

# Control in Crystal Structure of CdS Fine Powders by Chemical Bath Method

M.Inagaki and Y.Yashiro

Graduate School of Engineering, Hokkaido University, Kita-ku, Sapporo 060, Japan  
Fax: 81-11-706-6575, e-mail: ina@eng.hokudai.ac.jp

**Abstract:** The effect of precipitation condition on the crystal structure of CdS particles by chemical bath method was studied by using three sulfide compounds, thiourea (TU), thioacetamide (TAA) and Na<sub>2</sub>S, and two additives, triethanolamine (TEA) and tetramethylammonium hydroxide (TMAH). Reaction rate between cadmium and sulfide ion was found to govern the crystal structure of CdS; rapid reaction resulted in zincblende-type structure with poor crystallinity and slow reaction in wurtzite-type structure with relatively high crystallinity. The effects of starting ratio of sulfide compounds to cadmium ions (S/Cd) and pH value of the solution were not appreciable. Titration of sulfide compound solution into cadmium solution gave wurtzite-type CdS and zincblende-type one was obtained in the reverse way. By annealing, zincblende-type structure transformed to wurtzite-type at 300°C, therefore the former being metastable phase at room temperature, and a pronounced growth of wurtzite crystals was observed above 500°C.

**Keywords:** cadmium sulfide, chemical bath method, crystal structure, titration, phase transition

## 1. Introduction

Cadmium sulfide, CdS, has been attracted attention as the material for a variety of optoelectronic devices, such as an electrode in thin film solar cells etc. It can be easily precipitated as fine particles from aqueous solution containing cadmium ions by babbling hydrogen sulfide gas. For the application as the parts of electronic devices, however, it was required to be a thin film. Therefore, different techniques have been applied to prepare the thin film of CdS, such as vacuum evaporation [1], sputtering [2], spray pyrolysis [3] and electrolysis [4,5].

Recently, so-called chemical bath deposition (CBD) method was developed to deposit CdS thin film on some substrates, of which the principle was the same as the conventional precipitation method from aqueous solutions, but the nucleation on the substrate had to be controlled [6-9]. In these precipitation methods, the direct control of crystal structure and their crystallinity was not easy, even not taken care in most works, though they were expected to have certain influence on electronic properties. In CBD method, most of the as-prepared CdS films were a mixture of two phases, wurtzite- and zincblende-types, and were often annealed at high temperatures to make it a single phase of wurtzite-type and to eliminate any defects such as stacking faults [8,9].

On the other hand, the process for mono-dispersed CdS particles from concentrated solution was also investigated [10,11]. Though the formation mechanism of mono-dispersed CdS particles was expected to relate with the concentration of cadmium and sulfide ions, the relation between the concentration of either cadmium or sulfide ions in the solution and the crystal structure obtained was not studied in detail.

In the present study, the effects of different conditions, involving different reagents of sulfide ions, pH of the solution and methods for mixing reagents, on the crystal structure of the precipitates were studied in order to obtain a single crystalline phase of CdS fine powders. The structural change in CdS powders by annealing at high temperatures was also examined.

## 2. Experimental

The powder samples of CdS were obtained by mixing three aqueous solutions of cadmium, sulfur and additives. Cadmium acetate in reagent grade was selected as cadmium source. As sulfur source, thiourea ((NH<sub>2</sub>)<sub>2</sub>CS, TU), thioacetamide

(CH<sub>3</sub>CS(NH<sub>2</sub>), TAA) and sodium sulfide (Na<sub>2</sub>S) were used. TU has frequently been used for preparing CdS thin film by its slow decomposition [6-9] and TAA for preparing mono-dispersed CdS particles with rapid precipitation [10,11]. Na<sub>2</sub>S emits sulfide ion due to its abrupt dissociation and gives rapid precipitation of CdS. As additives, triethanolamine (N(CH<sub>2</sub>CH<sub>2</sub>OH)<sub>3</sub>, TEA) and tetramethylammonium hydroxide (N(CH<sub>3</sub>)<sub>4</sub>OH, TMAH) were used.

In most cases for preparing CdS particles, cadmium solution with its concentration of 0.05 mol dm<sup>-3</sup> and additive solution with 0.40 mol dm<sup>-3</sup>, 20 cm<sup>3</sup> each, were mixed and stirred at room temperature for 1h in order to make the concentration of cadmium hydroxide and cadmium complexes in equilibrium state. This mixed solution was heated up to 70°C and then mixed with 20 cm<sup>3</sup> of 0.05 mol dm<sup>-3</sup> sulfur solution which was heated to the same temperature in advance. After mixing, the solution was shaken for 1 h at 70°C. The precipitates formed were filtered and dried at room temperature for a day. The powder samples thus obtained were characterized by X-ray diffraction (XRD) measurement by using Cu K $\alpha$  radiation.

Some of the samples obtained were annealed at 200, 300, 400 and 500°C for different period in N<sub>2</sub> flow with 200 cm<sup>3</sup> min<sup>-1</sup> rate and quenched to room temperature. The change in crystal structure of CdS powders with annealing temperature was examined by XRD.

In the case of determination of precipitation rate, the cadmium ion concentration in the supernatant solutions in the course of reaction was measured by inductively coupled plasma with atomic emission spectrometry (ICP-AES) by referring to a standard solution. In the sample solutions for this analysis, the acetic acid was added right after the sampling to stop the further reaction between sulfide and cadmium.

## 3. Results and Discussion

### 3.1. Precipitation rate

In Fig. 1, the extent of reaction, which are calculated from cadmium concentration remained in supernatant solution, is plotted against reaction time when TU and TAA are used as sulfur source. A remarkable difference between TU and TAA is observed in their reaction rate with cadmium; the reaction of TAA proceeds so rapidly, whereas that of TU relatively slowly. When Na<sub>2</sub>S was used, the precipitation occurred as rapidly as the

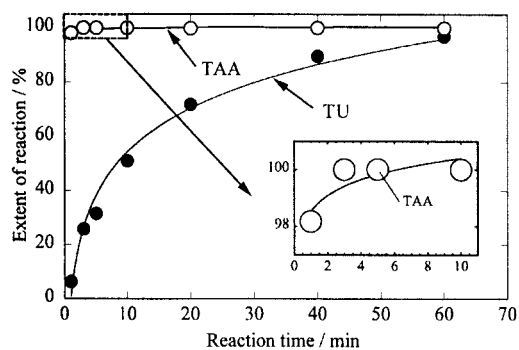
case of TAA.

XRD patterns are measured on the samples which are finally obtained from these sulfur sources and shown in Fig. 2. The XRD patterns of the samples obtained from TAA and Na<sub>2</sub>S may be able to be indexed with zincblende-type structure, but it has to be pointed out that all diffraction peaks are so broad. On the other hand, the sample from TU can be concluded to have wurtzite-type structure and its diffraction peaks are relatively sharp.

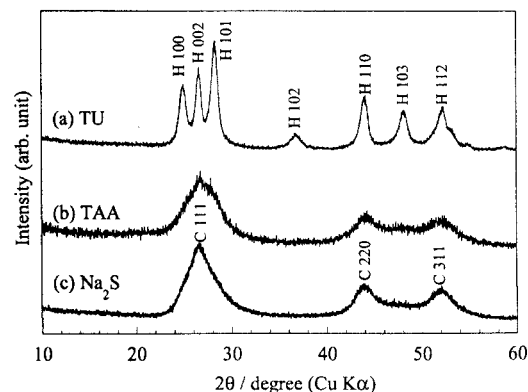
It may be concluded from these results that the rapid emission of sulfide ions in cases of TAA and Na<sub>2</sub>S allows to give zincblende-type structure with a large amount of lattice distortion for CdS precipitates and the relatively slow emission like TU gives wurtzite-type structure.

### 3.2. Effect of S/Cd ratio in the solution

In Fig. 3, XRD patterns are shown on the samples prepared from the solutions with different starting ratios of sulfide compounds to cadmium ions (S/Cd). It is seen that the ratio S/Cd in the starting solution has little effect on the structure of CdS; wurtzite-type structure was obtained from TU but zincblende-type from both TAA and Na<sub>2</sub>S. Small change in the line profile is observed on the samples obtained from S/Cd of 10; in the case of TU relative intensity of the peak at 26.5° in 2θ increases, suggesting the formation of small amount of zincblende-type structure in the matrix of wurtzite-type one, and in the cases of TAA and Na<sub>2</sub>S a slight modification of broad band around 26.5° which may suggest the formation of small amount of wurtzite-type in



**Fig. 1** Changes of reaction extent with time after quick mixing of cadmium solution with the sulfide solutions of TU(●) and TAA(○), where TEA was used as additives.



**Fig. 2** XRD patterns of samples as final products obtained from the solution of (a) TU, (b) TAA and (c) Na<sub>2</sub>S, when TEA was used as additives. In the index for each line, C stands for cubic zincblende-type structure and H for hexagonal wurtzite-type one.

zincblende-type matrix.

In the case of TU, though the ratio S/Cd increases from 1 to 10, expecting that the emission rate of sulfide ions becomes larger, the main phase of the product remains wurtzite-type.

This result implies that the difference in the emission rate of sulfide ions between TU and other two (TAA and Na<sub>2</sub>S) is very large, which seems to be consistent with the above-mentioned experimental results on reaction rate.

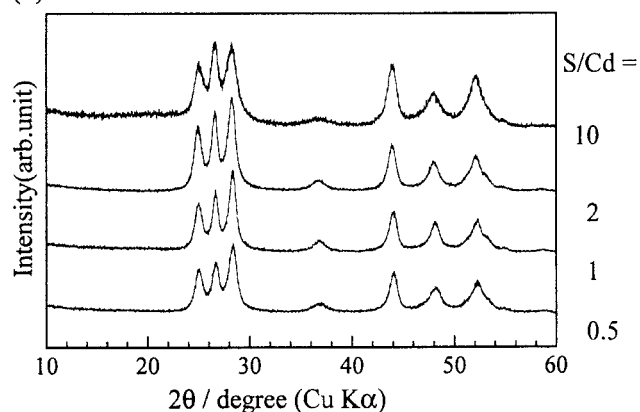
### 3.3. Effects of additives and pH

Fig. 4 a) shows XRD patterns of samples obtained from TAA with additives, TMAH and TEA, and without additives. The pH value of the starting solutions is also indicated for each XRD pattern. There are remarkable difference in XRD patterns between samples obtained with and without additives. The samples obtained with additives have zincblende-type structure, even though pH-values are different in two solutions. The sample without additives, however, is supposed to be a mixture of two structures, zincblende- and wurtzite-types, though pH-value of the starting solution without additives is only a little different from that with TEA.

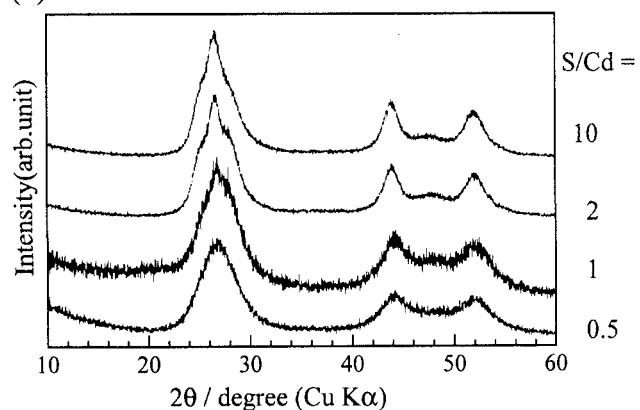
It is clear that the existing species of sulfide ions (*i.e.* H<sub>2</sub>S, HS<sup>-</sup> and S<sup>2-</sup>) formed by dissociation from Na<sub>2</sub>S strongly depend on pH of the solution. In Fig. 4 b), XRD patterns of samples obtained from Na<sub>2</sub>S solutions of different pH-values with different additives are shown. No difference in structure is observed, indicating no effect of sulfide ion species on crystal structure of the precipitate CdS.

Therefore, pH-value of the starting solution seems to

#### (a) TU-TEA



#### (b) TAA-TEA



**Fig. 3** XRD patterns of samples obtained from sulfide solutions with different starting ratios of sulfide to cadmium ions (S/Cd).

have little effect on the crystal structure of the final product CdS.

### 3.4 Effect of way of mixing

In the experiments described above, the addition of sulfide solution to the cadmium solution carried out within 2 seconds. This way of mixing may make the reaction heterogeneous because of so rapid reaction rate of TAA. So, the titration was adapted for mixing two solutions. In Fig. 5, XRD patterns are shown on the precipitates obtained by adding the sulfide solution (TAA) to the cadmium solution with a rate of  $1 \text{ cm}^3 \text{ min}^{-1}$  and also by adding

the cadmium solution to the sulfide compound solution with the same rate.

The way of mixing is found to affect strongly on the crystal structure of the sample obtained. In the case of the addition of sulfide solution to cadmium one, wurtzite-type CdS appears with relatively high crystallinity, but the main structure of zincblende-type CdS in the reverse way. In the case of cadmium titration, cadmium ions is dropped into largely excess of sulfide compounds and so reaction between these two ions seems to occur immediately to give poorly crystallized zincblende-type CdS. In the case of sulfide compound titration, however, sulfur compound (TAA) has to be hydrolyzed after being dropped into the solution containing excess amount of cadmium ions and also it seems to be

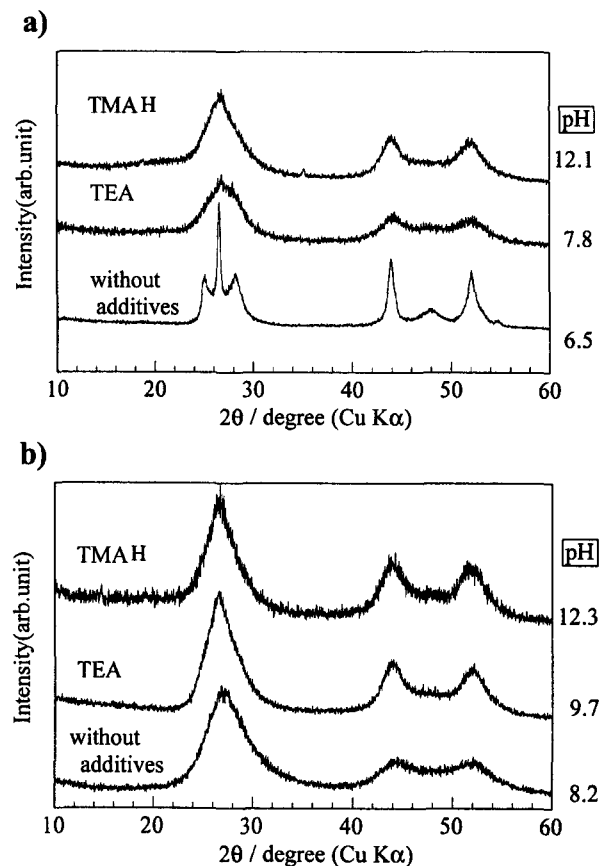


Fig. 4 XRD patterns of samples obtained from solutions of (a) TAA and (b)  $\text{Na}_2\text{S}$  with or without additives. The pH values of starting solutions are also indicated.

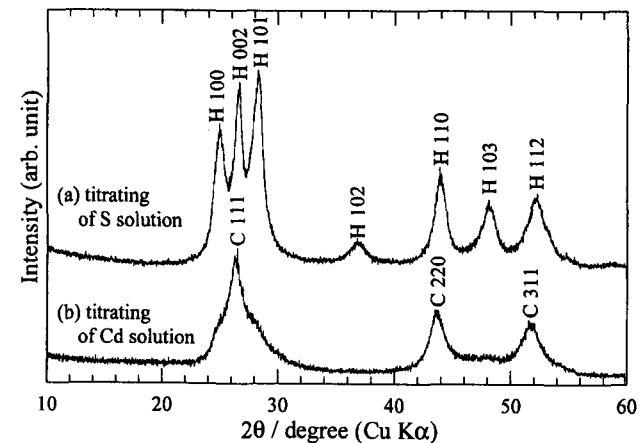


Fig. 5 XRD patterns of samples obtained by adding (a) sulfide solution (TAA) to cadmium solution and (b) cadmium solution to sulfide solution (TAA) with a titration rate of  $1 \text{ cm}^3 \text{ min}^{-1}$ .

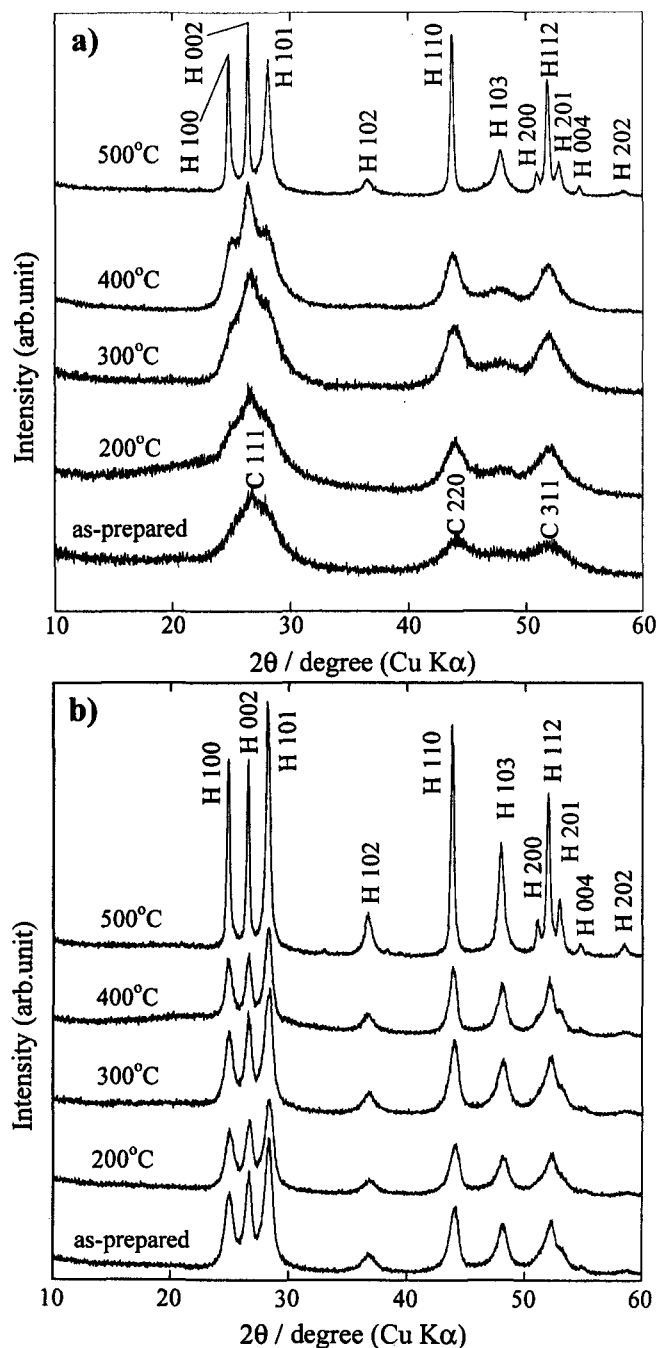


Fig. 6 Change of XRD patterns of samples with annealing at various temperatures for 1 h in  $\text{N}_2$  flow, starting from (a) wurtzite-type CdS obtained from TU and (b) zincblende-type CdS from TAA.

in diluted state, and, as a consequence, the rate of reaction between cadmium and sulfide seems to be slow, mainly because of slow hydrolysis of TAA. By using Na<sub>2</sub>S in spite of TAA, the same results were obtained.

### 3.5. Structural annealing

In Fig. 6, changes in crystal structure with annealing temperature are shown on two samples, zincblende-type CdS obtained by using TAA and wurtzite-type one by using TU. Zincblende-type structure of CdS starts to be transformed to wurtzite-type structure above 300 °C. At this temperature, however, further annealing for 1 week has no effects on XRD pattern. After annealed at 500°C marked sharpening of diffraction lines, *i.e.*, crystal growth, is observed, but some of diffraction lines, mostly *h0l* lines, appear still to be broad, which may suggest the presence of some stacking faults, as observed on various metal sulfides [9,12]. Crystallinity of wurtzite-type structure is improved appreciably above 500 °C. This experimental result indicates that zincblende-type CdS obtained is metastable phase.

### 4. Conclusion

Experimental results in the present work show that the reaction rate between cadmium and sulfide ions governs the crystal structure of the product CdS; rapid reaction produces metastable phase with zincblende-type structure and slow reaction results in crystalline CdS with stable wurtzite-type structure. Reaction rate is governed by the emission rate of sulfide ion from sulfur compounds and so depends primarily on sulfur compounds, whether TU or TAA and Na<sub>2</sub>S; the former emits sulfide ions slowly, but the latter very rapidly. The rapid reaction to form CdS is reasonably supposed to lead to small crystallite size of precipitates and large amount of distortion in the crystallites,

which is main reason why metastable zincblende-type structure with very broad X-ray diffraction lines is obtained.

### References

1. I. Gnal and M. Parlak, *J. Mater. Sci.: MATERIALS IN ELECTRONICS*, **8**, 9-13(1997).
2. C. T. Tsai, D. S. Chuu, G. L. Chen and S. L. Yang, *J. Appl. Phys.*, **79**(12), 9105(1996).
3. H. Chavez, M. Jordan, J. C. McClure, G. Lush and V. P. Singh, *J. Mater. Sci.: MATERIALS IN ELECTRONICS*, **8**, 151-154(1997).
4. E. Fatas, P. Herrasti, F. Arjona and E. G. Camarero, *J. Electrochem. Soc.*, **134**(11), 2801(1987).
5. H. Konno, J.-C. Lai and M. Inagaki, *this journal* in press.
6. I. Kaur, D. K. Pandya and K. L. Chopra, *J. Electrochem. Soc.: SOLID-STATE SCIENCE AND TECHNOLOGY*, **127**(4), 943(1980).
7. P. J. Sebastian, J. Campos and P. K. Nair, *Thin Solid Films*, **227**, 190-195(1993).
8. M. E. Oezsan, D. R. Johnson, M. Sadeghi, D. Sivapathasundaram, G. Goodlet, M. J. Furlong, L. M. Peter and A. A. Shingleton, *J. Mater. Sci.: MATERIALS IN ELECTRONICS*, **7**, 119-125(1996).
9. D. Lincot, B. Mokili, M. Froment, R. Cortes, M. C. Bernard, C. Witz and J. Lafait, *J. Phys. Chem. B*, **101**, 2174-2181(1997).
10. T. Sugimoto, G. E. Dirige and A. Muramatsu, *J. Colloid and Interface Sci.*, **176**, 442-453(1995).
11. T. Sugimoto, G. E. Dirige and A. Muramatsu, *J. Colloid and Interface Sci.*, **182**, 444-456(1996).
12. M. Onoda, M. Saeki and I. Kawada, *Acta Cryst.*, **A36**, 952-957(1980).

Received January 19, 1998

Accepted February 10, 1998