Extended Abstracts of the 17th Conference on Solid State Devices and Materials, Tokyo, 1985, pp. 225-228



# Single Crystal Growth of ZnS by the MBE Method Using $H_2S$ Gas Source

Shigeo Kaneda, Shuji Satou, Takao Setoyama, Shin-ichi Motoyama
Meiso Yokoyama† and Norio Ota†

Technological University of Nagaoka, Kamitomioka, Nagaoka 949-54 Japan
†Nippon Seiki Co. Ltd., Higashizao, Nagaoka 940 Japan

Crystal growth of ZnS by the inherent MBE apparatus having $H_2S$ gas source is performed. It is considered that this method has much advantages compared to ordinary MBE method using Knudsen cell. Namely, it can be not only prevent the unnecessary contamination by sulfur vapor but also easily select the molecular beam ratio $S_1$ and $S_2$ by the controls of inlet gas pressure and cracking temperature. These facts seems to be very usuful to improve the crystal quality and dopant control of impurity. Single crystal film having fairly high quality is obtained under the suitable conditions.

## 1. Introduction

Up to date, various methods for crystal growth of ZnS have been attempted. Among them, MBE method is very effective to grow the thin crystal film. Yao et al[1] performed it by the ordinary MBE method using Knudsen cell. We have constructed special type MBE apparatus having $H_2S$ gas cracking cell for the supply of sulfur molecular beam.

In this paper, various properties of this apparatus, growing characteristics of ZnS crystal and crystalline evaluations of ZnS crystal grown are described.[2]

## 2. Considerations of $H_2S$ gas cell

Temperature dependences of vapor pressures for materials relating to this work are shown in Fig.1. These characteristics have much important meaning in MBE method as well-known as the method of three temperatures. Apparent from this figure, each sticking property of $S_1$ or $S_2$ on ZnS is very different. And also, the growing mechanism becomes quite different for each case of $S_1$ or $S_2$ molecular beam. Cracking pattern of $H_2S$ gas for thermal equilibrium is already given.[3] One of the calculated results for $10^{-6}$ Torr. is shown in Fig.2, and the detailed pattern for the region of practical use is shown in Fig.3. Choosing the suitable conditions of gas pressure and cracking temperature,

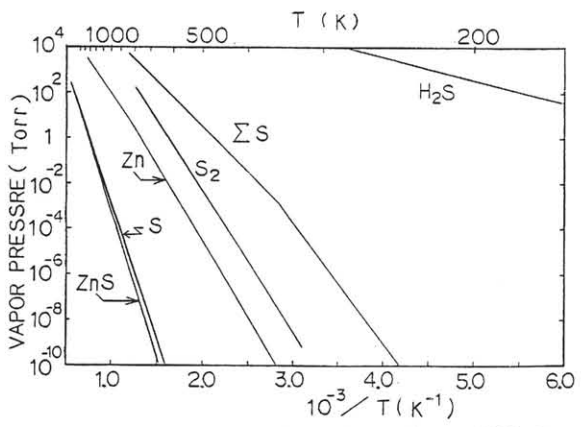



Fig.1 Vapor pressures for thermal equilibrium of the materials relating to the MBE growth of ZnS.

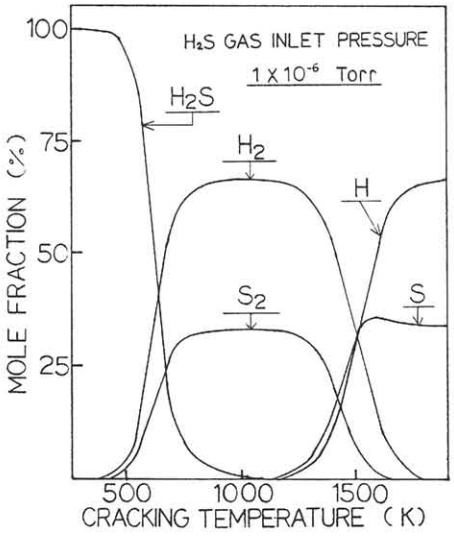



Fig.2 Theoretical cracking pattern of $H_2S$ gas for the thermal equilibrium state.

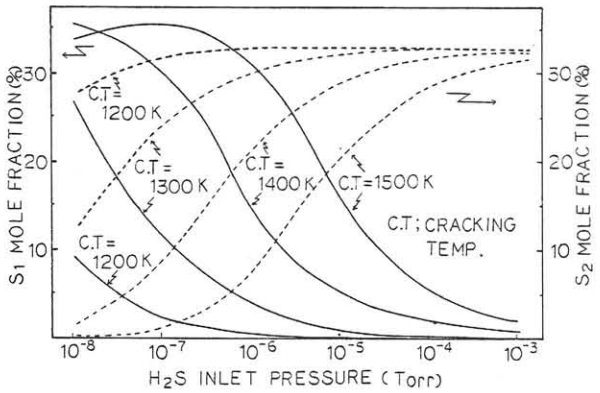



Fig.3 Theoretical cracking patterns of $S_1$ and $S_2$ versus inlet gas pressure of $H_2S$ for the region of practical use.

one can select an arbitrary molecular beam ratio of $S_1$ and $S_2$. This fact seems to be very effective to improve the crystal quality. Moreover, it will become very useful for the practical crystal growth, for instance, the adjustments of growth rate and dopant control of impurity and so on.

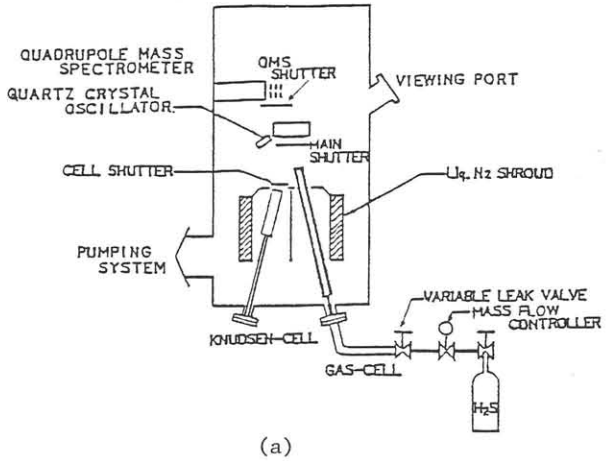
## 3. Experimental

Schematic diagram of experimental apparatus is shown in Fig. 4(a). The base vacuum is the order of $10^{-10}$ Torr. The apparatus contains the inherent gas cell for $H_2S$ as shown in Fig. 4(b). It has an identical construction proposed by Calawa[4] for $AsH_3$ gas cell. For the supply of Zn molecular beam, Knudsen type cell with a cracking heater located near the exit portion as shown in Fig. 4(c) is used.

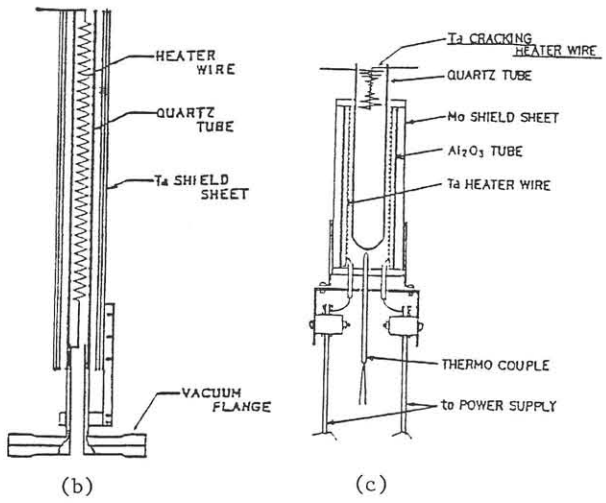
Distribution patterns of total sulfur and zinc molecular beams from each cell are shown in Figs. 5 and 6 respectively. These patterns are approximated by the well-known cosine law[5] as the form of $\cos^n\theta/d^2$ (explanations of $\theta$ and d are shown in the figures). Approximate expressions for n=16 and 40 shown by dashed lines are corresponding to the cases of $H_2S$ gas cell and Zn Knudsen cell respectively.

As the substrate, GaAs and GaP wafers whose crystal faces (100) and (111) are used. Several methods of crystal characterizations are performed in parallel with the experiments of crystal growth. X-ray microanalysis (XMA) is used to examine the composition ratio Zn/S (atomic ratio) of specimens. RHEED, X-ray diffraction, SIMS and SEM analyses are used for crystalline evaluations.

Refering the results of these analyses, the experiments are systematically carried to find out the optimum growing conditions changing the sub-




(a)




(b) (c)

Fig.4 Experimental apparatus (a) schematic diagram of main part of apparatus, (b) $H_2S$ gas cracking cell and (c) Knudsen type cell for Zn.

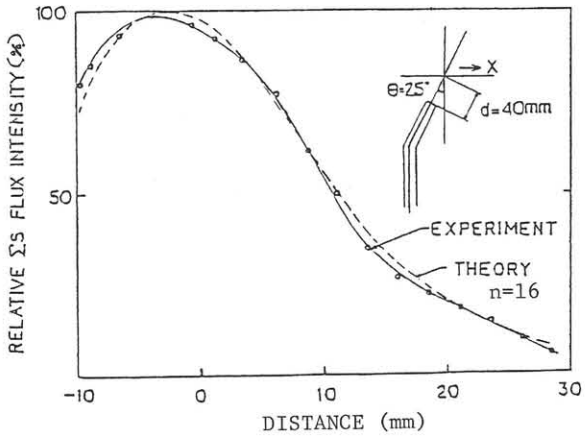



Fig.5 Distribution pattern of total sulfur molecular beam intensity exited from $H_2S$ gas cracking cell.

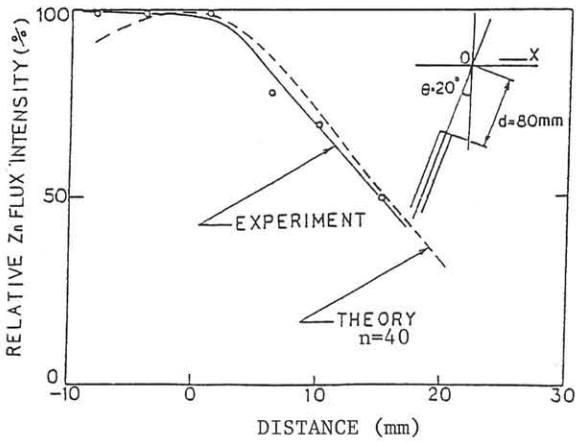



Fig.6 Distribution pattern of zinc molecular beam intensity exited from Zn Knudsen cell.

strate temperature $T_{sub}$, Zn beam flux intensity $J_{Zn}$, inlet gas pressure $P_{H_2S}$ and also both cracking temperatures of Zn and $H_2S$ as the parameters.

The experiments for the crystal growth of undoped ZnS are attempted under the conditions as shown in Table 1. The values of parameters denoted in this Table and the following figures are only the measured values in our experimental system. In the practical measurements, there exist various restrictions. Namely, $P_{H_2S}$ is only the equilibrium pressure measured at some separated position and $T_{cr}(H_2S)$ is the temperature of cracking cell near the exit portion. Still more, the state of gas near the substrate would not be equilibrium state. According to these reasons, it is considered that the correspondences between the experimental data of these parameters and the calculated values shown in Figs.2 and 3 would not be always coincident. These facts have been suggested from the various results measured by mass-spectrometer. Growth rate of ZnS versus $T_{sub}$ is shown in Fig.7. It begins to adruptly decrease at the region of $T_{sub}=360°C$. But it is verified that single crystal can be enough grown in the region of $T_{sub}=360°C$ as shown in Table 1. Fig.8 shows one of the typical results of zinc or sulfur atomic percent versus $J_{Zn}$. The content of zinc is increased in proportion to $J_{Zn}$ from sulfur rich state to zinc rich state. So, the perfect stoichiometric crystal can be obtained by the selection of suitable value of $J_{Zn}$. For the cases of different inlet pressure and cracking temperature of $H_2S$, the suitable value of $J_{Zn}$ is more or less shifted. According to the results of

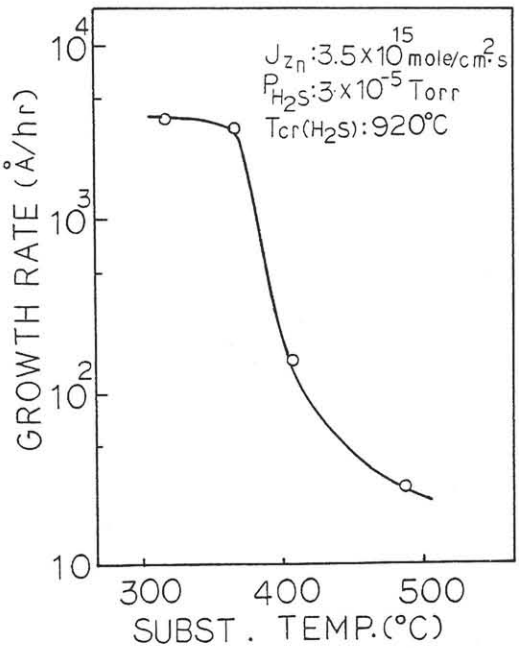



Fig.7 Growth rate of ZnS crystal versus substrate temperature $T_{sub}$.

| Tsub (°C) | $P_{H_2S}=3\times10^{-5}$(Torr) $J_{Zn}$ (x$10^{15}$mole./cm$^2$·sec) | | | | | $J_{Zn}=3.5\times10^{15}$(mole./cm$^2$·sec) $P_{H_2S}$ (x$10^{-5}$ Torr) | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 1.3 | 2.5 | 3.5 | 6.0 | 9.0 | 0.8 | 2.0 | 3.0 | 6.5 |
| 310 | | | △ | | | | | △ | |
| 360 | △ | □ | ○ | ◎ | ◎ | △ | □ | ○ | ○ |
| 375 | | | | | ○ | | | | |
| 400 | | | ○ | | | | | ○ | |
| 480 | | | ○ | | | | | ○ | |

Table 1 A table showing the crystalline characteristics for ZnS crystals grown under the various conditions at $T_{cr}(H_2S)=920°C$.

△ : Poly crystal □ : Single crystal contains the twin
○ : Single crystal ◎ : Nearly perfect stoichiometric single crystal.

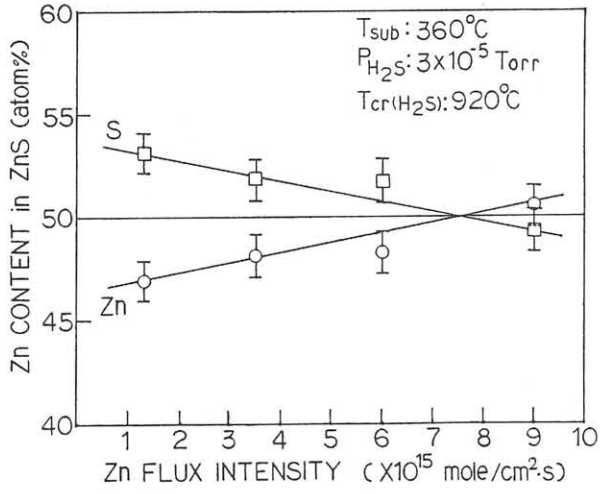
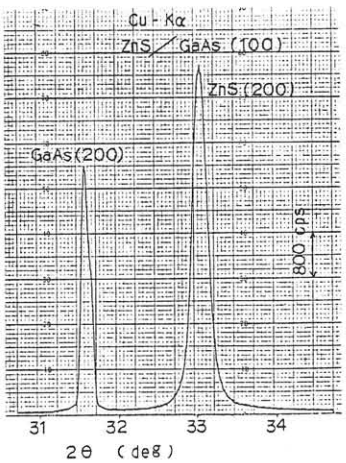
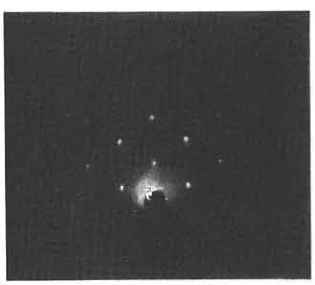



Fig.8 Atomic percent of Zn or S in ZnS crystal versus flux intensity of Zn molecular beam $J_{Zn}$.




(a)



(b)

Fig.9 Crystal analyses of stoichiometric ZnS crystal grown under the conditions:
$T_{sub}$=360°C, $P_{H_2S}$=3.5X10$^{-5}$ Torr.
$J_{Zn}$=9X10$^{15}$(mole/cm$^2$.sec)
(a) X-ray diffraction pattern and
(b) RHEED pattern.

these series of experiments, it is possible to say that one of the conditions to obtain the nearly perfect stoichiometric single crystal are as follows; $T_{sub}$=360°C, $P_{H_2S}$=3X10$^{-5}$ Torr., $T_{cr}(H_2S)$=920°C, $J_{Zn}$=6~9X10$^{15}$ mole/ cm$^2$·sec.

One example of X-ray diffraction patterns for single crystal film satisfied stoichiometry is shown in Fig.9(a). This is the case of specimen grown on GaAs (100) surface. The peak of ZnS (200) is as sharp as the peak of GaAs (200) and its half width is about 0.21°. This value is by no means inferior comparing to another crystal grown by MO-CVD method[6]. Fig.9(b) shows the RHEED pattern for the same crystal. It can be considered that the single crystal of fairly high quality is obtained.

## 4. Conclusion

Single crystal growth of undoped ZnS is succesfully accomplished. But there exist some problems to solve for future work. Namely, it is very difficult to obtain the exact properties of thermal cracking process of $H_2S$ gas due to the various restrictions in the practical measurements mentioned above.

Conclusively, it can be described that the MBE method using gas cell is very effective to grow the thin ZnS crystal film. Moreover, we belive that the crystal growth of more high quality and also the dopant control of impurity would be accomplished by the selection of suitable operating condition of gas cell.

## Acknowledgement

This study was supported by the Ministry of Education, Science and Culture under Grant-in-Aid "Co-operative Reserch".

We would like to thank Ass. Prof. N. Fujii for his aid relating to analysis of $H_2S$ gas characteristics. A part of crystalline evaluations is done in Analysis Center of our university.

## References

1) T. Yao et al : J. Cryst. Growth 53 (1981) 423.
2) S. Kaneda et al : Annual Meeting of Jap. Appl. Phys., 30aY2, 31aZA1, 31aZA2 (1985-03).
3) S. Gordon et al : NASA SP-273 N71-37775, National Tech. Inf. Service (1971).
4) A. R. Calawa : Appl. Phys. Lett., 38 (1981) 701.
5) H. Kumagai et al : "Physics and application of vacuum", Shokabo, (1983) (in Japanese).
6) S. Fujita et al : Jap. J. Appl. Phys. 22 (1983) L583.