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APPLICATION OF PHOTOACOUSTIC SPECTROSCOPY FOR *IN SITU* MEASUREMENT OF SEMICONDUCTOR ELECTRODE REACTIONS

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An application of photoacoustic spectroscopy (PAS) for semiconductor electrode reactions is described. A cathodic decomposition of a CdS single crystal electrode and an electrochemical deposition of Cd^{2+} on the CdS electrode were measured by PAS technique *in situ*.

A number of applications of photoacoustic spectroscopy (PAS) have been reported as a new tool for the study of various materials.[1-4] Especially in dense materials, PAS has been emphasized as an advantageous method, because absorption spectra of the dense materials can be obtained easily.

In previous publications, we showed an application of PAS for an *in situ* measurement of metal electrodes by the use of a new type photoacoustic cell.[5,6] A conventional PAS technique is available for the measurement of the absorption spectra of solid samples only in an inactive atmosphere, because the samples have to be placed in a sealed chamber containing a suitable gas, *e.g.*, air. In the PAS cell, which was newly constructed for the *in situ* measurement, the sample was mounted outside the chamber and the heat change on the surface, resulting from a radiationless transition due to irradiation, was detected after being transported to the rear of the sample. We could measure the absorption spectra of the sample, the surface of which was in contact with any surrounding situations, by the use of this type of PAS cell.

In this work, we investigated the PAS-semiconductor electrode system upon its spectroscopic property and its sensitivity in detecting a surface change in the course of a cathodic decomposition of a CdS single crystal electrode as a model sample. Since reactions of semiconductor electrodes are much influenced by the surface conditions,[7-11] PAS is advantageous for the study of the semiconductor electrodes with rough surface, *e.g.*, an etched surface of CdS, to which other spectroscopic methods are hardly applicable on account of light scattering problems.

In Fig. 1, the photoacoustic cell used is shown. The structure of the photoacoustic cell and the experimental procedure were modified for the semiconductor electrode. The PAS cell was constructed from stainless steel, and its outside surface was coated by epoxy resin for the purpose of insulation against the electrolyte. The pyrex window was provided at one side of this cell, and light, which was not absorbed by a sample electrode, passed through the window. A sample electrode, a CdS single crystal with a donor concentration

N_D = 1.6 x 10^{16} cm^{-3} (Teikoku Tushin), was polished to a thin plate with a thickness of less than 0.5mm because the amplitude of a photoacoustic signal depends on the thickness of the sample, especially in semiconductors which have smaller thermal conductivities than metal. Before measurements were taken, the surface of the CdS electrode was etched with concentrated hydrochloric acid for a few seconds. After the etching treatment, the surface of CdS became dull, and light-scattering was increased.

Experimental instruments were similar to those used in the case of metal electrode.[5,6] In the semiconductor electrode, a fairly large phase angular shift was observed in the lock-in detection due to the heat conduction from the surface to the rear side of the electrode. The phase angle was adjusted before the spectroscopic measurements.

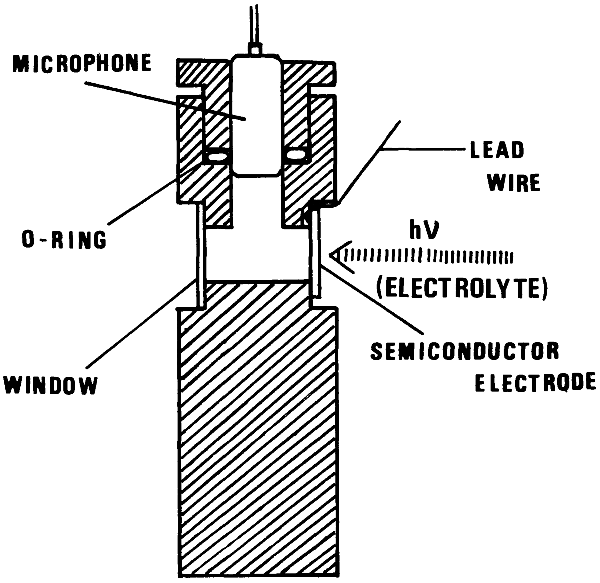

Fig. 1 PAS cell for semiconductor electrode

The cathodic decomposition of a CdS single crystal electrode was studied by Kolb and Gerischer through the use of a differential reflectance spectroscopy.[12,13] However, only polished surfaces were examined because the surface had to be flat in the reflectance technique. The cathodic reaction can be written as follows;

$$CdS + 2e^- \longrightarrow Cd + S^{2-}$$

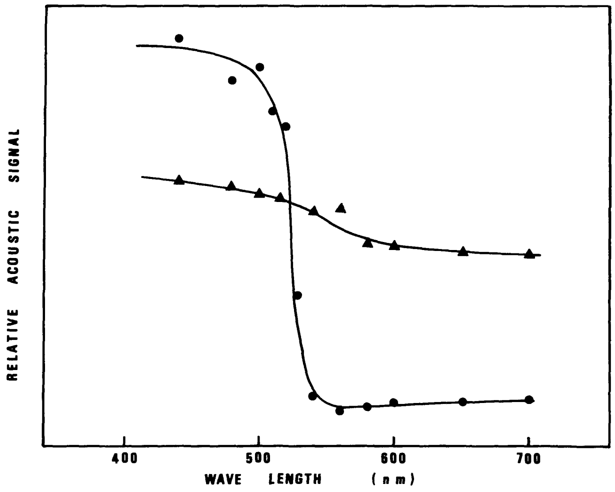

Fig. 2 Photoacoustic spectra of CdS electrode, before (-●-) and after electrolysis at -2.0 V (-▲-).

Figure 2 shows the photoacoustic spectra of the CdS electrode before and after electrolysis at -2.0 V versus SCE in a 1 M KCl electrolyte. Both spectra were measured under the condition that the surface of the electrode was in contanct with the electrolyte solution. As shown in Fig. 2, we could obtain the information concerning the absorption of the electrode, though some of the background absorption was present in the wavelength region longer than the absorption edge in the spectrum of CdS before the electrolysis. The spectrum was changed after the electrolysis at -2.0 V, where the CdS electrode might decompose and the

CdS surface might be covered with a metallic Cd layer. After electrolysis, the shape of the spectrum became flat, that is, the absorption at the longer wavelength region increased, and in the intrinsic absorption region the absorption bacame a small value. These results confirm that we can use the photoacoustic signal change as a probe for the detection of the change at the CdS electrode.

Figure 3 shows the current-potential and the relative acoustic signal-potential curves of the CdS electrode in a 1 M KCl electrolyte. The wavelength of the incident light, for a photoacoustic measurement, was 610 nm. At this wavelength, no photochemical reaction takes place at the CdS electrode. In the current-potential curve, the reductions of dissolved oxygen and hydrogen evolution were recognized at about -1.0 V and -1.4 V ,respectively. However,a well defined peak of the cathodic decomposition of CdS could not be observed on account of a large cathodic current of hydrogen evolution. On the other hand, the signal increased at -1.5 V in the photoacoustic signal-potential curve, and then it became constant at about -2.0 V. This means that CdS was decomposed, and the electrode surface was covered with Cd below -1.5 V. The photoacoustic signal was scarecely disturbed by the hydrogen evolution or reduction of oxygen in the sensitivity range of this study. On the anodic scan, a sharp anodic current peak which was attributed to the dissolution of deposited Cd into the solution appeared at -0.8 V. At around this potential, the photoacoustic signal began to decrease, and reverted to the initial value. This behavior indicates that the deposited Cd layer was completely dissolved during the anodic scanning.

On the second scan, another cathodic current was observed at -0.78 V in the current-potential curve. This current seems to have been attributed to the electrochemical deposition of Cd^{2+}, which was formed at the first scan, and, at the same potential, the photoacoustic signal once increased.

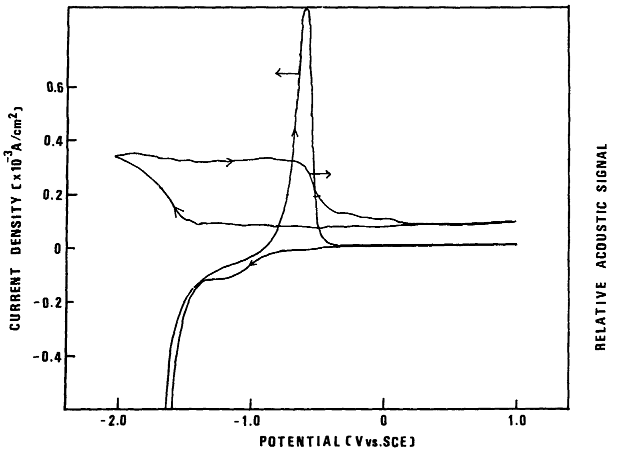

Fig. 3 Photoacoustic signal potential and current potential curves of CdS electrode. 1M KCl, potential sweep rate 40 s/V, λ=610nm (Rh-6G Dye Laser).

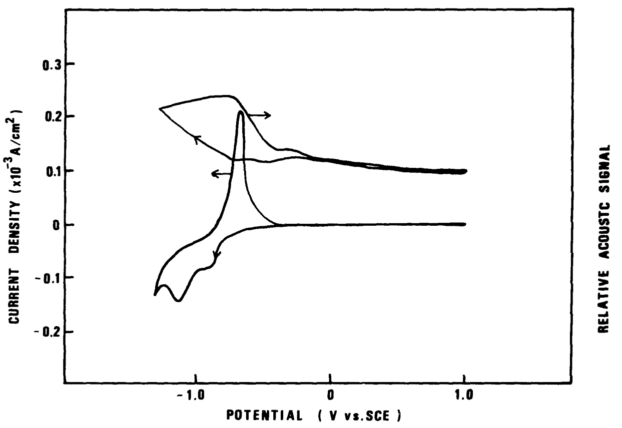

Fig. 4 Photoacoustic signal-potential and current-potential curves of CdS electrode in the presence of 5×10^{-5}M Cd^{2+}, 1M KCl, potential sweep rate 40 s/V, λ=610nm (Rh-6G Dye Laser).

Figure 4 shows the current-potential and photoacoustic signal-potential curves of the CdS electrode in a 1M KCl electrolytic solution containing 5×10^{-5}M Cd^{2+}. The range of potential scanning was from 1.0 to -1.4 V, in which the CdS electrode did not decompose. A cathodic current at - 0.78 V was attributed to the deposition of Cd^{2+} on the CdS surface from the electrolyte solution, and at this potential, the photoacoustic signal began to increase. Assuming that the deposited layer was uniform, the thickness of the deposited layer was estimated to be about 7 Å at -1.4 V from the amount of charge passed for the electrochemical deposition.

We could detect the change during the cathodic decomposition of the CdS electrode also by the use of intrinsic absorption wavelength irradiation (514.5nm) as a probe, on the basis of the absorption change in the cathodic decomposition as shown in Fig. 2. When the intrinsic absorption light was irradiated on CdS, photoacoustic signal-potential behavior was different from the result shown in Fig.3. That is, the photoacoustic signal decreased at -1.5 V as a result of the Cd deposition contrary to the results in Fig. 3.

It was confirmed that a photoacoustic spectroscopy-electrode system was applicable to the *in situ* measurement of semiconductor electrode reactions and that it was sensitive enough to detect the deposit of a few layers of metal atoms when using laser irradiation. This new technique for the *in situ* observation of the electrode surface has some possibilities of application. One of applications is for the study of polycrystalline semiconductor electrodes, which are difficult to study with conventional spectroscopic techniques.

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