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A "DIP-GROWN" CdSe PHOTOANODE IN PHOTOELECTROCHEMICAL CELL

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CdSe films can be grown simply by dipping Cd metal in an SeO_2-containing acid solution. These film electrodes without any additional treatment exhibit fairly good photoanodic characteristics. This enables us to fabricate a large-scale photoelectrochemical cell very easily.

Recently, there has been a great deal of interest in utilizing semiconductor-based electrochemical photovoltaic cells for the conversion of the sunlight to electrical and/or chemical energies. In view of the practical application, these devices require the use of thin film polycrystalline electrodes in order to minimize their costs. A number of recent works have been devoted to preparing photosensitive semiconductors at low costs.[1-9)] As to Cd-chalcogenide semiconductors, much attention has been paid to the electrochemical deposition of thin films, *e.g.* anodic oxidation[1,2)] and cathodic electrodeposition,[3,4)] because it potentially provides a convenient and inexpensive method to form thin films. During the course of our investigation on electrodeposited CdSe films, we found that a fairly photosensitive CdSe film could be grown simply by dipping a Cd metal in an SeO_2-containing acid solution. In this paper, we briefly describe the important results.

High purity Cd plates (99.999%) of thickness of 1 mm and the total exposed area of about 0.3 cm^2 were dipped in aqueous sulfuric acid solutions containing various concentrations of SeO_2. Polarization behaviour under illumination of the films thus obtained on Cd substrates was measured in an aqueous sulfide solution under potentiostatic condition with a Pt counter electrode and an SCE reference electrode. A 500 W Xe lamp was used as a light source. All measurements have been performed at room temperature.

A very thin film, visibly black, was formed immediately when the Cd plate was dipped in an SeO_2-containing sulfuric acid solution. The film thickness increased with dipping time. This film was identified as CdSe, which will be described later. The formation rate as well as the surface morphology of the film was different from sample to sample, depending mainly on the surface condition of the plate. The film formation apparently takes place faster at sites with flaws than at other sites. Reddish deposits, which was identified as Se, were sometimes found on the edges of the plate. According to the work already done,[4)] the reduction of Se(IV) to elemental Se can be described by either

$$H_2SeO_3 + 6H^+ + 6e \longrightarrow H_2Se + 3H_2O$$

followed by the chemical reaction

$$2H_2Se + H_2SeO_3 \longrightarrow 3Se + 3H_2O,$$

or

$$H_2SeO_3 + 4H^+ + 4e \longrightarrow Se + 3H_2O.$$

Thus, the formation of CdSe film can be explained by assuming a local cell mechanism, in which the cathodic reaction in the local cell is the reduction of Se(IV) to Se(-II) or Se(0).

Figure 1 shows the Cd and Se distribution across the Cd/film interfacial region of a sample by an X-ray microanalysis together with the SEM micrograph of the cross section. The Cd content gradually decreases from the interior to the surface, whereas the distribution of Se is rather uniform, indicating that the Cd/Se ratio gradually decreases toward the surface.

The film formation rate was unexpectedly high and it depended on the composition and temperature of dipping solution as well as on the Cd surface condition described above. In the case of the sample shown in Fig.1, the thickness of the film grown by dipping in a 2.5 M H_2SO_4 + 0.05 M SeO_2(M≡mol dm^{-3}) solution for 30 min was about 3 μm.

An X-ray diffraction pattern for the film grown by dipping for one day is shown in Fig.2. This film shows a comparatively sharp peak at $2\theta=25.4°$, which coincides well with the diffraction peak from (002) of CdSe. Hence the film formed on Cd was identified as CdSe. It is surprising that such a clear peak appears for a film grown at room temperature without any post-deposition heat treatment.

Figure 3 shows the polarization curves of these as-grown CdSe film electrodes under illumination in an aqueous sulfide solution. Anodic dark currents were negligibly small in all cases. These film electrodes exhibit fairly large anodic photocurrents, depending on the dipping conditions. Zero-photocurrent potentials were between -0.8 and -1.0 V vs. SCE, which are somewhat more positive than those for other CdSe electrodes reported so far.[10-12] One of the reasons for it is that the cathodic dark currents start flowing at relatively positive potentials.

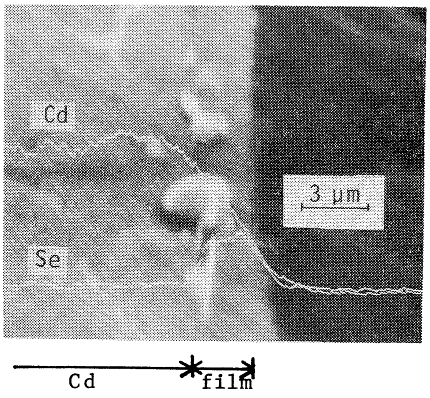

Fig.1 X-ray microanalysis of the cross-section of Cd/film system

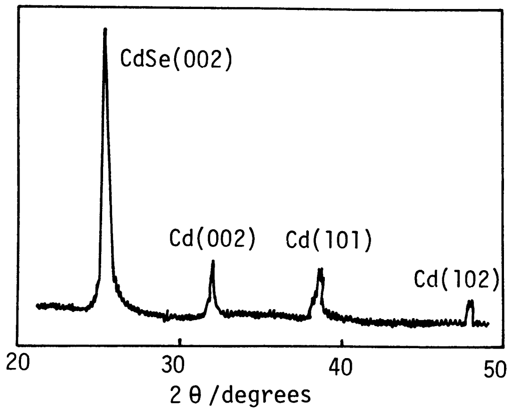

Fig.2 X-ray diffraction pattern of the film grown by dipping Cd in 2.5 M H_2SO_4 + 0.05 M SeO_2 solution for one day.

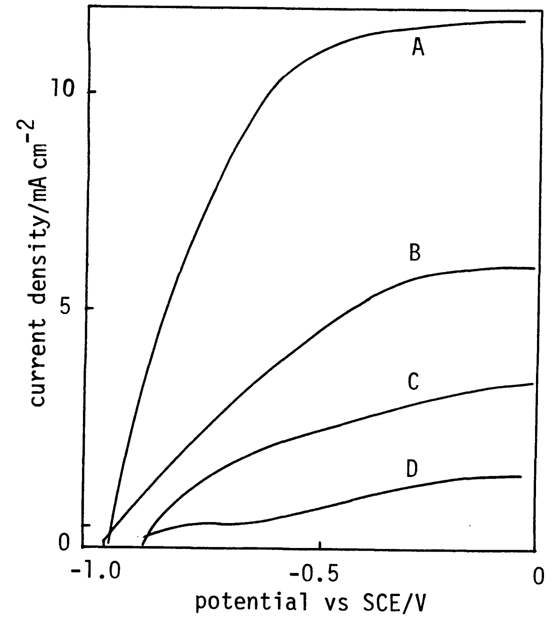

Fig.3 Potentiostatic current - potential curves for CdSe film electrodes under white light illumination in 0.1 M NaOH + 0.1 M Na_2S solution (light intensity; 100 mW cm^{-2})

Film preparation conditions

A; Dipped in 2.5 M H_2SO_4 + 0.05 M SeO_2 for 30 min.

B; Dipped in 0.25 M H_2SO_4 + 0.05 M SeO_2 for 30 min.

C; Dipped in 2.5 M H_2SO_4 + 0.05 M SeO_2 for 5 min.

D; Dipped in 2.5 M H_2SO_4 + 0.005 M SeO_2 for 30 min.

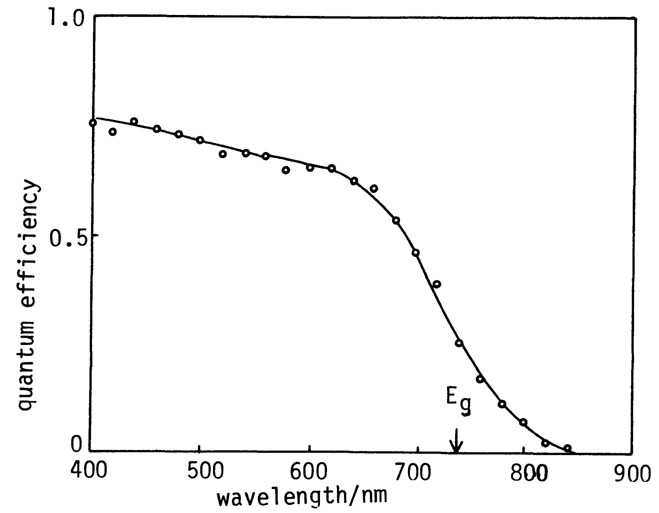

Fig.4 Quantum efficiency for anodic photocurrent - wavelength plots for a CdSe film electrode at 0 V vs SCE in 0.1 M NaOH + 0.1 M Na_2S solution. The film preparation condition is the same as that of Curve A in Fig.3.

Peeling off of the film from the substrate, which is often observed with vapour-deposited films, did not occur.

A typical example of the spectral dependence of the quantum efficiencies for the anodic photocurrent is shown in Fig.4. The quantum efficiencies of 50% or above under the anodic polarization were attained in the wavelength range of 400 -700 nm. Interestingly it depended on the light intensity for some electrodes; the quantum efficiency was higher at lower intensities. Detailed consideration on this effect is now in progress.

Two main features should be pointed out in Fig.4. One is that the response falloff in the short wavelength range was not observed,*i.e.* the response is relatively flat in a wide range of wavelength. The other is that it has a considerable response further out into the longer wavelengths than its bandgap energy (1.7 eV, 740 nm). This may be attributable to the absorption from band tail.$^{7)}$

The energy conversion efficiencies of the photoelectrochemical cells consisting of these CdSe film photoanodes, a Pt cathode, and a polysulfide electrolyte do not exceed 1% at present for white light from an Xe lamp, mainly because of the low photovoltage which can be attributed to the relatively positive zero-photocurrent potential mentioned previously (Fig.3). A short-circuit current of about 4 mA cm^{-2} for this cell under white light illumination of an Xe lamp was maintained during a 10-hour operation.

In spite of lower efficiency of this CdSe photoelectrochemical cell than those of other CdSe ones, this cell possesses important advantages over many other photoelectrochemical cells. One is that this CdSe photoanode without using any thermal and electrical energies is extremely simple and cheap to prepare. The other is that a large-scale photoelectrochemical cell can be fabricated quite easily. The latter is one of the most important features from the practical viewpoint.

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