An Ultramicrostructured Photoelectrode System Composed of TiO_2 Single Crystal and Layered SiO_2 and Pt Thin Film

Masahiro HIRAMOTO, Kazuhito HASHIMOTO[†], and Tadayoshi SAKATA*[††]

Chemical Process Engineering, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka 565

[†]Department of Synthetic Chemistry, Faculty of Engineering, The University of Tokyo,

Hongo, Bunkyo-ku, Tokyo 113

[††]Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta,

Midori-ku, Yokohama 227

An ultramicrostructured photoelectrode system composed of a TiO_2 single crystal and thin films of SiO_2 and Pt was prepared by exposing the vertical section of the layered SiO_2 and Pt film. The distance between the semiconductor and metal, i.e., the thickness of the SiO_2 layer is made very thin (ca.140 nm). This electrode showed photoresponse under irradiation in the presence of vapor of water, ammonia, ethanol and acetone. This is the first micro-photoelectrode system which can work in the gas phase.

Electrodes which have a microscopic structure are interesting from the view point, such as microelectrode,[1] electrochemical transistor,[2] photochemical conversion of solar energy,[3] etc.[4] To prepare the microstructure, photolithography technique is often used. Recently, we presented an ultramicrostructured electrode system prepared from the vertical section of the multilayered thin films.[5] The structure of the microstructured electrode which consists of metal and insulator (SiO_2) layers is shown in Fig. 1. Since the distance between the two electrodes, i.e., the thickness of the SiO_2 layer, can be made very thin (nm order), gas-phase electrochemistry[5] can be carried out by this electrode system. Here, we report the first microstructured photoelectrode system in which one of the two metal layers in Fig. 1 is replaced by a semiconductor (TiO_2).

We used TiO_2 and Pt as a semiconductor and a metal, respectively. Although in an ideal case, a TiO_2 film should be used as shown in Fig.1, a TiO_2 single crystal was used in the present study as a substrate as shown in Fig.2A, because of easiness of preparation. Since the characteristic feature of the microstructure shown in Fig. 1 is the very small distance between metal and semiconductor, similar effects as in the case of microstructured electrode of Fig. 1 are also expected for the microstructure of Fig. 2A. Before use, the TiO_2 single crystal
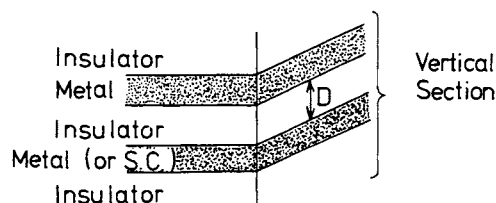

Fig. 1. An ultramicrostructured electrode system prepared from the vertical section of alternating layers of metal and insulator. In the present work, one of two metal layers is replaced by a semiconductor (TiO_2).
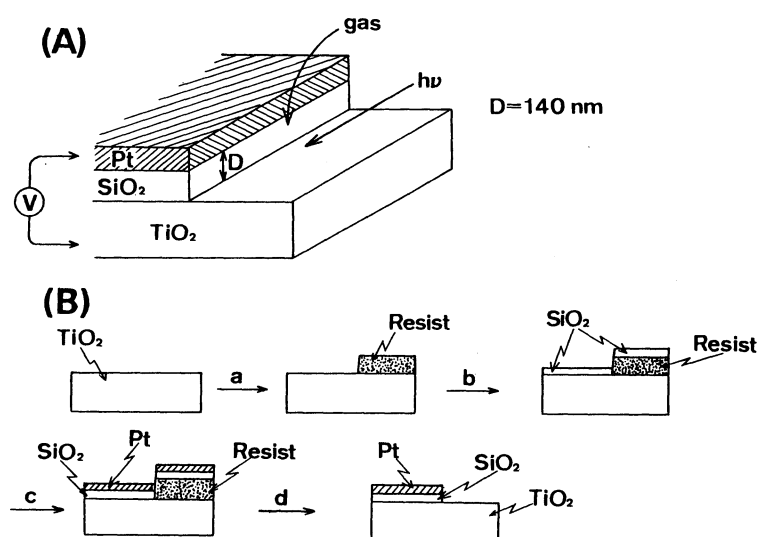
Fig. 2. (A) The structure of $TiO_2/SiO_2/Pt$ microstructured photoelectrode used in this study. (B) Preparation procedure of the $TiO_2/SiO_2/Pt$ microstructure.
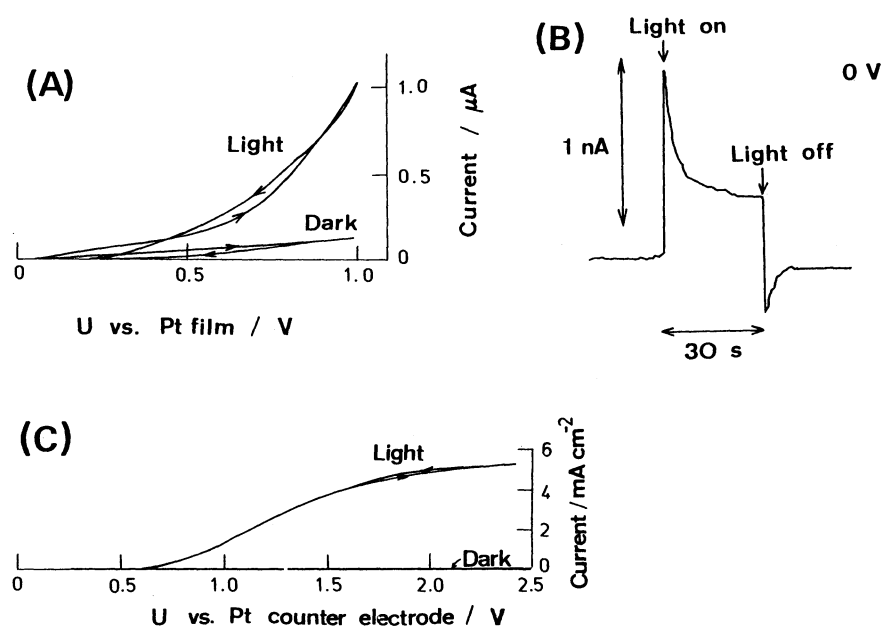

Fig. 3. (A) Photocurrent (i)-Voltage (U) curves of $TiO_2/SiO_2/Pt$ microstructured photoelectrode under water vapor (19 Torr). (B) Photoresponse at U = 0 V. Here, U is the electrode potential of TiO_2 with respect to the Pt film. (C) Photocurrent(i)-Voltage(V) curve for the same TiO_2 photoelectrode immersed in an aqueous electrolyte solution.

was reduced under H_2 atmosphere at 600 °C. Preparation procedure of the microstructure is shown in Fig. 2B. A part of the optically flat TiO_2 surface was covered with a photo resist (Tokyo Ohka Kogyo, Co., Ltd., OMR-83)(a). Next, a SiO_2 film (140 nm thick) was deposited on the whole surface by using plasma CVD (Samco, model BP-1, deposition condition; N_2O 80 ml/min, SiH_4 10 ml/min, substrate temperature 140 °C, 13,56 MHz)(b). A Pt film (250 nm thick) of rectangular shape (1 mm x 3.5 mm) was deposited by using Ar^+-ion sputtering (Ar 6 x 10^{-3}Torr, 100 W)(c). This Pt electrode is crossed over the border of the surface covered with the resist and the resist free surface. Finally, the resist was removed by using the resist stripper (Tokyo Ohka Kogyo Co., Ltd.)(d). We call this as a $TiO_2/SiO_2/Pt$ microstructured photoelectrode. An ohmic contact was made to the back surface of TiO_2. The potential between the TiO_2 single crystal and the Pt film was controlled by a potentiostat (Hokuto, HA501). The microstructured electrode was set in an optical cryostat (Oxford Instruments Ltd., CF1104) and the photocurrent-voltage curves were measured under vacuum (1×10^{-3}Torr) and under various gas atmospheres. A 500 W mercury lamp was used as a light source.

Under various gas atmospheres, $TiO_2/SiO_2/Pt$ microstructured photoelectrode showed photoresponse. Figure 3 shows photocurrent (i)-voltage (U) curves in the presence of H_2O vapor of 19 Torr. A small dark current due to the leak current through pinholes in the SiO_2 film between TiO_2 and Pt was observed as shown in Fig. 3A. However, under irradiation with ultraviolet light, a clear and stable photocurrent was observed.

By evacuating water vapor the photocurrent disappeared. Nearly the same i-U curve was observed for the same TiO_2 photoelectrode immersed in an aqueous electrolyte solution (Fig.3C). Typical photoresponse at U = 0 V is shown in Fig. 3B. The transient photocurrent was observed for $TiO_2/SiO_2/Pt$ microstructured electrode. This transient is explained by the back reaction of the photoproducts accumulated on TiO_2 surface.[6] These results strongly suggests that the water vapor adsorbed on the electrode surface was directly decomposed on the photoexcited TiO_2 surface of $TiO_2/SiO_2/Pt$ microstructured electrode.

Figure 4 shows dependence of the photocurrent on the vapor pressure of water. At U = 0 V, the photocurrent increased remarkably with increasing the vapor pressure from 1 to 5 Torr, and reaches saturation. This behavior seems to be caused by the different conduction mechanism between chemically adsorbed water layer and physically adsorbed one.[7] With increasing the applied voltage V, at U = + 0.5 V, the amount of the photocurrent increases about 100 times due to the development of the band bending near the TiO_2 surface and it monotonically increases with increasing the vapor pressure, presumably because of increase of the conductivity of the adsorbed water layer due to the increase of water layer thickness. This result suggests that this microstructured photoelectrode system can be used as a gas sensor.

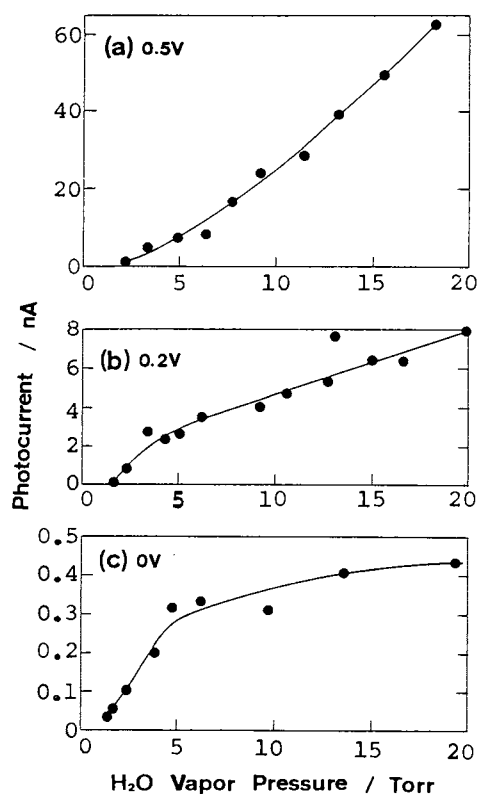Besides water vapor, this microstructured electrode system

Fig. 4. Dependence of the photocurrent on the vapor pressure of water at (a) U = 0.5 V, (b) U = 0.2 V, (c) U = 0 V.

showed photoresponse to various gases
such as ammonia, ethanol, and acetone
(Fig. 5). Interestingly, the photocurrent
depends sensitively on the kind of gas
molecules as well as the pressure.

The above results suggest that
the adsorbed gas molecules are directly
photodecomposed on the microstructured
photoelectrode system. This is because
of the very small distance between metal
and semiconductor (ca.140 nm).
Moreover, in the present system, any
kind of ion can act as a charge carrier.
This is another unique feature of this
system compared to the solid electrolyte

Fig. 5. Vapor pressure dependence of the photocurrent at U =
0 V. Vapors are water, ammonia, ethanol, and acetone.

in which the kind of active ion is restricted.[8] In the case of water vapor, the charge carriers are thought to
be H^+ and OH^-. When the TiO_2 is irradiated with ultraviolet light, OH^- ions are oxidized to oxygen on the
TiO_2 surface by the photogenerated holes and H^+ ions are reduced to hydrogen on the Pt surface. To our
knowledge, this is the first example of the water photoelectrolysis in the gas phase.

The role of the SiO_2 layer is quite important. If TiO_2 contacts directly Pt, most of the photogenerated
holes in TiO_2 easily transfer to Pt along the potential gradient of the valence band. Then we could not
observe the photocurrent due to the oxidation reaction on the TiO_2 surface.

The observed photocurrent is very small owing to the very small active area of TiO_2 and Pt because only
a small area near the SiO_2 layer can contribute to the photocurrent. Photocurrent density calculated from the
active area should be very large. This active area can be drastically increased if we enlarge the area of
vertical section by making use of photolithography technique. Moreover, this microstructured electrode system
can be used for the gas-phase electrochemical reaction which is difficult to carry out in the solution like N_2
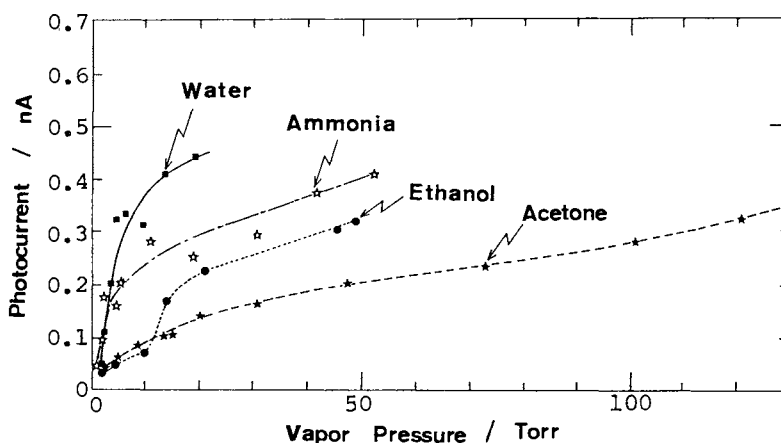fixation. The low temperature photoelectrochemistry is also possible as reported previously.[5]

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