased from

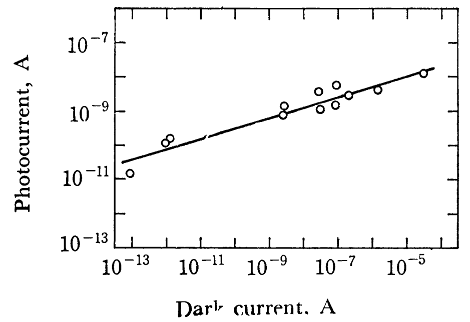

Fig. 10. Relation between the photocurrent at 405 mμ and the dark current at 25 °C.

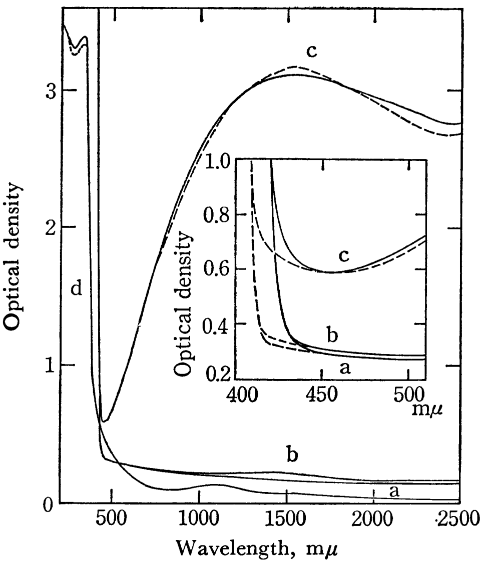

Fig. 11. Optical densities of a rutile single crystal and thin film treated under several conditions. Single crystal: (a) oxidation at 450 °C for 3 min, (b) reduction at 500 °C for 10 min, and (c) reduction at 500 °C for 3 hr. Thin film prepared by the oxidation of the evaporated film of titanium at 1100 °C: (d) oxidation and reduction at 500 °C. Full lines show the optical density measured at 25 °C and dotted lines at −133 °C.

room temperature to −133 °C. A broad absorption centered at 1.5 μ appeared upon the reduction with hydrogen and increased extremely remarkably with the reduction time, though the absorption edge did not change entirely. The absorption spectrum of a thin film of rutile showed maxima at 330 mμ and a slight peak at 1.1 μ. These peaks did not change with the temperature. The optical density near the band gap was not changed by the reduction, whereas the photoconductivity changed markedly.

It is clear from the results of the electrical conductivity and the photoconductivity that the electronic state near the surface of the rutile single crystal is changed remarkably by the contact with oxygen or hydrogen for a short time, while the electronic state in bulk is also changed. It has been considered that hydrogen atoms can diffuse into the bulk of rutile and act as donors.[7,30] However, the evacuation at a high temperature may remove the hydrogen atoms as in the case of ZnO.[31] The reversible change in the electrical conduction by the reduction-oxidation cycle indicates that oxygen atoms may be removed easily from the surface or bind to the surface even under the mild conditions studied. The change in the activation energy with the concentration of donors may be considered to depend on the position of the Fermi level in relation to the conduction band on the surface in addition to the effect of the interactions between donors.[3b] As oxygen atoms can not be removed below 300 °C, the increase in the electrical conductivity and

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29) K. Mizushima and S. Iida, *J. Phys. Soc. Jap.*, **31**, 950 (1971).

30) G. J. Hill, *J. Phys. D*, **1**, 1151 (1968).

31) G. Heiland, E. Mollow, and F. Stöckmann, "Solid State Physics," Vol. 8, ed. by F. Seitz and D. Turnball, Academic Press, New York, N. Y. (1959), p. 191.

photoconductivity when rutile is evacuated below that temperature suggests that the active oxo-structure produced by the condensation of hydroxyl groups on the surface can act as donors in the electrical conduction on the surface.

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