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DETERMINATION OF INTRINSIC QUANTUM EFFICIENCIES OF PHOTOELECTROCHEMICAL REACTIONS ON SEMICONDUCTOR ELECTRODES BY TEMPERATURE MEASUREMENT

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Quantum efficiencies of photoelectrochemical reactions on various semiconductor electrodes were easily determined by a new method - the measurement of temperature changes of the surface of semiconductor electrodes. The characteristics of this method were discussed, and the quantum efficiencies were compared with those by the usual chemical actinometric method.

The conversion of solar energy into electrical and/or chemical energy in an electrochemical photocell using a semiconductor electrode has been greatly studied.$^{1-6)}$ The energy conversion efficiencies and quantum efficiencies of the electrochemical photocell are very important factors in the effective utilization of solar energy.

Using a thermistor based on the technique of a new spectroscopic method called Photothermal Spectroscopy (PTS),$^{7)}$ we have measured the temperature change on the semiconductor electrode during photoelectrochemical reaction.$^{8)}$ When the semiconductor electrode is illuminated with a monochromatic light pulse having an energy E (eV/photon), with an average absorbed intensity I (photons/sec) for a time t (sec), the following equation (1) can be obtained by considering the energy balance within the semiconductor photoelectrode.

In the limiting photocurrent region,

$$E\,\frac{\Delta T}{\Delta T^{\circ}} = \frac{Q_{s.c.} + T\Delta S}{It} + \eta e\,(\,V - V_{fb})\qquad(1)$$

where ΔT : Temperature change of the semiconductor surface;
ΔT° : Temperature change of the semiconductor surface in the open circuit;
ΔS : entropy change of the semiconductor electrode reaction;
$Q_{s.c.}$: heat evolved in the semiconductor *via* recombination and radiationless processes;
η : quantum efficiency of photo-electrode reaction;
V : applied potential (V *vs.* reference electrode);
V_{fb} : flatband potential (V *vs.* reference electrode).

Under constant illumination conditions (EIt held constant), a plot of $E\,\frac{\Delta T}{\Delta T^{\circ}}$ against $(V - V_{fb})$ yields the quantum efficiency, η, from the slope of the straight line.$^{8)}$

To understand quantum efficiency obtained from the relationship between temperature change and applied potential, two model cases are shown in Fig. 1. When $\eta = 1.0$, the slope of $E\,\frac{\Delta T}{\Delta T^{\circ}}$ against $V - V_{fb}$ must be 1.0, because all the electrons excited into the conduction band by light irradiation move from the surface into the bulk of semiconductor through the space charge layer, resulting in heating. When, on the other hand, $\eta = 0.5$, the slope has to be 0.5, since half of the excited electrons are recombined with the holes in the surface region and therefore the heat due to electron movement through the space charge layer is half as much as that in case of $\eta = 1.0$.

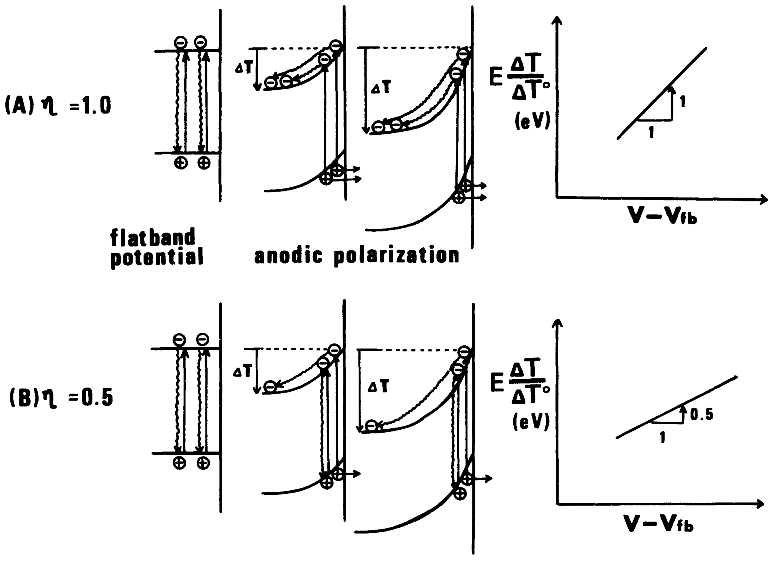

Fig. 1 Relationship between temperature change and applied potential

In this paper we report that the determination of the quantum efficiencies of various photoelectrodes —— semiconductors of n-type (CdS, CdSe, GaP, GaAs, TiO_2, ZnO, MoS_2) and P-type (GaP and GaAs) —— can easily be carried out by the direct measurement of temperature changes in the semiconductor electrodes.

Figure 2 shows a block diagram of the experimental apparatus. To measure the temperature changes, we used matched pairs of thermistors (Shibaura Electronics, Model BSB4 - 41A; nominal resistance 4 K ohm, sensitivity 0.052°C/ohm). The thermistors were used in a differential arrangement with one held against the front surface of the semiconductor electrode and the other positioned behind the electrode while not touching it. The cell was carefully positioned so that the monochromatic light beam struck only the electrode and not either of the thermistors. The temperature change of the electrode by irradiation caused a resisitive change in the thermistor and produced a voltage imbalance in the D.C. bridge. This small voltage was amplified and then displayed on a strip chart recorder. The temperature changes of the electrodes were measured under open circuit condition and applied potentials.

The light source used was a 500 W high pressure mercury lamp (Ushio Electric) and interference filters were employed to select wavelength of the exciting light. A shutter with two timers was used to fix precisely the irradiation time. The cell was equipped with a platinum counter electrode and a saturated calomel reference one. The current-potential and current-time curves were measured under potentiostatic conditions using a potentiostat and a potential programmer (Nikko Keisoku). To know the usual quantum efficiencies of the photoelectrodes a chemical actinometric method (potassium ferrous oxalate)[9] was used. Semiconductors used were single crystals (CdS, CdSe, GaP, GaAs, TiO_2, MoS_2) and polycrystals (ZnO, CdS). Ohmic contacts and surface etchings were doned with the most suitable methods for respective semiconductors.

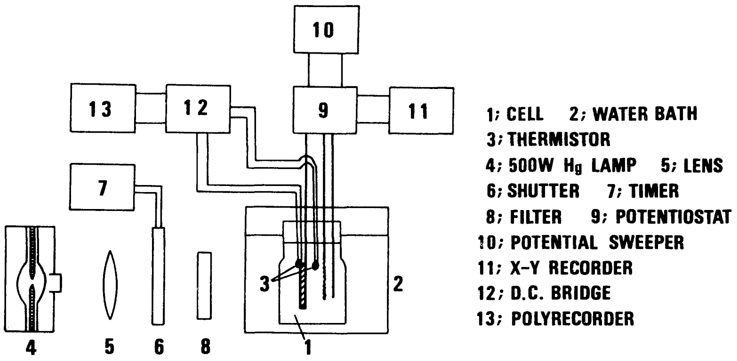

Fig. 2 Measurement assembly

Figure 3 plots $\frac{\Delta T}{\Delta T°}E$ against $(V - V_{fb})$ for an illuminated ZnO polycrystal electrode in a sodium sulfate aqueous solution in accordance with Equation (1), where the illumination conditions are constant (I: constant, E: 340 nm (3.6 eV), t: 20 sec). As shown in Fig. 3, in the limiting photocurrent region, a linear increase in temperature was observed with anodic polarization. The slope of a straight line was 0.85, indicating that the quantum efficiency for photo-dissolution10) of ZnO polycrystal electrode was 0.85. Even when light intensity was changed with neutral density filters, the slope of the ZnO polycrystal was constant 0.85 in the region of photocurrents between 500 μA and 7 mA. Wavelength effect of irradiation on the slope was measured using CdS single crystal photoanode in sodium sulfite aqueous solution. With the wavelengths (e.g., 340, 400, 490 nm) shorter than 525 nm (2.4 eV) corresponding to the band gap of CdS, the slopes obtained were the same, 1.0. Using this CdS-Na_2SO_3 system, the slopes were checked up with different irradiation times (*i.e.*, 5, 10, 20, 30 and 60 sec). Also, the slopes were 1.0 within these irradiation times.

In p-type semiconductor electrodes, the cathodic current increased with light irradiation. In the cathodic limiting photocurrent region, the relationship between temperature changes and the applied potential also can give information on the quantum efficiency. Figure 4 shows the results for p-GaP single crystal electrode. From the linear slope, it was possible to obtain the quantum efficiency of 0.80 for the hydrogen evolution reaction.

Table 1 provides a comparison of the quantum efficiencies (η_t) obtained from the temperature measurement of ten kinds of the semiconductor surfaces. Usual quantum efficiencies (η_a) calculated from the numbers of electrons flowed against the numbers of incident photons which were counted by the chemical actinometry are also cited in Table 1. In the case of CdS, TiO_2, and CdSe, both quantum efficiencies, η_t and η_a, show nearly the same values, respectively. On the other hand, in the cases of ZnO, GaP, GaAs, and MoS_2, the values of η_a were smaller than η_t. On these semiconductors, incident light might not be completely absorbed due to reflectance or scattering on the semiconductor surfaces. Especially in the case of MoS_2, the surface has so metallic luster that the reflectance is fairly large.11)

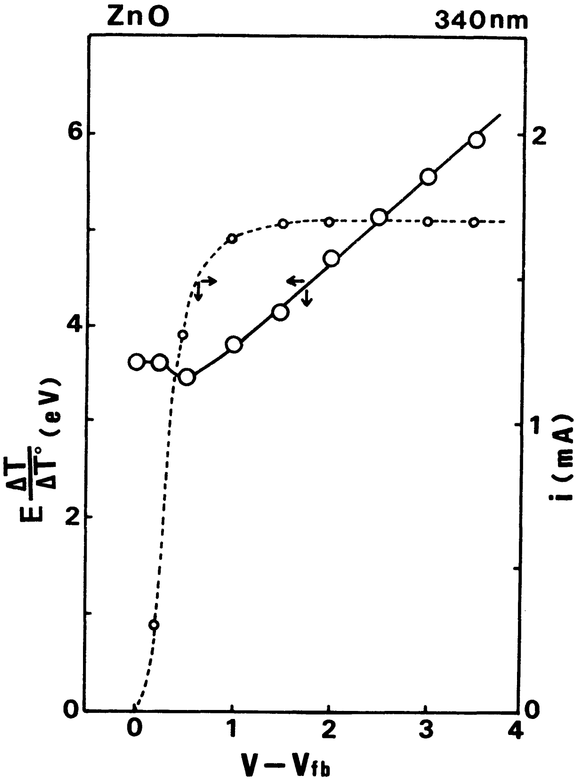

Fig. 3 Standardized temperature change *vs.* potential and photocurrent *vs.* potential of ZnO polycrystal electrode in 0.2 mol dm^{-3} Na_2SO_4.

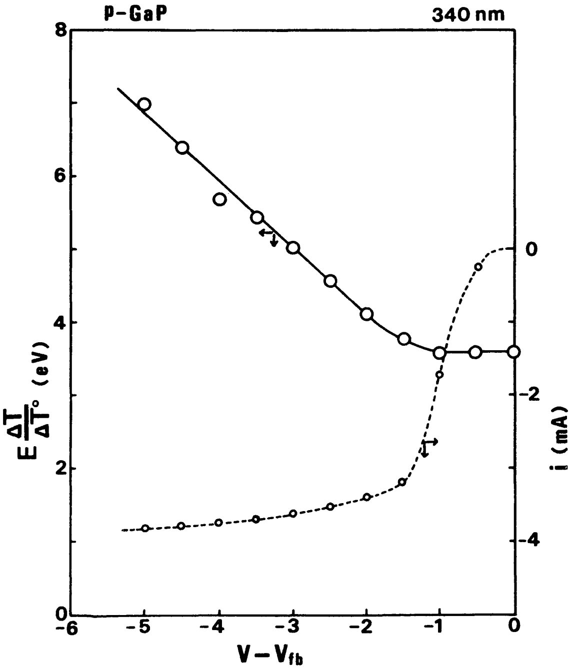

Fig. 4 Standardized temperature change *vs.* potential and photocurrent *vs.* potential of p-GaP single crystal electrode in 0.5 mol dm^{-3} H_2SO_4.

For these lustrous semiconductors, it is very difficult to estimate the actual quantum efficiency of the photoelectrode reaction by the usual method of counting the photon numbers. This temperature method, however, counts only the photons which are absorbed in the surface of the semiconductor. Therefore, the quantum efficiency thus obtained may be taken as the intrinsic quantum efficiency.

This temperature method has several advantages over the usual actinometric method, including; i) great simplicity; ii) no need to count the number of photons irradiated and/or absorbed; iii) the possibility of obtaining intrinsic quantum efficiencies even for semiconductors which have great surface reflectance and/or scattering.

Table 1 Comparison of quantum efficiencies

340 nm

ELECTRODE	η_t	η_a	ELECTROLYTE
n-CdS s	1.00	1.00	Na_2SO_3
n-CdS p	0.67	0.67~0.70	Na_2SO_3
n-CdSe s	0.42	0.40~0.42	Na_2S
n-GaP s	0.85	0.62	Na_2S
n-GaAs s	0.80	0.47~0.49	Na_2S
n-TiO_2 s	0.70	0.70	H_2SO_4
n-ZnO p	0.85	0.76~0.78	Na_2SO_4
n-MoS_2 s	1.00	0.54	Na_2SO_4
p-GaP s	0.80	0.60~0.66	H_2SO_4
p-GaAs s	0.80~1.00	0.56~0.59	H_2SO_4

η_t : Quantum efficiency by temperature measurement

η_a : Quantum efficiency by actinometry

S : Single crystal P : Polycrystal

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