—Communication—

ESR Investigation on the Surface Transient in Particulate Photoelectrochemistry of CdS

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1 INTRODUCTION

Photoelectrochemical properties of metal sulfide semiconductors such as CdS are of interest for their potential use in the storage of solar energy. Numerous studies have been reported for the photocatalytic reactions with metal sulfide particles. In order to observe the reaction intermediate, electron spin resonance (ESR) spectroscopy has been applied.[1-3] Although the ESR spectra of holes trapped on sulfur ions were reported for ZnS,[1] only a preliminary report is available in the literature for CdS.[3] In the present study, ESR measurements were carried out for some kinds of illuminated CdS. The observed spectra that depend on the crystal structure were attributed to the trapped holes.

2 EXPERIMENTAL

Two kinds of powdery CdS were employed. One was synthesized from a $CdSO_4$ aqueous solution by bubbling H_2S at around 100 ℃.[4] Another was obtained from Nacalai Tesque Co. X-ray diffraction measurements revealed that the crystal structures of these CdS were entirely zinc blende and wurtzite, respectively. These CdS samples were immersed in a methyl viologen (MV) aqueous solution and dried in vacuo. The amount of MV impregnated was 0.1 mol % of CdS.

The ESR tube containing the sample was evacuated and the spectra were measured with an X-band ESR spectrometer (JEOL RE2X) at 77K. During the measurements, the sample was irradiated with a 500W mercury lamp (Ushio USH-500D) through a 360-nm band pass filter (Toshiba UV-D36C).

3 RESULTS AND DISCUSSION

The ESR spectra obtained from the wurtzite and zinc blende CdS are shown in Fig.1-a and b. These spectra are labeled (A) and (B), respectively. Spectrum (B) includes a broad signal around g=2.039 and a concavity at g=2.030 beside a fairly large signal around g=2.007. On the other hand, spectrum (A) consists of only the signal around g=2.007. This observation suggests that the difference in the crystal structure originates in the chemical structure of radical species produced at the illuminated CdS. The radical species are suspected to be the hole trapped at sulfur atom. Although absorption of photons by semiconductors generates pairs of electron and hole, the electrons probably reduce Cd^{2+} into Cd^0,[5] which affords no ESR signal.

In order to confirm that the observed signal arises from the trapped hole, ESR measurements were done for CdS loaded with an electron acceptor MV. For zinc blende CdS, the spectrum is shown in Fig.1-c. A new intense symmetric signal appeared around g=2.003 with the line width ΔH of 1.39 mT, and is labeled (C). Besides signal (C), the broad signal (B) around g=2.039 increased with the addition of MV. When the microwave power of the ESR spectrometer was varied, saturation of signal (C) occurred at a 10-fold lower power than that of (B). This observa-

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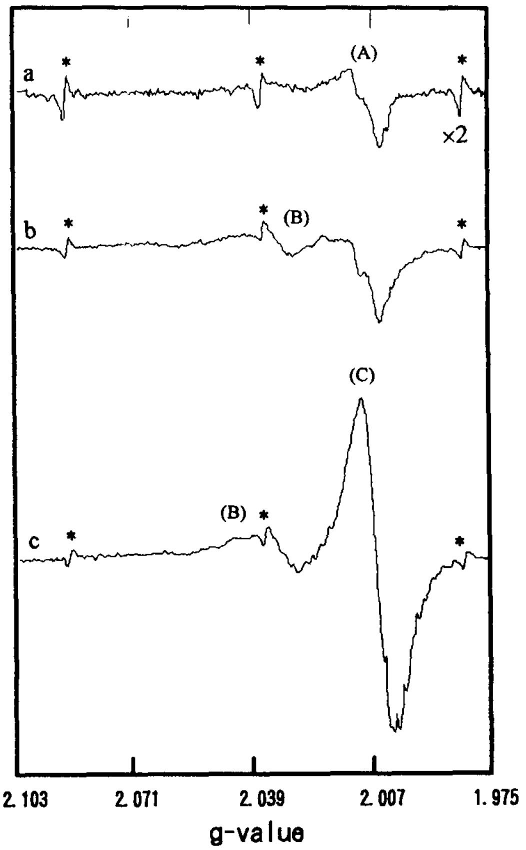

Figure 1 Light-induced ESR spectra obtained at 77K for CdS powders having the crystal structures of wurtzite (a) and zinc blende (b), and for zinc blende CdS loaded with electron acceptor molecules MV(c). The signals (*)are from Mn^{2+} of the g-value marker.

tion shows that (C) has a longer spin relaxation time, suggesting that it is an organic radical.6) Moreover, by comparing with the reported ESR spectra of MV radical formed on a polymer film, 7) the g-value of (C) is identical and the ΔH is consistent with the reported values of 1.25 - 1.66 mT. The formation of MV radical implies the utilization of photoinduced conduction band electrons. Then, the increase of signal (B) with the formation of MV radical indicates that the signal originates in photoinduced valence band holes.

For wurtzite CdS, similar formation of MV radical was observed. However, increase of signal (A) could not be recognized because of the large signal of MV radical. When an electron donor, 2-propanol, was contacted with wurtzite CdS, signal (A) disappeared. This fact suggests that the radical of signal (A) has an oxidation ability, and hence can be assigned to the trapped hole.

Micic and coworkers3) reported an ESR signal obtained for CdS particles in acetonitrile after irradiation with several thousands of 308-nm excimer-laser pulses. The signal is analogous to (A). Although they attributed the signal to the hole trapped on sulfur ions, no experiment was reported to confirm the assignment. Shono measured g-values of the hole localized on the sulfur ions in an electron-irradiated ZnS single crystal. The large anisotropy of g-values reported is similar to that of (B). The large anisotropic g-value stems from the large spin-orbital coupling constant of sulfur atom.

In conclusion, we have observed two types of ESR signals formed at irradiated CdS of different crystal structures. The signals are attributed to the trapped holes. Further investigations directed to the surface reaction are under way.

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