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ELECTROCHEMICAL PHOTOCELL USING CdS-ZnSe SOLID SOLUTION FILM ANODE

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Epitaxial films of CdS-ZnSe solid solution were prepared by vacuum evaporation from the source composed of equimolar amounts of CdS and ZnSe onto the (111) thin films of a NaCl-NaBr solid solution system. The action spectrum of the electrochemical photocell using these epitaxial films as photoanodes in a S^{2-}-containing electrolyte was shifted to the longer wavelength region by about 100nm compared with a CdS thin film anode. The open-circuit voltage and the short-circuit current were found to be 0.54 V and 0.7 mA/cm^2, respectively, under sunlight of 62 mW/cm^2.

Electrochemical photocells based on the cadmium chalcogenide in the chalcogenide/polychalcogenide redox electrolyte have been reported.[1)-5)] We have investigated some fundamental characteristics of the electrochemical photocell using a sintered electrode and a chemically sprayed film electrode of CdS.[6) 7)] The use of a narrow bandgap semiconductor anode is preferable for the effective utilization of solar energy. One of the methods to prepare semiconductors with a variety of bandgap energies is to alloy several compound semiconductors. It is possible to control the bandgap energy of II-VI compound solid solutions by changing their compositions. The films of the II-VI compound solid solutions have already been prepared by spray pyrolysis[8)] and vacuum evaporation.[9) 10)] However, the application of these films to the photoanodes in the electrochemical photocell have not been reported to date. In general, bandgap energy of a solid solution is monotonously dependent on its composition and has intermediate value between two components. We have found that the CdS-ZnSe solid solutions with appropriate compositions exceptionally have smaller bandgap energy than CdS (E_g=2.4 eV) and ZnSe (E_g=2.6 eV) and that nearly equimolar composition crystal has the smallest bandgap energy.[11)] In this paper, we describe some results on the preparation of epitaxial CdS-ZnSe solid solution film electrodes and the photoelectrochemical characteristics of these electrodes.

The epitaxial films of the CdS-ZnSe solid solution were prepared by vacuum evaporation technique. It was carried out through two steps to minimize the misfit between CdS-ZnSe film and the substrate. In the first step, the (111) of a NaCl-NaBr solid solution film was prepared by vacuum evaporation onto a cleaved mica from the solid solution of which molar ratio NaCl/NaBr was 0.68/0.32. This molar ratio was

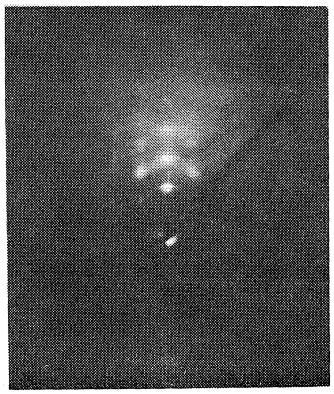

Fig.1 RED pattern of CdS-ZnSe epitaxial film

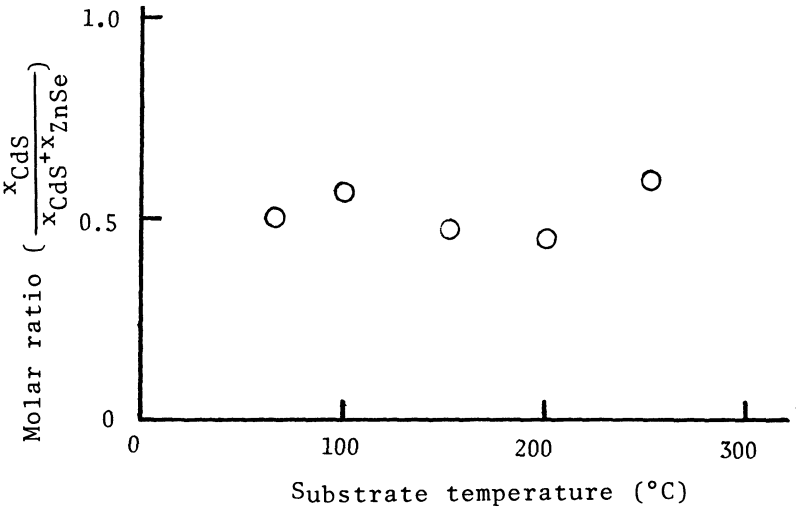

Fig.2 Molar ratio $x_{CdS}/(x_{CdS}+x_{ZnSe})$ in vacuum evaporated CdS-ZnSe film as a function of substrate temperature

selected to obtain the best fit to the interatomic distance, 4.07 Å, on the (0001) of the CdS-ZnSe solid solution and the (111) of the NaCl-NaBr solid solution. The electron diffraction pattern showed that a single crystal layer of this sodium halide solid solutioncould be obtained in the substrate temperature range of 250-350 °C. In the second step, vacuum evaporation onto the (111) of such a sodium halide substrate from the source of equimolar mixture of CdS and ZnSe was carried out at the controlled temperature in the range of 100-250 °C. Epitaxial films with about 1 μm in thickness were easily obtained. The electron diffraction patterns of these films indicated, as shown in Fig.1, that these films possessed a highly oriented (0001) and were regarded as a single crystal. The composition of the film was found to be nearly constant over various substrate temperatures by atomic absorption spectrophotometric analysis of the films, as can be seen from Fig. 2. The evaporated specimen was immersed in water to dissolve the sodium halide intermediate layer. Then, the CdS-ZnSe epitaxial film, which was floated on water, was scooped

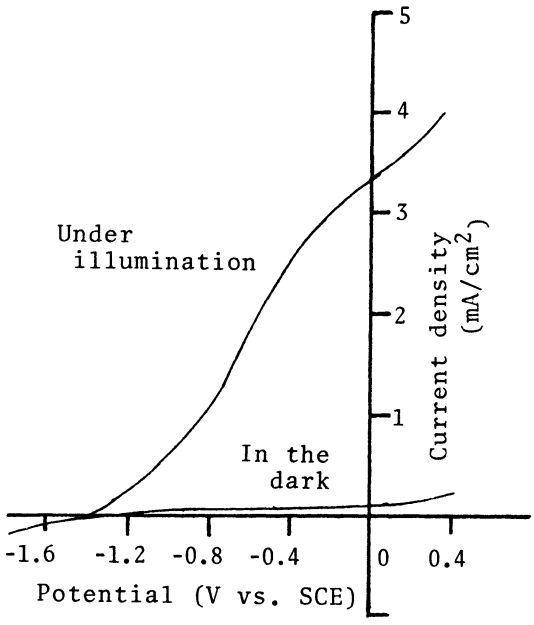

Fig.3 Current - potential curves for a evaporated CdS-ZnSe film electrode in 1 M NaOH + 0.5 M Na_2S solution

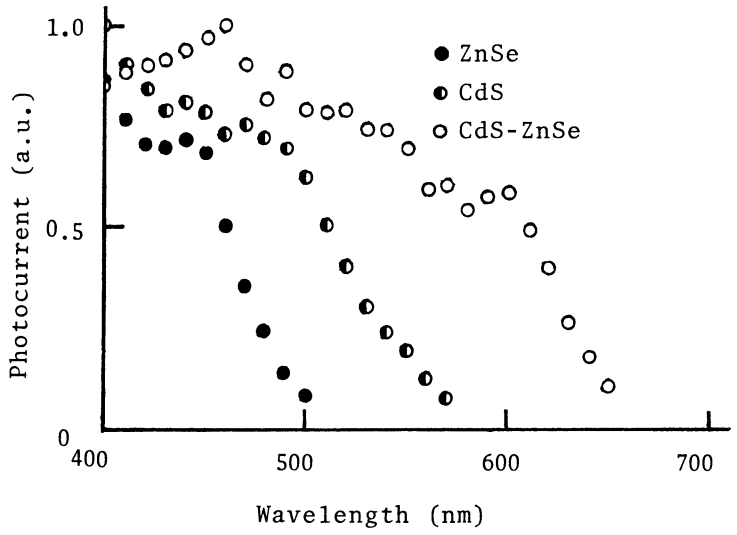

Fig.4 Spectral responses of the photocurrent for ZnSe, CdS and CdS-ZnSe film electrode
Photocurrents shown are corrected for variation in light intensity with wavelength.

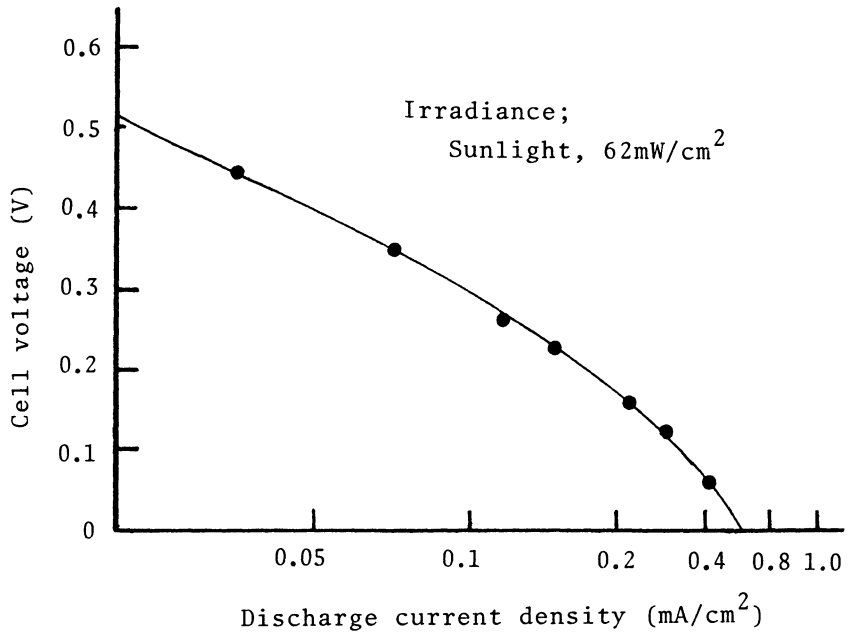

Fig.5 Current-voltage characteristics of CdS-ZnSe film/sulfide electrolyte/Pt photocell

up on a glass slide. A good ohmic contact was obtained by vacuum-evaporating indium onto the surface of the film. A copper wire was attached to the indium layer with a silver epoxy. After insulating this specimen, the film was detached from the glass slide. The test electrode thus obtained was used for the investigation of photoelectrochemical behaviors.

A standard three-electrode electrochemical cell was used for photoelectrochemical measurements and the solution used was 1 M NaOH + 0.5 M Na_2S. Spectral response of the photocurrent was determined by using monochromatized light from a 500 W Xe lamp.

Figure 3 shows typical polarization curves for a CdS-ZnSe solid solution film electrode in the dark and under illumination in an aqueous sulfide solution. The anodic

dark current is virtually zero in this potential region. Under illumination there appeared a large rise in anodic current commencing at about -1.4 V (vs. SCE). This photocurrent is attributed to the photoanodic oxidation of sulfide ions, as have already been reported for several n-type semiconductor electrodes.[1)-6)]

The action spectrum of this solid solution electrode was extended to the longer wavelength by about 100 nm compared with the CdS electrode, as can be seen from Fig.4. There appeared the drops in photoresponse at about 510 nm and 460 nm, which correpond to the bandgap energy of CdS and ZnSe, respectively. The extension of the action spectrum to the longer wavelength can be attributed to narrowing of the bandgap of this solid solution (2.3 eV)[11)] and the presence of the states within the forbidden band due to imperfections at the surface.[4)] The latter effect is specially prominent in the case of thin films.

The current - voltage curve of a typical cell using a CdS-ZnSe epitaxial film photoanode under sunlight is shown in Fig.5. The open-circuit voltage and the short-circuit current were 0.54 V and 0.7 mA/cm^2, respectively.

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