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The Photoconductivity of the Titanium Dioxide Crystal

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The photoconductivity of titanium dioxide (rutile type) synthesized by the flame-fusion method was studied. The photoconductivity spectra showed three peaks. The first is the maximum response around the edge of the fundamental absorption of rutile; the second is the peak at 630 mμ (1.98 eV), and the third is the broad-band spectra in the near infrared region of 1.0—1.9 μ. From the facts that Fe is found by chemical analysis to be a major impurity in rutile, that the peak at 630 mμ is enhanced by the increase in Fe concentration from 0.006 mol% to 0.02 mol%, and that the infrared quenching band of photoconductivity is observed at 1.23 μ (1.01 eV) in Fe-doped rutile, it is concluded that this peak at 630 mμ results from the excitation of the electron from the Fe^{3+} level. The broad-band spectra at 1.0—1.9 μ are enhanced by the reduction and are decreased by the oxidation of the crystal, so these excitation spectra are ascribed to lattice defects originating from the non-stoichiometry of TiO_2. These defects have much influence on the photoconductivity of rutile, *i. e.*, on the relation between the photocurrent and the electrical applied field, and on the change the photocurrent *versus* the time.

Titanium dioxide has a conduction band consisting of 2p orbitals of O^{2-}. In the case of rutile, the energy gap of the forbidden band is 3.01 eV—3.05 eV.[1] When titanium dioxide is exposed to the gap light of 420 mμ, it responds quickly to the irradiation with a considerable amount of photocurrent. It is generally considered that a material which has a d-conduction band cannot become a good photoconductor. The reason for this has not yet been clarified and the photoconductivity mechanism of the d-conduction band has not been studied in detail. In view of these points, the photoconductivity of titanium dioxide has many interesting problems. The photoconductivity of the rutile crystal was studied by Cronemeyer.[1] He reported that the photoconductivity spectra of rutile has a maximum response at a wavelength of around 400 mμ. However, he has not mentioned the detailed phenomena of photoconductivity of rutile. Therefore, we have studied the photoconductivity of titanium dioxide in detail, using a single crystal of rutile synthesized by the flame-fusion method. For this report we have studied the photoconductivity spectra for pure rutile, for Fe-doped rutile, and for slightly-reduced rutile, the relation between the photocurrent and the electrical applied field, the change in the photocurrent *versus* the time, and the infrared quenching of photoconductivity for Fe-doped rutile.

Experimental

The single crystal of titanium dioxide was synthesized by the flame-fusion method using highly purified titanium dioxide powder which had been made by firing ammonium-titanil-sulfate at 1000°C. The crystal structure and the direction of the *c*-axis were identified by X-ray deflection. The single crystal was chemically analyzed by spectral analysis. Original crystals grown in an oxyhydrogen flame did not have the stoichiometric composition. Therefore, the crystal was annealed in oxygen gas at 1000°C for 20 hr, and then cooled very slowly to room temperature. The resistivity of this rutile was around 10^{12} Ω cm. After the surface of single crystal plate had been polished with alumina powder to a mirror flatness, the electrodes were attached to this plate by the following procedures. Two parallel zones of silver paste, separated by 5 mm, were painted on one side of the plate, and the sample was heated at 500°C for one hour. Then silver was slightly diffused on the crystal surface, and the electrodes were fixed securely on the surface.

The photoconductivity was measured by the following methods: the sample was mounted on a copper block with silver paste and fixed on the measurement cell. After the air in the cell had been evacuated, the copper block was cooled with liquid nitrogen. The sample was exposed through a quartz window to the monochromic light produced by a monochromator of Carl Zeis, using a 500-W tungsten lamp as the light source. An electric field of 6×10^2 V/cm was applied to the sample, and the photocurrent was measured with an electrometer of the Keithley 610 B type. The infrared quenching spectra of the photoconductivity were measured by the double-beam method; that is, the first excitation light of 400 mμ, which was made by using an interference filter of VV-40 (this filter transmits between 350 mμ and 450 mμ), and the second excitation light of infrared, made by the monochromator, were irradiated on the sample simultaneously, and then the quenching of the photocurrent was measured.

1) D. C. Cronemeyer, *Phys. Rev.*, **87**, 876 (1952).

Results

The general photoconductivity spectra of the rutile crystal are shown in Fig. 1. The maximum of the response is located at the wavelength of 420 mμ at 300°K, but it shifts to 410 mμ at 77°K. The small peak at 630 mμ is observed at any temperature and always has a good reproducibility. The broad response spectrum is observed in the near infrared region of 1.0—1.9 μ at 77°K, but this peak greatly decreases with the increase in the temperature.

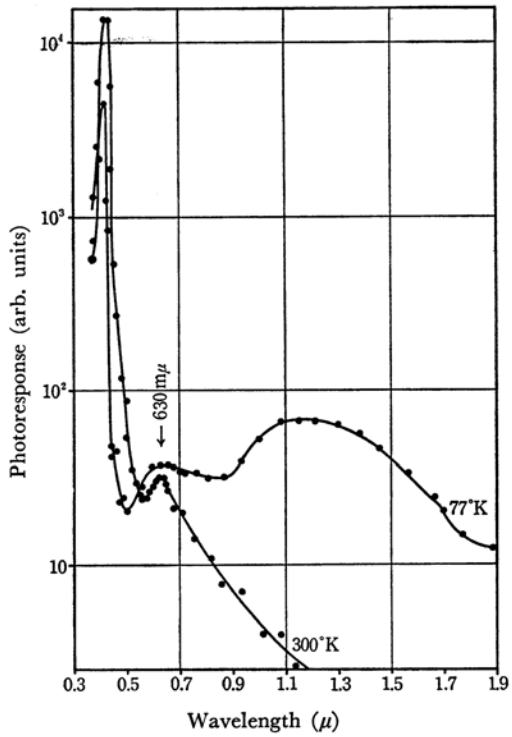

Fig. 1. Photoconductivity spectra for a rutile synthesized by the flame-fusion method.

Chemical analysis of the sample showed that the iron impurity is the major impurity; aluminium, nickel and cobalt are not detected. Therefore, we produced a single crystal doped with 0.02 mol% of iron and measured the photoconductivity spectra. As is shown in Fig. 2, in this sample the peak at 630 mμ is observed clearly, and it is enhanced by the increase in Fe concentration from 0.006 mol% to 0.02 mol%. The broad excitation spectra at 1.0—1.9 μ also appear in the Fe-doped sample, and it can be noticed that the dependence of these broad spectra on the temperature is same as in the case of undoped rutile.

If the rutile crystal is heated at 400°C under the reduced air pressure of 10^{-2} mmHg, the broad response spectra at 1.0—1.9 μ are greatly enhanced. The photoconductivity spectra of slightly-reduced

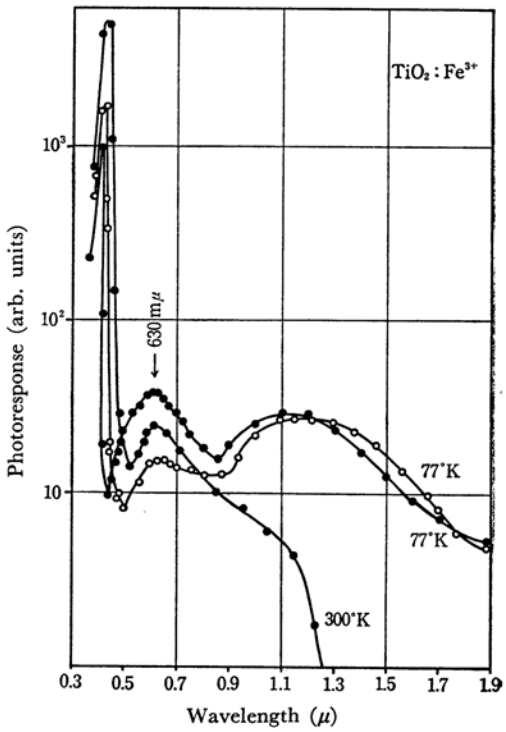

Fig. 2. Photoconductivity spectra for TiO_2 : Fe.
—○—○— TiO_2 : Fe (0.006 mol%)
—●—●— TiO_2 : Fe (0.02 mol%)

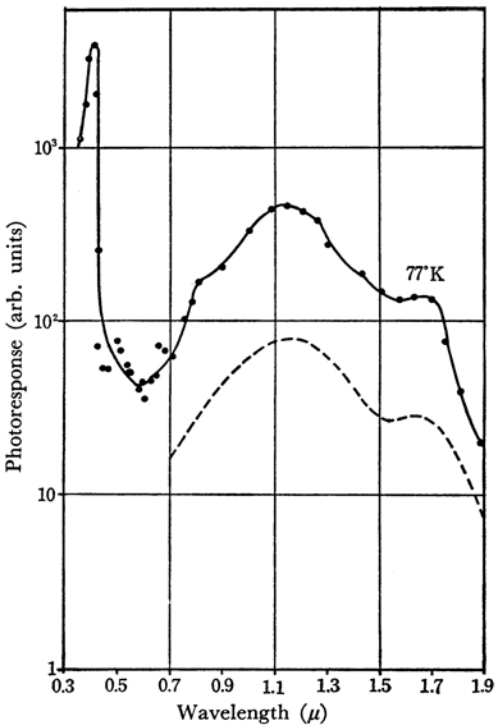

Fig. 3. Photoconductivity spectra for the reduced rutile. The dotted line represents the infrared absorption spectra of the reduced rutile which were reported by Cronemeyer.[2]

rutile, the resistivity of which is around $10^7\ \Omega$ cm, are shown in Fig. 3. It can be noticed that two peaks are found in the broad excitation spectra. One is at 1.2 μ, and the other is at 1.7 μ. The dotted line represents the infrared absorption spectra of reduced rutile measured by Cronemeyer.[2] From these curves it can be recognized that these two peaks, at 1.2 μ and at 1.7 μ, coincide with two peaks of the infrared absorption spectra.

The photocurrent dependencies of rutiles on electrical fields are shown in Fig. 4, using the light of

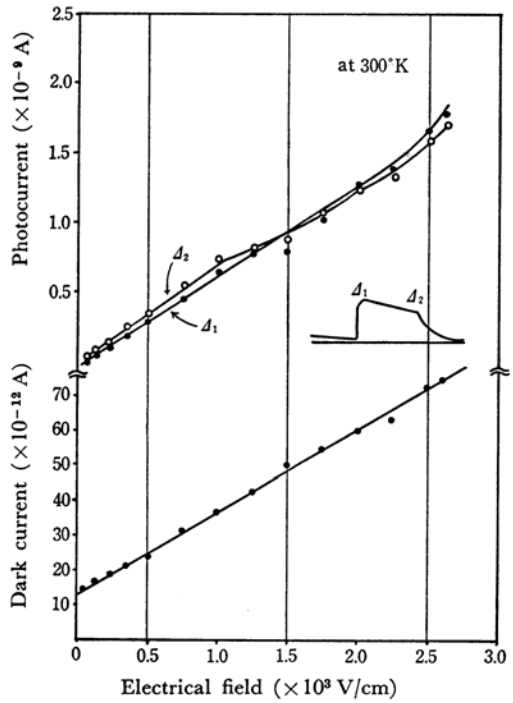

Fig. 4. Photocurrent and dark current dependencies on the electrical field. The notations of Δ_1 and Δ_2 mean the photocurrent measured two seconds and ten seconds respectively after the turn-on of the excitation light.

410 mμ as the excitation beam. The photocurrent increases proportionally to the applied field up to the field strength of 2×10^3 V/cm. The notations Δ_1 and Δ_2 represent the photocurrent measured two seconds and ten seconds respectively after the turn on of the excitation light. The saturation of the photocurrent does not appear even at the field of 2.6×10^3 V/cm. On the contrary, the dark current is exactly proportional to the applied field.

The changes in the photocurrent of a rutile with the time are shown in Fig. 5. As can be seen from the figure, the photocurrent increases rapidly with the time at first, and then it gradually saturates. If these excitations are repeated several times, the

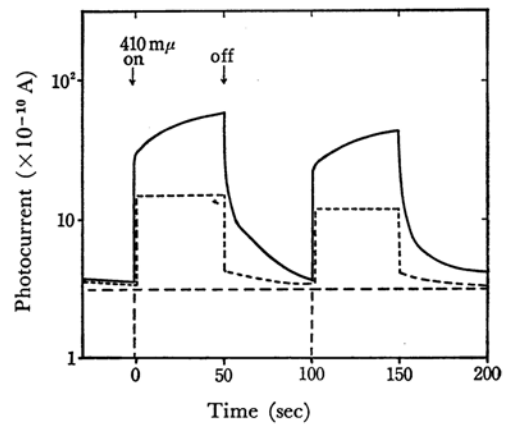

Fig. 5. The change in the photocurrent *versus* the time. The dotted line represents the change in the Fe-doped rutile.

absolute value of the photocurrent decreases gradually. In the case of an Fe-doped rutile, the shape of the photocurrent rather resembles that of the rectangular wave.

In Fig. 6, the infrared quenching spectrum of the photoconductivity of an Fe-doped rutile measured at 77°K by the double-beam method is shown. The infrared quenching band due to the hole trapped at the Fe impurity is observed at 1.23 μ. The dotted line represents the case of pure rutile. This spectrum does not have a quenching band. The degree of infrared quenching is represented by the notation of δ, which is an arbitrary statement of the difference between the full line and the dotted line.

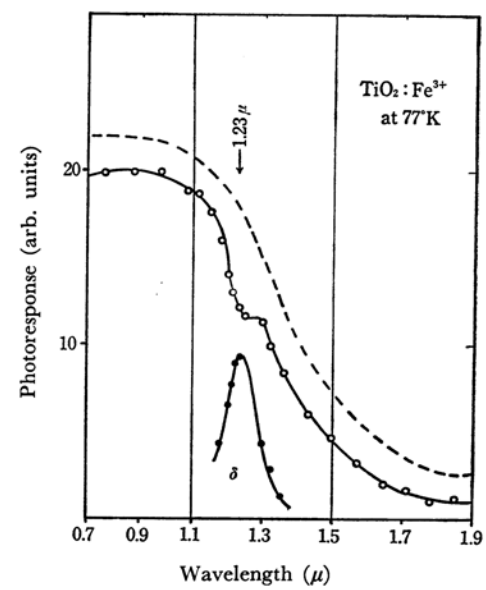

Fig. 6. Infrared quenching spectrum of the photoconductivity for the Fe-doped rutile measured at 77°K.

2) D. C. Cronemeyer, *Phys. Rev.*, **113**, 1222 (1959).

Discussion

The analysis of the conduction mechanism of 3d band is quite complicated because the character of the 3d conduction band has not yet been clarified. Generally speaking, most compounds which are composed of transition elements do not have a photoconductivity. Titanium dioxide has the 3d conduction band of Ti^{3+}, but it has a good response to photoconductivity. This means that the 3d conduction band does not hinder the photoconductivity and that an excited electron can move considerably freely in the 3d conduction band. As a matter of fact, the single crystal produced by the flame-fusion method has many imperfections in its lattice, such as oxygen vacancies[3,4] and interstitial Ti^{3+} ions.[5] These centers become traps or recombination centers, and they have rather more influence on the photoconductivity of titanium dioxide than does the 3d conduction band.

The photoconductivity spectra have three peaks, between 300 mμ and 2.0 μ, as shown in Fig. 1. The first maximum, around 410 mμ, is referred to the edge of the fundamental absorption of rutile, the second small peak, at 630 mμ, has been little influenced by the temperature, while the third peak, at 1.0—1.9 μ, decreases considerably if the temperature increases to 300°K. These latter two maxima may be ascribed to lattice defects in the rutile crystal. Here let us consider what kind of lattice defects exist in the rutile.

It may be said, from Fig. 2, that the peak at 630 mμ results from the excitation of the electron from the Fe impurity to the conduction band of rutile. As a matter of fact, it is very difficult to make a single crystal of rutile containing less than 0.0001 mol% of an iron impurity. Therefore, it can be understood that all the photoconductivity spectra of a single crystal synthesized by the flame-fusion method have a peak of Fe impurity at 630 mμ, and that this impurity acts as a recombination center for the electron and the hole. The ESR measurement for the Fe-doped rutile has been performed by Carter and Okaya.[6] From their ESR results it is clear that Fe occupies the Ti site as a trivalent ion. The ground state of the free Fe^{3+} ion is ^6S. The crystal field of the Ti site is the rhombic field of D_{2h},[7] and the state of ^6S splits into three levels in this crystal field.[8] We can say, from the results of photoconductivity spectra, that the ground state of the Fe impurity lies 1.98 eV (630 mμ) below the conduction band.

From the facts that the broad excitation spectra at 1.0—1.9 μ are enhanced by the reduction and are decreased by the annealment of the crystal in oxygen gas, it may be said that these spectra are due to the lattice defects caused by oxygen deficiency in the rutile crystal. The two peaks, at 1.2 μ and 1.7 μ, ofslightly-reduced rutile coincide with the two peaks of the infrared absorption of reduced rutile as measured by Cronemeyer.[2] He has explained that these two peaks correspond to the ionization energy of two electrons captured by the oxygen vacancy. On the other hand, the measurement of ESR for reduced rutile was performed by Chester,[4] Yamaka[7] and Date,[9] and they concluded that the ESR signal at the g-value of 1.98 is the signal of the interstitial Ti^{3+} ion. Considering these results, we cannot easily deduce defect models with reference to these spectra. The only thing we can say is that the single crystal synthesized by the flame-fusion method has many defects caused by the nonstoichiometry of TiO_2, and that these defects are excited by the light at 1.0—1.9 μ.

Therefore, it is expected that these defects should have much influence on the photoconductivity of rutile. The facts that the photocurrent depends linearly on the electrical field applied up to 1.0×10^3 V/cm, while over that the linear proportionality is not maintained, and the fact that the saturation of the photocurrent at a certain applied field is not observed are general tendencies of a semiconductor which has shallow traps; these facts can be interpreted by saying that the photocurrent observed is due not only to the initial photocurrent but also to the secondary photocurrent caused by the shallow traps.

On the other hand, the linearity of the dark current *versus* the applied field shown in Fig. 4 ensures us a good ohmic contact between the sample and the silver electrodes.

The change of the photocurrent of the rutile *versus* the time, shown in Fig. 5, may be interpreted as follows. The first rise in the photocurrent corresponds to the initial photocurrent, while the next gradual rising process is to be ascribed to the secondary photocurrent resulting from the effect of shallow traps. It the curve of the photocurrent of the Fe-doped rutile *versus* the time (Fig. 5), the effect of the secondary photocurrent does not appear. As we have mentioned above, Fe acts as a recombination center. It might be said that Fe has so large a capture cross-section for the electron and the hole that the effect of shallow traps is very small in the process of the photoconductivity in the Fe-doped rutile.

The impurity center of Fe can also capture a free

3) R. Hashiguti, *J. Phys. Soc. Japan*, **16**, 2223 (1961).
4) H. J. Becker and W. R. Hosler, *ibid.*, **18**, 152 (1963).
5) P. E. Chester, *J. Appl. Phys.*, **32**, 866 (1951).
6) D. L. Carter and A. Okaya, *Phys. Rev.*, **118**, 1458 (1960).
7) E. Yamaka and R. G. Barnes, *ibid.*, **135**, A. 144 (1964).
8) D. L. Carter, *J. Appl. Phys.*, **32**, 2541 (1961).
9) M. Date, *Bussei*, **1**, 22 (1960).

hole from the valence band. If this Fe is excited by the irradiation of the infrared region, the hole captured in Fe is excited to the valence band and it recombines with a free electron in the conduction band, thereby decreasing the photoconductivity. This phenomenon is called the infrared quenching of the photoconductivity. As is shown in Fig. 6, the infrared quenching band appears at 1.23 μ (1.01 eV) in rutile doped with 0.02 mol% of Fe. Therefore, we can find that the energy difference between the impurity level of Fe and the valence band is 1.01 eV. This value agrees with the result obtained from the photoconductivity spectra shown in the second figure.