Mechanism for CdS electrodeposition from fused salt

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Electrodeposition of CdS on a graphite substrate from LiCl–KCl eutectic melt containing $CdCl_2$ and Na_2SO_3 has been examined. It has been found that the cathodic deposition of CdS onto a graphite substrate occurs in competition with the formation of CdS particles by homogeneous precipitation in the bath. We have proposed as a deposition mechanism that the underpotential deposition of cadmium occurs under the influence of some sulphur species. We have also found that crystals of solid solution of CdS–CdSe are electrodeposited by adding selenium powder in the bath.

1. Introduction
The cadmium chalcogenides (CdX; X = S, Se, Te) are one of the most promising classes of semiconductors in solid-state as well as in liquid-junction solar cells. Various kinds of preparation techniques have been reported in recent years [1].

We have been studying fused salt electrolysis as a novel technique for obtaining CdX films. The morphology, crystal structure and chemical composition of CdSe and CdTe films prepared with this technique have already been reported, and a deposition mechanism has been proposed [2–4]. Electrodeposition at an elevated temperature has an advantage of obtaining deposits with a high crystallinity due to the additional (thermal) energy supplied to the system. Accordingly, the as-deposited CdSe films thus obtained give solar energy conversion efficiencies higher than 6.1% [2]. As to the reaction mechanism, we have found that the reaction is initiated with the cathodic deposition of selenium or tellurium, followed by the underpotential deposition of cadmium [3, 4]. This mechanism, however, does not seem to apply to the CdS deposition because of a difficulty in depositing sulphur.

Recently, Illieva's group has reported that CdS films can be deposited from a fused salt containing $CdCl_2$ and Na_2SO_3, and has outlined the effects of some variables on the morphology and crystal structure [5, 6]. The reaction mechanism, however, has not been described yet.

In this paper we describe our attempt to deposit CdS onto graphite by means of fused salt electrolysis and discuss the reaction mechanism in comparison with that of CdSe and CdTe electrodeposition.

2. Experimental procedure
The experimental apparatus is identical with that in our previous paper [2].

$CdCl_2$ (0.005 mol) and Na_2SO_3 (0.005 mol) were added to the LiCl–KCl solvent (23 g) of the eutectic composition (LiCl 0.236 mol, KCl 0.172 mol) as the source materials of cadmium and sulphur, respectively. All chemicals used were reagent grade.

The electrolysis was performed under potentiostatic conditions using a conventional three-electrode configuration, as we have previously found the potential-dependent deposition of CdSe and CdTe [3, 4]. As an Ag/AgCl electrode was used as a reference electrode, all potential values in the present paper are expressed with respect to this electrode. Both the working electrode (substrate) and the counter electrode were graphite plates, in which the latter had a larger surface area than the former. Nitrogen gas was carefully purified by passing through $Mg(ClO_4)_2$, ascarite, concentrated H_2SO_4 and copper powder heated at 250° C, and was introduced into the Pyrex chamber to prevent oxidation of the deposits and to prevent moisture from reacting with the fused salt. After the electrolysis was completed, the working electrode was slowly pulled up from the bath, cooled in a purified nitrogen atmosphere and then dipped in a 1% HCl solution followed by rinsing thoroughly in distilled water to remove solvents and solutes stuck to the deposits.

The crystal structure and the morphology of the deposits were examined using an X-ray diffractometer (Rigaku Denki 2024) with a copper target X-ray tube and nickel filter, and a scanning electron microscope (SEM) (Akashi Seisakusho ISI-40W), respectively.

3. Results and discussion
3.1. Structure and morphology of electrodeposits
In the initial experiments, electrolysis was carried out at various potentials (−0.4, −0.5, −0.6, −0.7, −0.8, −0.9 and −1.0 V) in LiCl–KCl melts containing 0.005 mol $CdCl_2$ and 0.005 mol Na_2SO_3 at 450° C. The first finding was that CdS could not always be deposited onto graphite electrodes in contrast to the case of CdSe and CdTe deposition. The second finding was that CdS precipitates were formed in the bath at
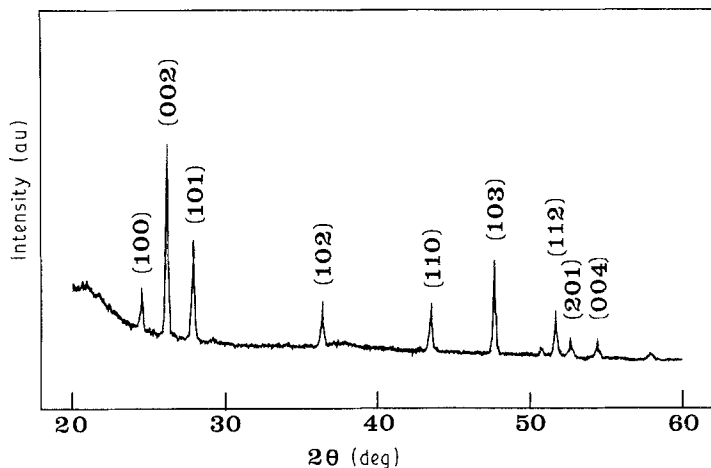
all potentials examined, and that apparent current efficiencies of forming such precipitates were independent of current density, and higher than 100% in some cases. Deposits with a yellow colour were found on graphite electrodes only when electrolysed at − 0.5 V. The electrolytic potential was fixed at − 0.5 V in the following experiments.

An X-ray diffractogram of as-grown deposits formed on a graphite electrode at a potential of − 0.5 V is shown in Fig. 1. All peaks belong to the α-CdS (hexagonal) phase. This agrees with the previous reports of Markov *et al.* [5, 6]. But in contrast with their results, the deposits obtained in our experiments showed no marked preferential growth along the *c*-axis. This may be attributed to the difference in substrates used; copper or silver in their experiments, and graphite in our experiments. In our earlier experiments on CdSe (hexagonal) electrodeposition from the fused salt, we have previously reported that the crystallinity of the deposits depends upon the electrolytic potential and that a very strong and sharp peak assigned to (0 0 0 2) of CdSe appears in X-ray diffractograms of the deposits obtained at relatively positive electrolytic potentials [2]. This indicates a high crystallinity and a preferential crystal growth along the *c*-axis even on porous graphite substrates. Similar dependence of the crystallinity of deposits on potential might also be observed in the case of CdS deposition, if the deposition occurs in a wider range of potentials.

The morphology of the deposits is seen in SEM micrographs in Fig. 2. A graphite substrate is covered with plenty of hexagonal-shaped crystals, the size of which is around 5 μm. Hexagonal hollow crystals are also deposited. Such a morphology resembles that of CdSe (hexagonal) deposits obtained from a fused salt [2]. Thus we suggest that hollow crystals tend to grow in the fused salt electrolysis.

On occasion, no deposit was found even under the same experimental conditions, which suggests a poor reproducibility in obtaining CdS electrodeposits. Also, a repetitive use of the same fused salt resulted in no electrodeposition of CdS. This may imply that substances in the melt are changed by certain chemical reactions at this temperature. As mentioned earlier, yellow precipitates were formed in the bath, which were identified as CdS powder. This reaction occurs without applying voltage between electrodes. This means that CdS can be formed by certain chemical reactions of cadmium and sulphur at 450° C in this melt. The cessation of deposition during electrolysis, and the poor reproducibility in obtaining CdS electrodeposits, could then be attributed to a lack of cadmium and/or sulphur sources due to such chemical reactions. We observed with the naked eye the gradual formation of a yellow substance after adding $CdCl_2$ and Na_2SO_3 in the LiCl–KCl melt.

Figure 3 presents SEM photographs of the precipitates in the melt. No peak was found other than CdS (hexagonal) in the X-ray diffraction patterns of the precipitates. We have reported the synthesis of ternary Cu–In–S compound semiconductor powder by the homogeneous precipitation technique in an aqueous
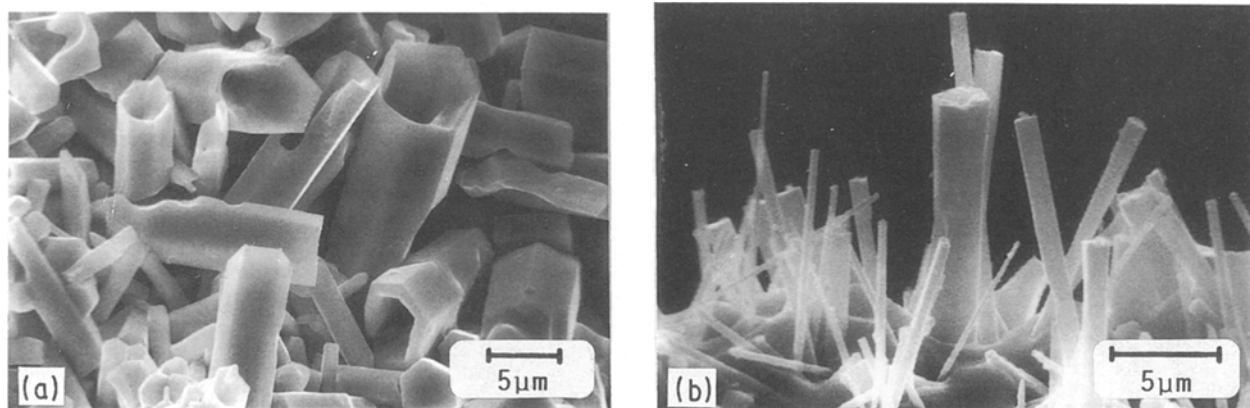

Figure 2 SEM micrographs of deposits. Deposition potential, − 0.5 V. (a) From above, (b) cross section.
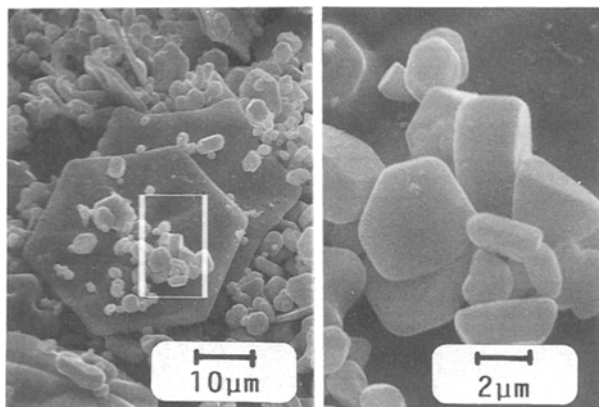
Figure 3 SEM micrograph of precipitates in the bath at 450° C.

solution [7–9]. The above formation of CdS precipitates can be regarded as a kind of homogeneous precipitation technique in a fused salt. This may apply to the formation of other compound powders of interest.

3.2. The mechanism for CdS electrodeposition

Examining in more detail the chemical reactions occurring in the bath would help to clarify the mechanism for the CdS electrodeposition. Taking into account the result that CdS is precipitated in the bath, it is apparent that S^{2-} ions are formed by chemical reactions in the bath at an elevated temperature.

To discover the other products of the chemical reactions, $BaCl_2$ was added to the supernatant solution which was prepared by dissolving the solidified salt in distilled water and filtering. White substances were then precipitated. The X-ray diffractogram of the precipitates is shown in Fig. 4. All the peaks in this figure, which are not strong, can be assigned to BaS_2O_7. Thus it is reasonable to assume that SO_3^{2-} ions decompose into S^{2-} and $S_2O_7^{2-}$ ions by the disproportionation reaction at this temperature, which may be expressed as

$$8SO_3^{2-} \rightleftharpoons 2S^{2-} + 3S_2O_7^{2-} + 3O^{2-} \qquad (1)$$
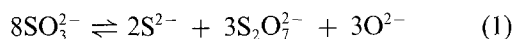
As this reaction proceeds, S^{2-} ions are formed, react immediately with dissolved Cd^{2+} ions, and form CdS precipitates. As S^{2-} ions are thus removed as the precipitate, reaction 1 proceeds to the right-hand side so long as Cd^{2+} ions are left in the bath.

The equilibrium of this disproportionation should depend upon the reaction temperature. So we measured the yield of CdS precipitation as a function of bath

temperature. The results are shown in Fig. 5, where reaction time was fixed at 1 h in all cases. The reaction yields in Fig. 5 were calculated on the basis of the assumption that dissolved SO_3^{2-} ions decompose according to reaction 1, and the S^{2-} ions thus formed completely change to CdS. So the reaction yield of 100% means that SO_3^{2-} ions added completely decompose to form CdS precipitates. It can be seen from Fig. 5 that at higher temperatures the reaction yields approach 100% and it becomes impossible to deposit CdS electrolytically because of a lack of SO_3^{2-} ions in the bath. Conversely, it is expected that by lowering the bath temperature, the equilibrium of reaction 1 is shifted to the left and, in turn, successive electrodeposition of CdS can occur. Based on this consideration, electrolysis was carried out at a bath temperature of 380° C. As a result, electrodeposits of CdS on graphite substrates were obtained with better reproducibility, confirming the validity of reaction 1. But even at this temperature, CdS precipitation occurs slowly, resulting in the cessation of electrodeposition from the same bath. It is virtually impossible to use lower temperatures than this as long as the LiCl–KCl eutectic solvent is used, as the melting point of this solvent is 352° C.

It is concluded from the above results that (i) electrodeposition of CdS competes with a chemical formation of CdS, and (ii) SO_3^{2-} ions participate in the electrodeposition of CdS, whereas S^{2-} ions, formed by reaction 1, take part in the chemical formation of CdS.

We shall now consider the mechanism for electrodeposition of CdS. As in CdSe deposition, the galvanostatic electrolysis was carried out in the melt containing only the cadmium source ($CdCl_2$) at a current density of $-45\,mA\,cm^{-2}$, followed by adding Na_2SO_3 during electrolysis.

As shown in Fig. 6, the potential of a graphite working electrode before adding Na_2SO_3 is about $-0.6\,V$, which coincides well with the redox potential of Cd/Cd^{2+} reported ($-0.589\,V$; [10]), indicating the occurrence of stationary cadmium electrodeposition. The electrode potential shifts gradually toward the positive direction after Na_2SO_3 is added into the melt and reaches about $-0.5\,V$. CdS deposit was found on the graphite electrode in this case. Note that the electrodeposition onto a graphite electrode takes place only at $-0.5\,V$ in the potentiostatic electrolysis experiments, as described in 3.1 above.

On the other hand, electrode potential under similar electrolysis conditions in the melt containing only the sulphur source (Na_2SO_3) was unstable, and no change
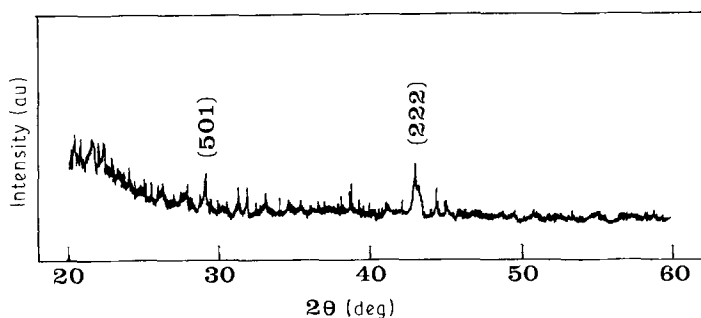

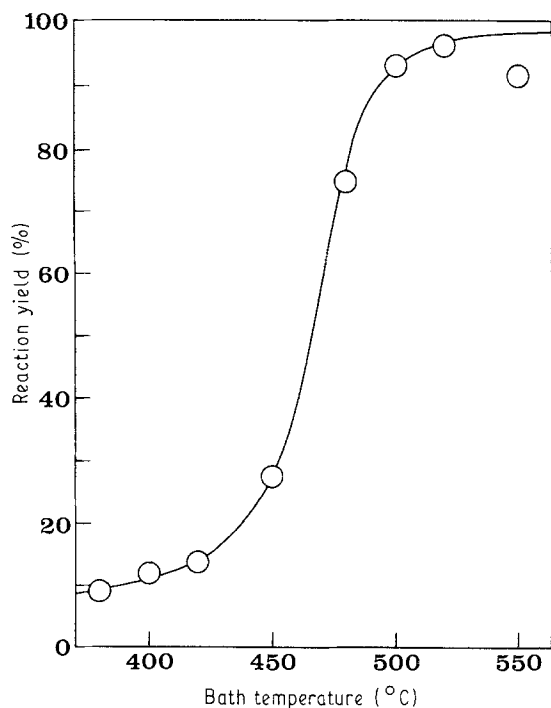*Figure 4* X-ray diffraction pattern of the BaS_2O_7 precipitate.

Figure 5 Bath-temperature dependence of reaction yield for CdS precipitation in the bath. Reaction time, 1 h.

shown in Fig. 6, probably because of a strong affinity of cadmium and sulphur sources.

The occurrence of the reaction of cadmium and with a sulphur species in a SO_3^{2-}-containing melt was confirmed by our result that the addition of cadmium plates and Na_2SO_3 into the KCl–LiCl melt leads to the formation of a small amount of CdS precipitates.

From the analysis of the reaction mechanism, the first experimental result that CdS electrodeposits are found only when electrolysed at $-0.5\,V$ can be explained as follows. At potentials more positive than $-0.5\,V$, the reduction of cadmium ions should not occur. On the other hand, at potentials more negative than $-0.6\,V$, the electrodeposition of cadmium takes place quickly, even from a bath free from sulphur source. So it is probable that the electrodeposits at these potentials are a mixture of cadmium metal and CdS. Cadmium metal thus deposited is in a liquid state at 450°C and so tends to fall down in the bath. Our observation in the first experiment is thus explained.

Figure 7 shows the weight of electrodeposits on a graphite substrate against the electric charge passed during electrolysis at $-0.5\,V$. The linearity suggests the constancy of the current efficiency during CdS electrodeposition. From the slope of this straight line, the apparent number of electrons transferred during this process was estimated to be about three. Considering that some of the CdS deposits fall down during the thorough rinsing of the deposit in a diluted HCl solution, it must be less than three. This value is not inconsistent with the deposition mechanism proposed above.

in the electrode potential by the addition of $CdCl_2$ during electrolysis was observed. In this case, no CdS deposit was found.

In our previous paper [3] we proposed that the initial stage for CdSe electrodeposition from the fused salt is selenium deposition, followed by the underpotential deposition of cadmium. We conclude from the results presented here that in the case of CdS deposition, in contrast, the initial step is cadmium deposition, followed by the reaction of the deposited cadmium with a sulphur source, resulting in CdS formation. Ignoring the fact that Cd^{2+} ions may be complexed with solvent molecules or anions, this electrodeposition process can be expressed as

$$Cd^{2+} + 2e + S\ species \rightarrow CdS \qquad (2)$$

although the exact chemical formulae of sulphur species are not clear yet. The underpotential deposition of cadmium also occurs in this case, as is evident from the potential shift by the addition of Na_2SO_3
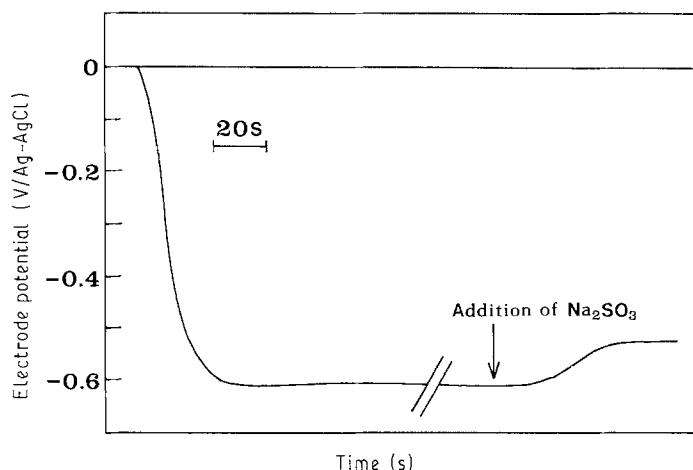
3.3. Electrodeposition of CdS_xSe_{1-x}

The theoretical energy conversion efficiency for a liquid-junction solar cell depends upon the band-gap of the semiconductor and the flat-band potential of the semiconductor in the electrolyte. In this respect, it is interesting to examine the possibility of obtaining the mixed CdS–CdSe materials by this technique, because incorporation of selenium into CdS can change both the band-gap and the flat-band potential of CdS.

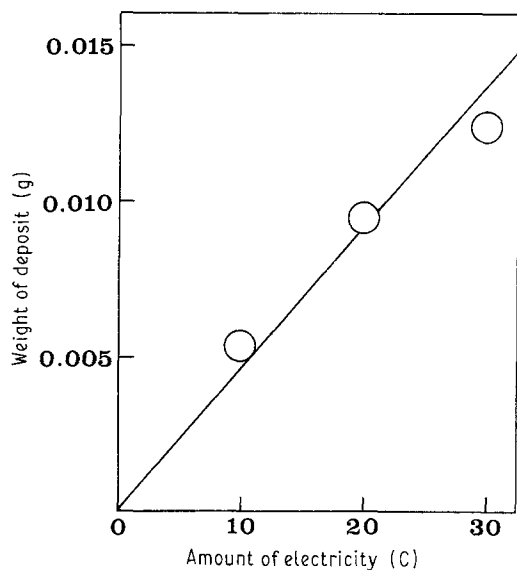As a preliminary experiment in obtaining CdS_xSe_{1-x} film, a small amount of selenium powder

Figure 6 Electrode potential change with time under galvanostatic electrolysis of $-45\,mA\,cm^{-2}$ in the bath containing $CdCl_2$.

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Figure 7 Weight of deposit against amount of electricity during electrodeposition of CdS at −0.5 V.

was added to the melt together with $CdCl_2$ and Na_2SO_3, and potentiostatic electrolysis was carried out under the same conditions as for CdS electrodeposition. Brownish electrodeposits were found on a graphite substrate electrolysed at −0.5 V. Peaks in X-ray diffractograms of the deposits are at diffraction angles between those of CdS and those of CdSe. Such shifts of X-ray diffraction peaks show that the obtained deposits are solid solution of CdS and CdSe

(CdS_xSe_{1-x}), as expected from the colour of the deposits. Further work on obtaining CdS_xSe_{1-x} with various x values is now in progress.

Acknowledgement

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