Local Atomic Structure and Electronic State of ZnS Films Synthesized by Using CBD Technique

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We have succeeded in synthesizing ZnS films on substrates such as glass or Si wafer by using CBD (chemical bath deposition) method. These semiconductor films were photocatalytic and showed high productivity of hydrogen gas from the solution containing HS⁻ ions. From observation of SEM/TEM, it was found that the cluster film consisted of 100 nm sized agglomerated particles composed of nano-crystals. The result of EDS analysis for the cross-section of the film prepared by using FIB showed the presence of small amounts of oxygen along with zinc and sulfur. The information of the local quantum structures obtained from EXAFS/XANES analysis suggested that the cluster film has unique atomic-distribution and metastable electronic state different from bulk ZnS and ZnO. Based on the results of the above analysis, the relation between local quantum structures and properties was proposed.

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1. Introduction

Semiconductors, becoming more essential in various fields as functional materials, are expected to have useful properties, which are not observed in bulk state, especially in nanometer-sized cluster. ZnS is a typical II–VI semiconductor with band gap of 3.5 eV in bulk, therefore, it creates excited electrons by the light irradiation of wavelength under 350 nm. The photo-excited electrons can be used in some redox reactions in aqueous solutions.

The photo-exciting and moving the electrons inside, or the electronic interaction with outside species are thought to be deeply related to the local quantum structures, such as the atomic distribution or the electronic state in the semiconductor. In recent years, renewed interest is being shown towards the photochemical reaction processes at semiconductor-electrolyte interfaces to convert solar energy into electrical or chemical energy. In the photocatalytic hydrogen generation, it was reported that a submicron-sized particle with what is called the “stratified” structure, such nanolayer consisted of nano-clusters, has been reported to show high activity.¹ When we consider the use of semiconductor clusters as a photo-functional material, the film form is suitable for effective photo acceptance and easiness in handling compared to fine particles. Among various film synthesis methods, the chemical bath deposition (CBD) is a potential technique because of its simplicity and low reaction temperature. CBD method has been used to synthesize various semiconductor films, particularly chalcogenide materials such as CdS, CdSe, PbS, and so on. Generally in the CBD process, a complexing agent is used to regulate the precipitation of the corresponding bulk metal compounds into the solution. The metal complex ion buffers the reaction solution with the free metal ion at low concentrations. Substrates are immersed in the solution containing the metal ion, the complexing agent, and the chalcogenide source. Then, the compound films are deposited by heterogeneous reaction at the surface of the substrates. In this paper, we report the synthesis of ZnS film with high photocatalytic activity by CBD and discuss the relation between local atomic structure, electronic state and photocatalytic activity.

2. Photocatalytic Reaction by Semiconductors

In general, when a semiconductor is exposed to light radiation energy higher than its band gap, the electron in the valence band (VB) is excited to the conduction band (CB). As a result, a free electron exists in the CB and a hole is created in the VB. In the photocatalytic reaction scheme, the free electron in the CB moves to the surface of particle and reduces the ion at the interface. On the other hand, the hole accepts an electron from the ions that are oxidized at the interface. It has been reported that ZnS show high photocatalytic activity, when the transfer of electron to the hole through the oxidation of a reducing agent and hydrogen evolution through the reduction of proton in water take place in pair.² Here, Na₂S has been used as the reducing agent. In neutral to weakly alkaline region, Na₂S dissociates according to reaction (1); Na₂S + H₂O → 2Na⁺ + HS⁻ + OH⁻. The HS⁻ ions, produced in this reaction, act as the reducing agent by getting oxidized to form poly-sulfide Sₓ⁻ ions according to reaction (2); 2HS⁻ + 2h⁺ → 2H⁺ + S²⁻. The electron and the hole produced in the semiconductor are consumed in reactions (2) and (3); 2H⁺ + 2e⁻ → H₂. As a result of these reactions in the presence of light irradiation, hydrogen is evolved.

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3. Experimental

3.1 Synthesis of samples

In most cases of the CBD process, ammonia (NH₃) has been used as the complexing agent. However, heterogeneous reaction onto substrate in the case of ZnS was prevented by the very high stability constant of the zinc tetraammine complex ion ([Zn(NH₃)₄]²⁺). The deposition of ZnS thin films by CBD was possible with the use of hydrazine (N₂H₂) in addition to ammonia.³

The reagents used in present work are zinc sulfate heptahydrate (ZnSO₄·7H₂O), thiourea (SC(NH₂)₂), 25% ammonia solution, ammonium sulfate ((NH₄)₂SO₄), and 100% hydrazine monohydrate (N₂H₄·H₂O) and they were all of high commercial quality (Wako Chemical Co. Ltd.). The experimental procedure for the synthesis of ZnS film was as follows: 100 mL of chemical bath solution containing various reagents with specific concentrations prepared at room temperature was introduced into a beaker. After the substrate was immersed in the solution, the beaker was heated up to 85°C, and maintained at this temperature for 10 min. Then, the substrate was allowed to remain in the solution for 6 h at room temperature. 100 nm thick ZnS film can be achieved by repeating the experiment three times under similar conditions.

We used three forms of samples, namely bulk, coprecipitated nano-particles and stratified particles to compare with the CBD film. The bulk ZnS was used as a reference sample having the crystal structure of zinc blende type (Kojundo Chemical Lab Co. Ltd.). The coprecipitated ZnS was synthesized using solutions of 0.1 kmol/m³ ZnSO₄·7H₂O and 0.1 kmol/m³ Na₂S. Synthesis procedure of the stratified-ZnS is as follows:¹ After 4 N of 5N ZnO (Kojundo Chemical Lab Co. Ltd.) was introduced to 100 mL of distilled water and sonicated, 100 mL of 0.2 kmol/m³ Na₂S solution was added and mixed for 48 h.

3.2 Evaluation of photocatalytic activity

The photocatalytic activity of the ZnS film was evaluated from the amount of hydrogen produced when the film deposited on soda lime glass plate with 20 mm × 30 mm size was immersed in 0.1 kmol/m³ Na₂S solution and exposed to 500 W high-pressure mercury lamp. To transmit UV light, the reaction cell was made of quartz glass.

3.3 Characterization

The grain sizes and the photo-absorption spectroscopic properties were measured by X-ray diffractometer (MultiFlex, Rigaku Co.) and the UV-VIS photospectrometer (U-3300, Hitachi Co.). The morphology of the ZnS film was observed by the scanning electron microscopy (SEM) (Hitachi S4100) and the transmission electron microscopy (TEM) (HF2000, Hitachi Co.). The elemental distribution in the film was analyzed by the energy dispersive X-ray spectrometer (EDS) (VANTAGE, NORAN Instruments). In order to analyze the cross section of samples, the focused ion beam (FIB) (FB-2000A, Hitachi Co.) was used. The electronic state of the zinc ions and the local atomic structure of the film were determined by the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) spectra obtained by using the X-ray absorption spectrometer (R-EXAFS 2100S, Rigaku Co.).

4. Results and Discussions

4.1 Morphology

Figure 1 shows the X-ray diffraction (XRD) profiles of three ZnS powder samples. All of them had a crystal structure of zinc blende type. It was showed that coprecipitated ZnS had the smallest grains and the stratified-ZnS had medium one in the three samples considered here. In case of the CBD ZnS film, no diffracted peak was detected in the XRD profile. Figure 2 shows the morphology of CBD ZnS film synthesized under the following conditions: The composition of the chemical bath solution was 0.01 kmol/m³ ZnSO₄·7H₂O, 0.01 kmol/m³ SC(NH₂)₂, 0.5 kmol/m³ NH₃, 1.0 kmol/m³ N₂H₄, and 0.1 kmol/m³ (NH₄)₂SO₄. The SEM observation revealed that the ZnS film consisted of 100 nm sized agglomerated particles, and the film thickness was equal to the diameter of the agglomerates. When this film was analyzed for its structure using XRD, no peak was recorded due to nanometer sized fundamental structure units of the agglomerates. This was confirmed from the TEM photograph of the cross-section of CBD film fabricated by using FIB as shown in Fig. 3. The size of these fine particles was about 5 nm or less and each grain showed high crystallinity. From the EDS analysis, it was confirmed that this film contained zinc, sulfur, and small amount (10–20 at%) of oxygen.

4.2 Photocatalytic property

The UV-VIS absorption spectrum of the film (Fig. 4) showed a broad absorption edge around 350 nm of wavelength and this corresponded to the band gap of bulk ZnS. This result showed that the excitation of electron has occurred in the CBD ZnS film by UV light. The rate of hydrogen produced was constant at 2.5 mL/h per 1 cm² of irradiated area, for 500 W high-pressure mercury lamp as the source of light. For comparison, similar measurements were carried out for bulk, coprecipitated and stratified ZnS powders, and the rates were mere 0.5, 1.0 and 2.0 mL/h, respectively, despite total absorption of the irradiated light.
4.3 Local atomic structure and electronic state

To investigate the atomic distribution around Zn and electronic state of the CBD ZnS film, the X-ray absorption spectroscopic measurements were carried out at Zn K absorption edge (9663 eV) in fluorescence-mode at low incidence angle. Figure 5(a) shows the XANES spectrum of the CBD film along with structural standard samples of ZnS and ZnO powders. It was easily found that the XANES profile for the CBD film was different to that of ZnO, ZnS, or their mixture. There was little characteristic peak in the spectrum of the CBD film. In addition, it should be noted that considerable edge shift of about 2 eV toward higher energy side was also observed. Similar feature was observed in the XANES spectrum of stratified-ZnS particle as shown in Fig. 5(b). However, the coprecipitated-ZnS showed a profile similar to the reference sample in spite of nanometer-sized particle. Therefore, these results showed the features in the electronic state of CBD film and stratified-ZnS were not due to fine particle size or large surface area. Figure 6 shows the Fourier transforms of $k^3$ weighted EXAFS spectra for the wave vector $k$ space between 25 and 120 nm$^{-1}$ of ZnS and ZnO standard powders, and the CBD film. These correspond to radial distribution function and indicates the atomic distribution around Zn. Zn–S and Zn–O distances calculated by least-square parameter fitting of the Fourier filtered spectra from nearest neighbor correlation peak in Figs. 6(a) and (b) are 0.234 and 0.195 nm, respectively. Broken lines in Fig. 6 show calculated atomic-pair correlations of Zn–S and Zn–O. In the CBD film, the contribution due to atomic ordering in long range was not large. From comparison with the profiles for Zn–S and Zn–O correlations, it seemed that the nearest neighbor atom around Zn was oxygen, and not sulfur. This was confirmed fitting Zn–O pair than Zn–S with the experimental data. It had been reported that the reaction with hydroxide ions as well as with chalcogen ions occur at the surface of the substrates in the CBD chalcogenide film growth process for such as CdS, ZnSe. From these considerations, existence of ordered oxygen atoms and disordered sulfur atoms in distance from Zn atom should be considered. On the other hand, both coprecipitated and stratified ZnS powder samples were almost similar to standard ZnS in the radial distribution around Zn atom.

Observed features in the XANES profile of the CBD film and the stratified ZnS particles reflected the electronic state of Zn, and the above features remained even after exposed to the UV light irradiation and constant rate of hydrogen evolution for over 4 h. In the coprecipitated ZnS particles whose local quantum structures resembled the bulk ZnS, the photocatalytic activity was considered mostly due to large surface area. The XANES results suggested that the CBD films and the stratified ZnS particles had certain metastable electronic state and this was the key for improved photocatalytic activity as shown Fig. 5(c). It could be considered that the metastable state was induced by the atoms surrounding Zn, and in case of the CBD films, we can consider that relatively ordered oxygen and disordered sulfur distribution around Zn induce the...
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Fig. 5 XANES spectra for (a) the CBD film comparing with standards ZnS and ZnO, (b) coprecipitated and stratified ZnS powder samples comparing with standard ZnS, and (c) is schematic figure of electronic states in bulk and stratified/CBD-film ZnS.

Fig. 6 Fourier transform of \( k^3 \) weighted EXAFS spectra \( k^3 \chi(k) \) for standards of ZnS (a) and ZnO (b), and the CBD ZnS film (c). Calculated atomic pair correlations of Zn–S and Zn–O were drawn by broken lines.

5. Conclusion

The CBD film, which showed high photocatalytic activity, had the local atomic structure and electronic state different to the bulk ZnS. As a result, it could consequently be said that in the CBD film (a) the electronic state of Zn was different from the one in either bulk ZnS or ZnO, and (b) oxygen atoms around Zn were relatively much ordered than sulfur. These features observed in the CBD ZnS films were not found in even though coprecipitated ZnS consisted of nanometer-sized particles. Especially, the shift of Zn K absorption edge toward higher energy side in the XANES spectrum of the CBD film suggested that the potential of outer shell’s orbital was upheaved by the unique atomic distribution around Zn. Consequently, the transformation of the photo-excited electrons to protons at the surface of the film in aqueous solution was achieved more easily and the CBD film showed high photocatalytic activity.

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