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Photoelectrochemical Reactions at $SrTiO_3$ Single Crystal Electrode

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Electrode characteristics of strontium titanate ($SrTiO_3$) single crystal have been investigated under illumination with light of its intrinsic absorption region. It has been found that the photosensitized electrolytic oxidation of water, known heretofore uniquely on the TiO_2 electrode, can proceed also at the $SrTiO_3$ electrode whose anodic dissolution being negligible. Although the photosensitivity of the $SrTiO_3$ electrode is confined to a little shorter wavelength region than that of the TiO_2 electrode, the formal quantum efficiency of the photosensitized electrolytic oxidation of water is comparable for these two semiconductor electrodes under intrinsic absorption. In contrast to the case of the TiO_2 electrode, the electrochemical photocell consisted of the $SrTiO_3$ anode and platinum cathode can work efficiently even when the pH values of the anodic and cathodic compartments are close to each other. This point is discussed in terms of the flatband potential of these semiconductor electrodes.

We previously reported on the photosensitized electrolytic oxidation of water at the TiO_2 (n-type semiconductor) single crystal electrode,[1,2)] and its utilization in an electrochemical photocell[3,4)] where water is decomposed to hydrogen and oxygen gases through the light absorption by the electrode. However, no other semiconductor electrodes of this type have ever been reported so far.

Boddy and co-workers[5,6)] studied the electrode characteristics of oxide semiconductors such as TiO_2, $KTaO_3$, Ta_2O_5 and $SrTiO_3$ without intended irradiation of the electrode surface. They noted oxygen evolution at the surface of these electrodes under strong anodic polarization, and elucidated this phenomenon on the basis of a tunneling of electrons from the surface oxide ions to the conduction band of the electrode. Since no evidence for the dissolution of the electrode surface was observed, they concluded that the surface oxide ions were supplied by water molecules. Provided that the electrode surface remains stable also at the excited state, the photosensitized electrolytic oxidation is expected to occur on these oxide semiconductor electrodes. However, the photoeffects on these electrodes, excluding TiO_2, have not been investigated in detail.

In the present study we carried out quantitative measurements of electrode characteristics of the $SrTiO_3$ single crystal under illumination with light of its intrinsic absorption range ($\lambda<390$ nm), and verified that the photosensitized electrolytic oxidation of water by surface holes does proceed effectively at the $SrTiO_3$ electrode.

Experimental

Electrode Preparation. Single crystals of $SrTiO_3$ were supplied by Fuji Titanium Industry, Ltd. The crystal was in the form of a platelet of 2.5 cm^2 in surface area and 1.0 mm in thickness. Prior to the preparation of the electrode, the crystal was treated at 600 °C under high vacuum (*ca.* 10^{-3} Torr) for several hours in order to increase the electric conductivity. After this treatment the crystal is colored in blue owing presumably to the formation of oxygen vacancies in the bulk of the crystal and the specific resistivity is found to be around 10^3 ohm·cm. The crystal was cemented with an epoxy resin in such a way that the (001) face of the crystal (perovskite-type) was exposed to the electrolyte solution. The opposite face was used for a barrier-free electrical contact with a conducting wire by means of electroplated indium. Before the measurements, the surface of the electrode thus prepared was polished with an alumina powder, washed with nitric acid and then with de-ionized water. A platinized platinum plate, having the apparent surface area of 10 cm^2, was employed as the counter electrode.

Experimental Setup. Figure 1 schematically shows the apparatus for photocurrent measurements. A 500 watt xenon lamp served as a light source. The wavelength of the illuminating light was selected by means of appropriate colored glass filters (Toshiba Kasei, Ltd.) or a monochromator (Shimadzu, Ltd.). The electrode-electrolyte interface was illuminated through a quartz window attached to the electrolytic cell. Photocurrents were detected by means of a potentiogalvanostat Type HA-101 of Hokuto Denko, Ltd.

The number of photons of the monochromatic light incident to the $SrTiO_3$ electrode surface was determined by the following procedure. (i) First, an exact number of photons at $\lambda=365$ nm was measured by means of chemical actinometry with 0.006 M potassium ferrioxalate aqueous solution, where the light leaving the monochromator was totally absorbed by the actinometer solution. (ii) Second, light energy was measured (in erg/s) at the same geometrical position as (i) in the wavelength range 350—600 nm by means of a JASCO thermopile, where 1 mm^2 of Au black absorbed the incident monochromatic light. Finally, the number of photons calculated from the results of (ii) was corrected on the basis of the results of (i). At the time of photocurrent measurements, the light flux reaching the surface of the $SrTiO_3$ electrode was the same as that incident to the actinometer cell.

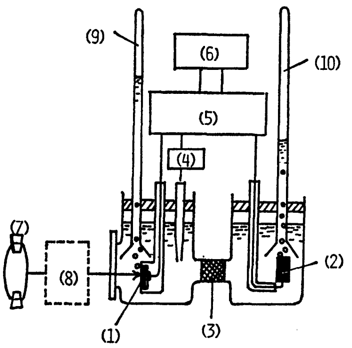

Fig. 1. Experimental setup.
(1) $SrTiO_3$ electrode (2) Platinum electrode (3) Agar salt bridge (4) SCE (5) Potentiostat (6) Recorder (7) Light source (8) Monochromator (9) Oxygen (10) Hydrogen.

Results and Discussion

Static Electrode Characteristics. The flatband potential of the $SrTiO_3$ single crystal electrode has been measured as a function of pH of the electrolyte solution. The determination of the flatband potential of an n-type semiconductor electrode is based on the application of the Mott-Schottky relationship[7)]

$$\frac{1}{C_s^2} = \frac{2}{q\kappa\varepsilon_0 N}\left(E - E_{fb} - \frac{kT}{q}\right) \qquad (1)$$

where C_s represents the space charge capacitance per unit area (measured by means of an AC bridge described elsewhere[8)]), q the electronic charge, κ the dielectric constant of the semiconductor (332 for $SrTiO_3$ at 25 °C[9)]), ε_0 the permittivity of vacuum, N the donor concentration, E the electrode potential against an appropriate reference electrode, and E_{fb} the flatband potential.

Figure 2 shows $1/C^2$ *vs.* E plots for the $SrTiO_3$ electrode at various pH values, from the slope of which the magnitude of N is calculated to obtain *ca.* 1.0×10^{19} cm^{-3}. From the intercepts of these curves on the E axis, the flatband potential of the $SrTiO_3$ electrode was determined and the results are shown in Fig. 3, together with those for the TiO_2 electrode reported elsewhere.[10)] As is clearly seen, the flatband potential of the $SrTiO_3$ electrode depends almost linearly on pH of the electrolyte solution with the slope of *ca.* −60 mV/ΔpH. Such a dependence supposedly results from a dissociation equilibrium of proton at the oxide electrode surface.[7,8)] The value of the flatband potential of the $SrTiO_3$ electrode at a given pH is about 0.30 volts more cathodic than that of the TiO_2 electrode. This point will be discussed later in connection with the electrochemical photocell characteristics of these two semiconductor electrodes.

Photosensitized Electrolytic Oxidation of Water. The reduced $SrTiO_3$ single crystal electrode behaves like a typical n-type semiconductor electrode. Figure 4 depicts the current-potential characteristics of the $SrTiO_3$ electrode at three different pH values. In darkness, owing to the formation of a depletion layer for the majority carrier (electrons) at the surface of the $SrTiO_3$ electrode, only a small current can be observed under anodic polarization. When the electrode surface is illuminated with light in the wavelength range

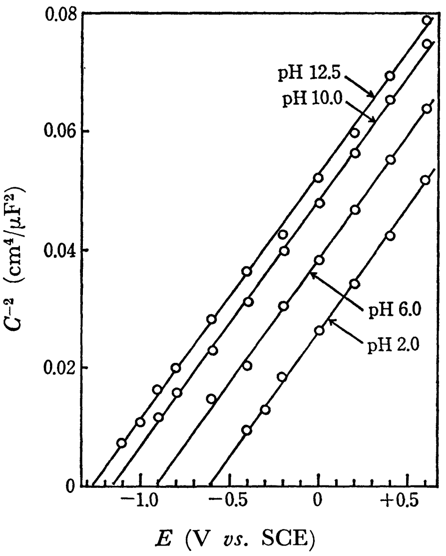

Fig. 2. Mott-Schottky plots for $SrTiO_3$ electrode.

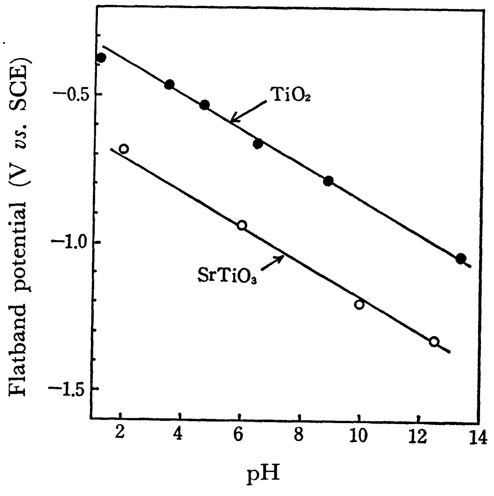

Fig. 3. Dependence of the flatband potentials of $SrTiO_3$ and TiO_2 single crystal electrodes on pH of the electrolyte solution.

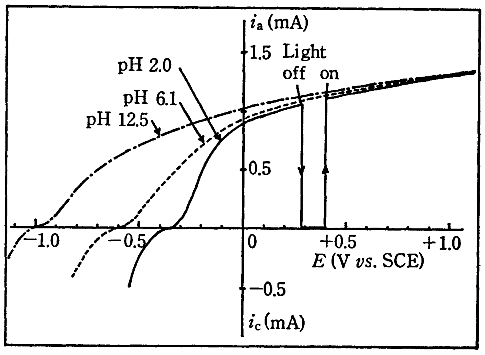

Fig. 4. Current-potential characteristics of $SrTiO_3$ electrode.

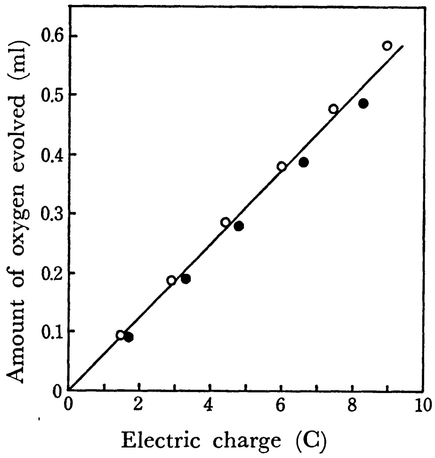

Fig. 5. Dependence of the amount of oxygen (as the standard state) evolved at the $SrTiO_3$ electrode surface on the amount of the electric charge passed through the external circuit. Solid line represents theoretical relationship.

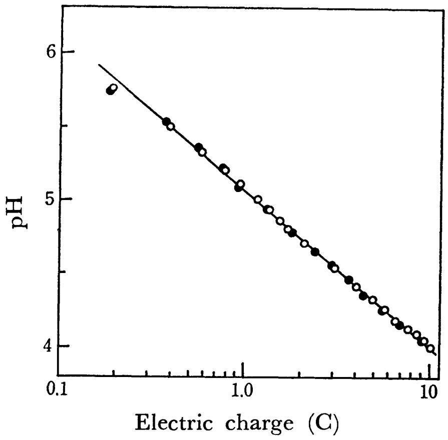

Fig. 6. Variation of pH value of the anodic compartment as a function of the amount of the electric charge passed through the external circuit.
—○—: $SrTiO_3$ (anode)-Pt (cathode) system; —●—: Pt (anode)-Pt (cathode) system under electrolysis.

$\lambda < 390$ nm, a large photocurrent is generated in the anodic polarization, while the cathodic branch remains practically unaffected. The electrode potential at which the anodic photocurrent starts to rise depends on pH of the solution with the slope of *ca.* -60 mV/ΔpH, which conforms to the pH-dependence of the flatband potential.

When the anodic photocurrent is flowing through the $SrTiO_3$ electrode, one can observe gases evolving from the surfaces of the $SrTiO_3$ electrode and of the platinum counter electrode with the apparent volume ratio of *ca.* 1 : 2. Through the examination on a gas chromatograph, these gases were found to be oxygen and hydrogen. The amounts of oxygen and hydrogen evolved have been measured as a function of the electric charge passed through the external circuit. Figure 5 shows the volume (as the standard state) of the oxygen gas evolved at the surface of the $SrTiO_3$ electrode as a function of the electric charge. The open and full circles represent independent measurements. From this figure it is evident that the current efficiency is approximately 100%. We could not notice any evidence for dissolution of the $SrTiO_3$ electrode surface during the electrolysis. The current efficiency for the hydrogen evolution from the platinum counter electrode was found in the range of 97±7%. These observations undoubtedly suggest that the photosensitized oxidation of water proceeds at the illuminated $SrTiO_3$ electrode surface as follows.

$$SrTiO_3 + h\nu \longrightarrow p^+ + e^- \tag{2}$$

$$4p^+ + 2H_2O \longrightarrow 4H^+ + O_2 \tag{3}$$

The residual electrons are transferred to the Pt electrode, where they react with protons to produce hydrogen.

$$2e^- + 2H^+ \longrightarrow H_2 \tag{4}$$

The occurrence of the reaction (3) can be verified by the fact that the value of pH of the anode ($SrTiO_3$) compartment is shifted by unity per decade increase in the amount of the electric charge passed through the electrode-electrolyte interface, as shown in Fig. 6. In this figure is also shown for comparison the variation of pH of the anode compartment for the Pt–Pt system during electrolysis.

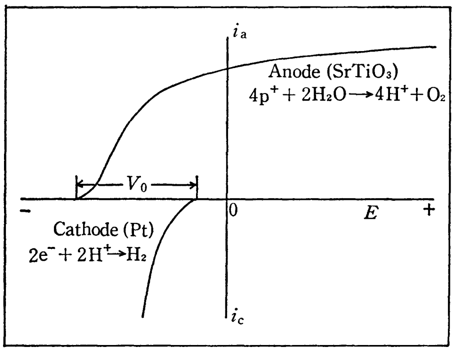

Fig. 7. Electrode reactions at $SrTiO_3$ (anode)-Pt (cathode) system under electrochemical photocell arrangement. V_0 represents the open-circuit cell voltage.

Table 1. Open-circuit cell voltages of $SrTiO_3$-Pt and TiO_2-Pt electrochemical photo-cells

	Common electrolyte solutions	Alkaline (anode)-acid (cathode) solutions
$SrTiO_3$-Pt	0.60 V (0.2 M Na_2SO_4)	1.25 V (1 M NaOH-0.5 M H_2SO_4)
TiO_2-Pt[4)]	0.30 V (1 M NaOH)	0.64 V (1 M NaOH-0.5 M H_2SO_4)

The electrochemical reactions occurring on the anode ($SrTiO_3$) and cathode (Pt) under the electrochemical photocell arrangement[3,4)] are summarized in Fig. 7. The electromotive force (and hence the value of the open-curcuit voltage, V_0) of the $SrTiO_3$ (anode)–Pt (cathode) electrochemical photocell is greater than that of the TiO_2–Pt system, owing to the fact that the flatband potential of the $SrTiO_3$ electrode is situated in the more cathodic region than that of the TiO_2 electrode. The data of V_0's for these semiconductor electrodes under the same illuminating light intensity are summarized in Table 1.

By illuminating the $SrTiO_3$ electrode surface with monochromatic light, the spectral response of the photocurrent has been measured. Since the forbidden gap width of $SrTiO_3$ is *ca.* 3.2 eV, the photosensitivity is confined to the wavelength range below 390 nm. For the estimation of the effectiveness of photocurrent production (and hence of the decomposition of water to hydrogen and oxygen gases), the formal quantum efficiency (*FQE*), defined by

$$FQE = \frac{\text{number of electrons flowing (s}^{-1}\text{)}}{\text{number of incident photons (s}^{-1}\text{)}} \tag{5}$$

was employed. The *FQE vs.* wavelength plot for the $SrTiO_3$ anode (0.0 V *vs.* SCE, in 1 M NaOH)–Pt (in 0.5 M H_2SO_4) system is shown in Fig. 8. The value of *FQE* reached 0.2 at 350 nm illumination. By the use of a common electrolyte solution (*e.g.*, 0.2 M Na_2SO_4) for both compartments, the values of *FQE* are lowered by a factor of about 1/2. This factor is much greater than that of the TiO_2–Pt system (*ca.* 1/30[4)]), owing presumably to the greater emf of the $SrTiO_3$ anode–

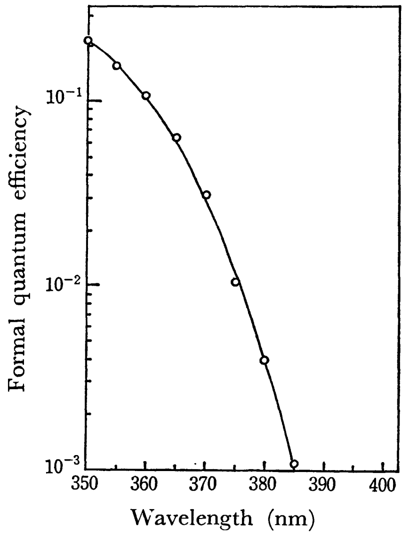

Fig. 8. Formal quantum efficiency of photocurrent production at $SrTiO_3$ anode (0.0 V *vs.* SCE) as a function of the wavelength of the incident light.

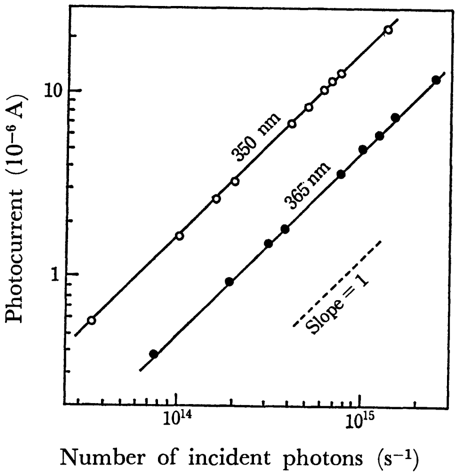

Fig. 9. Dependence of the photocurrent at $SrTiO_3$ electrode (0.0 V *vs.* SCE) on the intensity of the incident light.

Pt cathode electrochemical photocell than that of the TiO_2–Pt cell.

The true quantum efficiency would be much greater than *FQE* because of the high reflectivity of the $SrTiO_3$ crystal surface, whose precise measurement has not been carried out in the present study. For further enhancement of the quantum efficiency, it would be necessary to reduce the processes of electron trapping in the bulk of the semiconductor electrode and of the surface recombination of the charge carriers. These problems, possibly bearing on the thickness of the electrode[11] and/or the condition of the reduction treatment prior to the electrode preparation, are to be examined in the future investigation.

The magnitude of the photocurrent depends linearly on the incident light intensity, as depicted in Fig. 9. Even under the illumination by light with considerably high intensity (*e.g.*, 500 watt xenon lamp with no filters), the photocurrent did not show any saturation tendency.

Based upon the observations described above, it can be concluded that the $SrTiO_3$ single crystal is an excellent semiconductor electrode material for the decomposition of water by means of light energy.

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