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PHOTOVOLTAIC EFFECT ON THE SURFACE OF RUTILE SINGLE CRYSTAL

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The photovoltaic effect on the surface of rutile single crystal was studied at room temperature through producing the inhomogeneous distribution of oxygen vacancies by application of electric field at high temperatures. It was found from the photovoltage and the resistance that the barrier height near the positive electrode increases linearly with the applied voltage.

The photovoltaic effects of titanium dioxide have been studied on the barrier layers formed by the Schottky contact between the oxidized rutile single crystal and silver,1) on the anodic oxide films of titanium,2) and on the rutile electrode-electrolyte interface.3) In the present work, the photovoltaic effect of a rutile single crystal was observed on the surface with the inhomogeneous distribution of oxygen vacancies produced in the dc electric field at high temperatures.

The dimension of the rutile single crystal was $10 \times 10 \times 2$ mm^3. Gold was evaporated as electrodes onto the (110) plane so as to measure the electric behavior along the c-axis in the similar manner reported elsewhere.4) The distance between the electrodes was 7 mm. The sample connected with electrodes was set in a cell, followed by evacuation at 500°C and 10^{-5} Torr for three or four hours, and then dc voltage was applied to it at temperatures between 200° and 400°C for 2 hr. The voltage was varied from 1 to 10 V. The photovoltage was measured at room temperature in vacuo by using a high impedance electrometer after removing the dc bias. A halogen lamp and interference filters were used as a source of the illuminating light. Neither photovoltage nor rectifying action was observed when the electrodes were grounded at high temperatures.

The photovoltage was found to show spparently the same polarity as that of the potential which was applied to electrodes during the treatment and to be proportional directly to the intensity of the illuminating light. The spectral responses of the photovoltages of the rutile single crystal are shown in Fig. 1, where the applied dc voltage was 1.36 V. Each photovoltaic reponse showed a maximum at around 435 nm which corresponds to the band gap of rutile. This maximum was located at longer wavelength than that in the photoconductivity spectrum.[4] The photovoltage at the maximum increased with an increase in the treatment temperature. When a rutile single crystal is outgassed at temperatures around 500°C, oxygen vacancies rather than interstitial titanium ions are produced mostly on the surface.[4] These oxygen vacancies, which serve as donors, are ionized positively since the electrons present in vacancies are raised to the conduction band at high temperatures. Thus, the dc electric field may enable these oxygen vacancies to move toward the negative electrode.[5,6] Moreover, the diffusion coefficient of oxygen in the direction parallel to the c-axis is larger by several orders than that perpendicular to it.[7] Thus, the stronger the electric field and the higher the temperature, the greater may be the velocity of the oxygen vacancies along the c-axis on the surface.

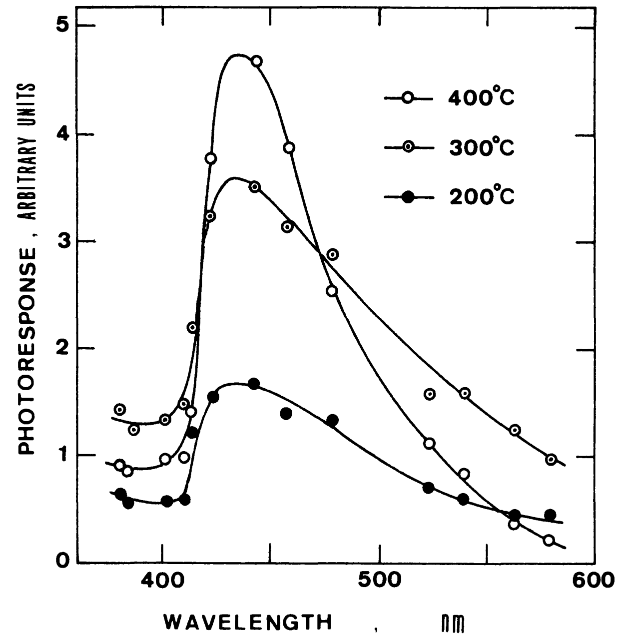

Fig. 1. Spectral responses of photovoltage of the rutile single crystal treated at several temperatures.

The photovoltaic responses at 425 and 525 nm are shown in Fig. 2 as a function of the voltage applied at 400°C. The rectifying action arose and developed remarkably as the applied voltage increased above 2.5 V. In the figure is also given the zero voltage resistance, R, obtained from the linear part of the current-voltage characteristic at low voltage.

From measurement of the voltage distribution on the surface of the rutile, it was found that a large voltage drop arose near the electrode to which the positive pole had been applied during the treatment. This may be caused by the accumulation of oxygen anions near the electrode as a result of the migration of the positively charged oxygen vacancies toward another electrode. Thus, the rutile surface near the positive electrode becomes stoichiometric composition, resulting in lowering the Fermi level. The inhomogeneous distribution of the oxygen vacancies causes a variation in the Fermi level which may create an electric field.[8] This difference in the Fermi level is considered to function in a similar manner as the potential barrier of height, V_d, in the general rectifying action, where V_d arises from the formation of space charge layer. Based on the assumption that the energy surface is spherical and that the donor level is composed of single level, the difference in the Fermi level between the region near the electrode and the main one can be expressed as follows:

$$V_d = (1/2)kT\ln(N_o/N_d) - (1/2)(E_d-E_o) = kT\ln(n_o/n_d) = kT\ln(R/R_o) \qquad (1)$$

where N is the concentration of oxygen vacancies, E the donor level measured from the bottom of the conduction band, n the concentration of free electrons, and the subscripts o and d represent each quantity before and after the formation of the barrier, respectively. If the barrier region is assumed to be 1 μ, R_o is calculated from the overall resistance to be 10^2 Ω.

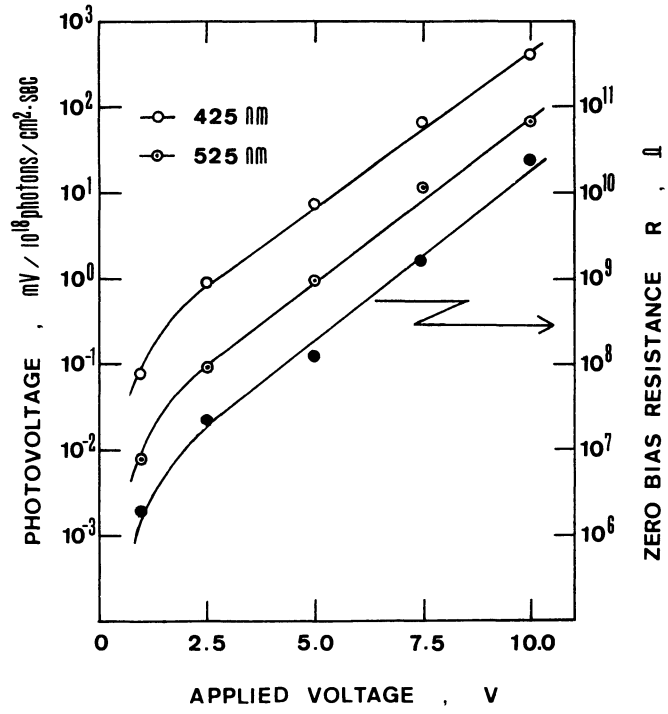

Fig. 2. Photovoltage and zero bias resistance of the rutile treated at 400°C as a function of the applied voltage.

When the intensity of the illuminating light is low, the photovoltage can be given as the product of R and the short circuit current which is the functions of hole-electron pairs generated, the diffusion length, and the width of the barrier layers.[9] As is seen in Fig. 2, it is worth noting that a linear relationship holds between the photovoltage and R, demonstrating the independence of the photocurrent on the applied voltage. Then, the electric power of the photovoltaic cell increases with an increase in the applied voltage.

It is evident from Fig. 2 and Eq. (1) that the barrier height is a linear function of the applied voltage when $R \gg R_0$. It should be noted, therefore, that the applied dc voltage makes the oxygen vacancies move toward the negative electrode, resulting in the formation of a potential barrier, the height of which increases linearly with the applied potential. On the contrary, information about the movement of the oxygen vacancies may be obtained from the measurement of the photovoltaic effect.

This barrier layer was considerably stable and disappeared only when the rutile was treated under grounding two electrodes at a high temperature, for example, for several hours at 400°C. The sample reduced strongly by hydrogen at 500°C showed a smaller photovoltage than that treated in vacuo, since a large excess of oxygen vacancies reduces the resistance and, in addition, the variation in the concentration of these oxygen vacancies near the electrode. These phenomena may also occur in other oxide semiconductors with a considerably ionic character.

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