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Sub-band-gap photoresponse of TiO_{2-x} thin-film—electrolyte interface

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When a TiO_{2-x} thin-film—electrolyte interface is illuminated by the monochromatic light in the sub-band-gap region, broad photocurrent peaks are observed at 462, 515, 1050, and 1258 nm. The energies of these peaks are in good agreement with the energies of defect levels of the TiO_2 single crystal due to oxygen vacancies. From these experimental results, the photoresponse of the TiO_{2-x} thin-film—electrolyte interface in the sub-band-gap region is interpreted as arising from electronic excitations between the trap levels which originate from the defects of the TiO_{2-x} thin film and the conduction band.

I. INTRODUCTION

The photoresponses of the titanium-oxide—electrolyte interface in the sub-band-gap region with the TiO_2 single crystal,[1–3] TiO_{2-x} thin film,[4] and TiO_2 ceramic[5] as photoanodes can be observed with monochromatic light of energy lower than the energy gap of TiO_2 ($E_g > h\nu$). The photocurrent peaks of the photoresponse in the sub-band-gap region reported until now are in the regions of 1260,[6] 980,[6] 800,[1] 750,[7] 650,[4] 589,[8] and 490 nm.[8] The generation mechanism of these photocurrent peaks has been explained by the electron transfer between the surface state and the band edge of TiO_2 (Ref. 4) or by the photothermal effect.[9]

From the measurement of the time constant of the photocurrent peaks in 589 and 490 nm, the author previously suggested that the photoresponse in the sub-band-gap region is caused by the electron transfer from the sub-band-gap state to the conduction-band edge rather than by the photothermal effect. But it is not clear how the electron transfer occurs from the sub-band-gap state to the conduction-band edge of TiO_{2-x} thin films.

In this report it is suggested that the sub-band-gap photoresponse in the TiO_{2-x} thin-film—electrolyte interface is generated by the electron transfer between the trap levels, which originates from the oxygen vacancies of the TiO_{2-x} thin film and the conduction band.

II. EXPERIMENTAL

The TiO_{2-x} thin-film photoanodes were prepared by the following procedures:[8] The titanium sheets (K-5330B, 99.9%, $3\times4\times0.05$ cm^3) from Electronic Space Product Inc. were mechanically polished, cleaned with detergent water in an ultrasonic cleaner, rinsed with detergent water, and then dried. The TiO_{2-x} thin film was grown by oxidizing the sheets in an electric furnace: Air in the furnace was purged with steam at 150 °C and the temperature of the furnace was gradually raised to 600 °C in 20 min and kept constant for 1 h. They were removed from the furnace quickly and then cooled to room temperature.

The x-ray diffraction pattern of the TiO_{2-x} thin film indicates that the oxide film is mainly composed of rutile with some anatase and brookite together with Ti_2O_3. The thickness of the TiO_{2-x} thin film measured by optical reflection method is approximately 210 nm. The film has the electrical resistivity of 10 Ω cm, and its conductivity type is *n* type. The TiO_{2-x} thin-film—electrolyte interface consists of a TiO_{2-x} thin-film photoanode, platinum electrode, saturated calomel electrode (SCE), 1*M* NaOH (pH, 13.2).

The lights from a 150-W Xe arc lamp and a 1-kW tungsten lamp were passed through the high-intensity grating monochromator (Bausch & Lomb, $f=25$ cm, Nos. 338676 and 338677) and illuminated to the TiO_{2-x} thin film. For the measurement of the photocurrent peaks in the $450 < \lambda < 650$ nm region, the monochromatic light was passed through the pure TiO_2 single-crystal plate of 2-mm thickness and a Corning No. 3-71(3385) glass filter in order to eliminate the ultraviolet harmonics, and for the peaks in the $650 < \lambda < 1400$ nm region, the filter was replaced by a Corning No. 2-59(2404) glass filter and Irtran filter (pure CdTe single-crystal plate, 1.5-mm thick) in order to eliminate the ultraviolet harmonics and the harmonics in (450—650)-nm region. Short-circuit photocurrent between the TiO_{2-x} thin-film photoanode and platinum cathode was measured with an electrometer (Keithly, model No. 610C).

III. RESULTS

A. Short-circuit photocurrent response

When the monochromatic light of sub-band-gap region was illuminated into the TiO_{2-x} thin-film—electrolyte interface, the photocurrent peaks of 465, 510, 585, 748, 1030, and 1262 nm observed in the $400 < \lambda < 1400$ nm region are shown in Fig. 1. These photocurrent peaks, except that of 510 nm, correspond to the previously reported peaks which are attributed to the sub-band-gap, but the small peak of 510 nm is not yet reported in pure samples.

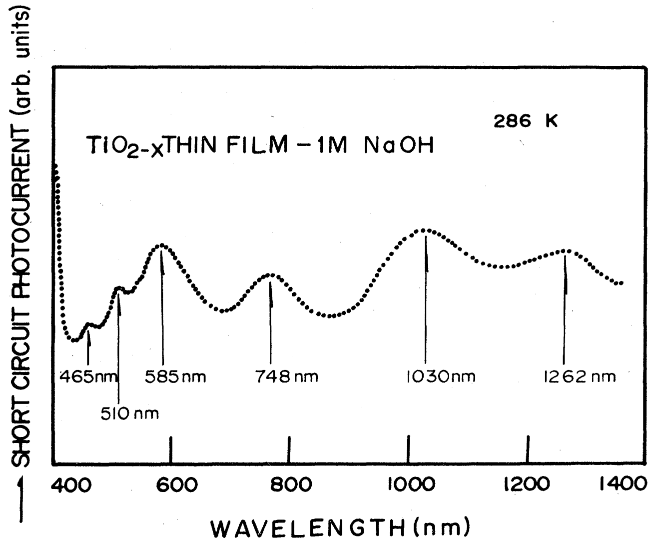

FIG. 1. Short-circuit photovoltaic response of TiO_{2-x} thin-film—1*M*-NaOH interface ($400 < \lambda < 1400$ nm).

B. Flat-band potential by the photocurrent method

The current-voltage characteristic of TiO_{2-x} thin-film—electrolyte interface with illumination of light of 310 nm to the TiO_{2-x} thin-film photoanode is shown in Fig. 2. The photocurrent increases sharply when the potential of the TiO_{2-x} thin-film photoanode is near -0.76 V (versus SCE).

In Fig. 3 the square of the photocurrent of Fig. 2 is plotted with the potential of the photoanode as the *x* axis. From the equation[10]

$$(J_p)^2 \sim \left[V - V_d - \frac{kT}{q} \right] , \tag{1}$$

the flat-band potential at 286 K is given to be -0.79 V (versus SCE), where J_p is the flowing photocurrent in TiO_{2-x} thin-film photoanode, V is the applied potential to the photoanode, V_d is the flat-band potential of the photoanode, q is the charge of an electron, k is the Boltzmann constant, and T is the ambient temperature.

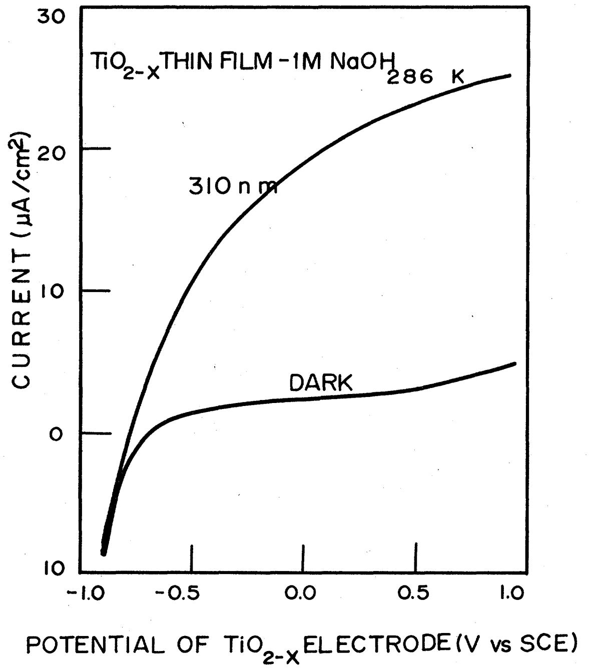

FIG. 2. Current-voltage characteristics of TiO_{2-x} thin-film—1*M*-NaOH interface.

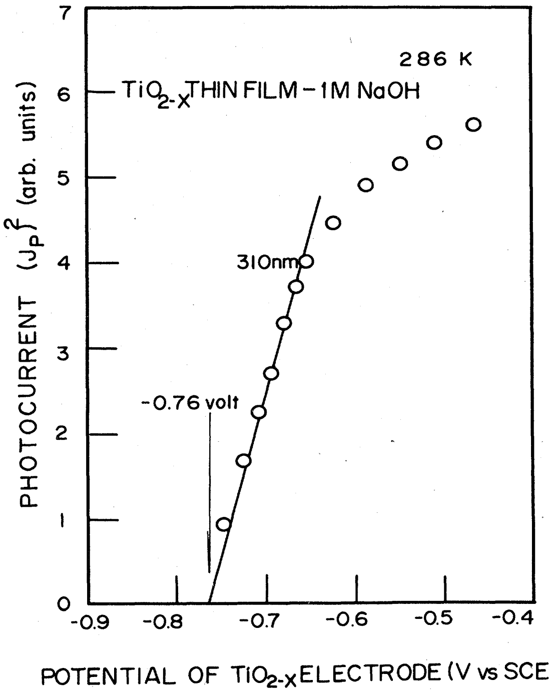

FIG. 3. Square of the photocurrent versus applied potential [vs saturated Calomel electrode (SCE)].

IV. DISCUSSION

TiO_{2-x} thin film has many trap levels because of the oxygen vacancies from nonstoichiometric defects inside the TiO_{2-x} thin film. These trap levels of TiO_{2-x} thin film might have the same optical properties as the trap levels of TiO_2 single crystal have. As is shown in Fig. 4, the photocurrent peaks of Fig. 1 are in agreement with the results of optical absorption,[11,12] photoconductivity, luminescence,[13] of the reduced TiO_2 single crystal, which were reported previously. From Fig. 4 the photocurrent peaks of the TiO_{2-x} thin-film—electrolyte interface can be separated into E_1, E_2, and E_3 groups.

A. S_{E_1} structure

The photocurrent peaks of S_{E_1} structure of the TiO_{2-x} thin-film—electrolyte interface are at 1262 and 1030 nm. The former corresponds to the strong optical absorption

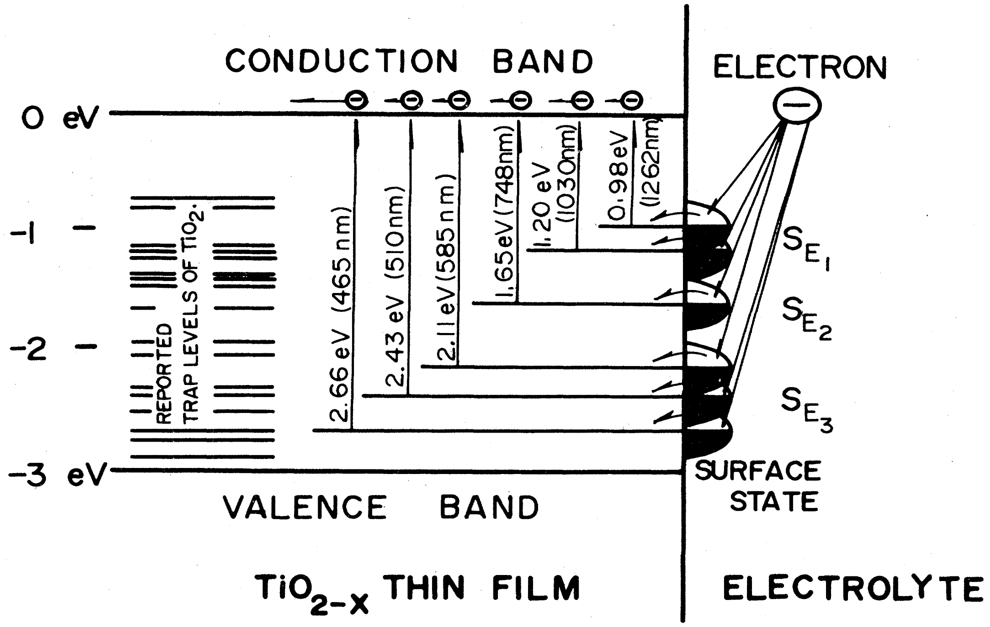

FIG. 4. Structure of the surface state and photocurrent peaks of TiO_{2-x} thin-film—electrolyte interface and the previously reported trap levels (Refs. 13 and 14) in TiO_2 single crystal.

band at 1500 nm while the latter corresponds to the donor level of the TiO_2 single crystal,[11,12] which lies 1.18 eV below the conduction band of the TiO_2 single crystal.

B. S_{E_2} structure

The peak of the S_{E_2} structure is at 748 nm and corresponds to the optical-absorption peak of the TiO_2 single crystal at 744 nm.[14] This photocurrent peak is observed with the titanium sheet oxidized under steam but not with that oxidized under air.

C. S_{E_3} structure

The photocurrent peaks of S_{E_3} structure are at 585, 510, and 465 nm. The peak at 585 nm corresponds to the optical-absorption band of the TiO_2 single crystal at 600 nm,[14] which is due to the oxygen vacancy. The peaks at 510 and 465 nm correspond to the optical ionization energy of the TiO_2 single crystal at 2.33 eV (530 nm) and 2.75 eV (450 nm),[13] respectively.

S_{E_3} structure of photocurrent peak corresponds to the E_1 and E_2 states which are obtained from photocurrent peaks in the undoped crystal of TiO_2.[15] Mizushima *et al.*[15] reported that the E_1 state seems to be the surface state in the photoelectrolysis of water and the E_2 state is due to the native defects in the bulk serving as the cation-vacancy acceptor state. But our experimental result shows that the E_2 state is also the surface state.

V. CONCLUSION

The photocurrent peaks of the TiO_{2-x} thin-film—electrolyte interface are observed with illumination of the monochromatic light of the sub-band-gap region and divided into S_{E_1}, S_{E_2}, and S_{E_3} states. These peaks are in good agreement with the results of optical absorption, photoconductivity, and luminescence, which are attributed to the oxygen vacancies of the bulk TiO_2 single crystal.

From these experimental results, it is found that the photoresponse in the sub-band-gap region is dependent on the trap level of the TiO_{2-x} thin film and the generation mechanism of photocurrent peaks are explained as follows.

The surface states shown in Fig. 4 are generated from the TiO_{2-x} thin-film—electrolyte interface and supplied electrons from the electrolyte, and transfer electrons to the trap levels. The trapped electrons are excited to the conduction band of the TiO_{2-x} thin film by the absorption of monochromatic light, and the repeated circulation of this process generates continuous flow of the photocurrent.

The generation mechanism of photoresponse in this sub-band-gap region explains that the photocurrent in sub-band-gap region depends linearly on the intensity of illuminated light and the degree of reduced TiO_2 crystal. And from the experimental result[6] that the photocurrent is independent of the supported electrolyte or the variation in pH and from the experiment[16] in TiO_2—electrolyte interface, we can conclude that this generation mechanism of sub-band-gap photoresponse is valid.

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