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Growth of ZnS Bulk Single Crystals and Homoepitaxial Growth of ZnS by Molecular Beam Epitaxy

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Bulk single crystals of ZnS were grown by the iodine chemical vapor transport method using a novel two-temperature technique (temperature-difference constant-temperature method). High-quality single crystals larger than 1x1x1 cm^3 in size with the etch pit densities of less than $2x10^4$ cm^{-2} were grown.

Homoepitaxial growth of ZnS was carried out on the ZnS single crystal substrate at temperatures between 200°C and 300°C by molecular beam epitaxy. Twin crystals were grown at a substrate temperature of 260°C and single crystals were grown at 300°C. From the result of photoluminescence characterization, the epitaxial layers at 260°C and 300°C have good quality.

1. INTRODUCTION

ZnS is a promising material for the application to short-wavelength light emitting devices covering a blue to ultraviolet region of the spectrum because of its direct-transition-type wide band gap (3.7eV at room temperature). High-quality single crystals are required to control opto-electronic properties and thus to realize light emitting devices. Many attempts have been made to grow II-VI compound films by using low-temperature growth methods such as metal-organic chemical vapor deposition (MOCVD) and molecular beam epitaxy (MBE) on heteroepitaxial substrates. But, heteroepitaxy possesses many inherent shortcomings, for example, lattice-mismatching, thermal-expansion-coefficient difference, cross-doping (contamination) between the substrate and the epitaxial layer.

In this study, we have chosen homoepitaxial growth by MBE. We developed a bulk single crystal growth technique using the iodine chemical vapor transport[1-3] and tried the homoepitaxial growth of ZnS by MBE[4-7]. In this report, at first, we describe the growth and characterization of bulk single ZnS crystals. Secondly, substrate orientation dependence of crystallographic quality, surface morphology and photoluminescence (PL) features of ZnS homoepitaxial films grown by MBE are presented.

2. EXPERIMENTAL

ZnS bulk single crystals were grown by a newly developed technique using the iodine chemical vapor transport[8]. The experimental procedure was described elsewhere[1,8]. Especially, the two zone furnace with strictly controlled constant temperatures was used. The growth (source) temperature was set at 850°C and the temperature difference was controlled between 2 and 10 degrees. Growth times were 1 to 3 weeks. Iodine concentration was varied from 0.02 mg/cm^3 to 10 mg/cm^3.

ZnS wafers with orientations of (100), (110), (111)A and (111)B were prepared by the conventional method. Homoepitaxy was performed using the ULVAC MBC 508 BASIC MBE system. Zn (6N) and S (5N) were used as source materials. The beam intensities were fixed at $1x10^{-6}$ Torr (Zn) and $5x10^{-6}$ Torr (S). During operation, the back ground pressure was 10^{-9}-10^{-10} Torr. Growth temperatures were between 200 and 300°C. Growth times were 1-3 hours.

3. RESULTS AND DISCUSSION

3.1 Bulk Single Crystal Growth

Figure 1 shows the transport rate of ZnS versus iodine concentration in the ampoule. The transport rate is the total transported ZnS devided by the growth time. Open circles indicate experimental results and closed ones show calculation. The calculation is carried out using the equilibrium vapor pressures of ZnI_2, S_2, I_2, I, appropriate binary diffusion constants, the temperature difference of 10 degrees, the diffusion length of 150mm, the ampoule cross-sectional area of $7cm^2$. Since the experimental and the calculated results agreed quite well, the transport mechanism is considered to be a diffusion limited one.

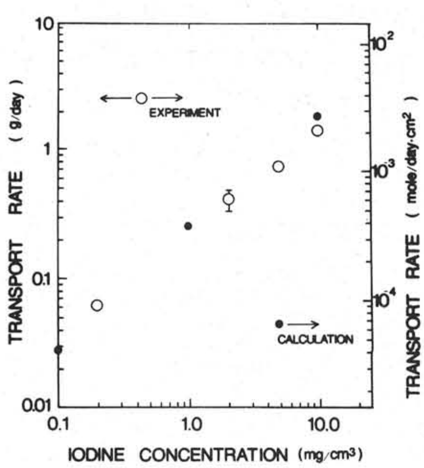


Fig.1 Transport rate versus iodine concentration in the ampoule.

In our experiments, we could grow a single crystal when the iodine concentration was less than about 2 mg/cm^3. The crystal was composed of two or more twinning parts, but the largest single crystal part extended over more than 90% of the grown crystal.

Crystal structure examined by X-ray Laue photograph and Electron Spin Rēsonance is purelycubic.Figure 2 shows the (111) ZnS wafers cut from a bulk single crystal. Figure 3 shows a photograph of the (100) wafer etched in HCl-HNO_3 mixed solution and Br(1%)-MtOH solution.The etch pit density was typically less than $2x10^4$ cm^{-2}. Since etch pit densities of 7-$9x10^4$ cm^{-2} were previously reported in ZnSe and $ZnS_{0.5}Se_{0.5}$ crystals[1], the new growth method proposed here is superior to the previous one.

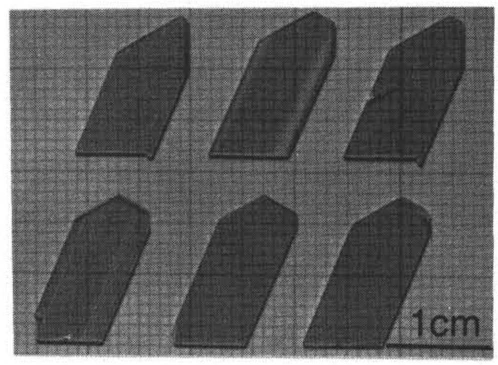


Fig. 2 A photograph of (111} ZnS wafers

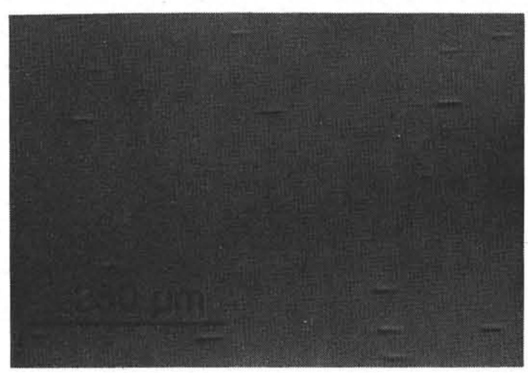


Fig. 3 A photograph of etch pits on the (100) surface. E.P.D.=$1x10^4$ cm^{-2}.

Figure 4 shows the PL spectrum of the wafer at 77 k with an excitation of 325 nm line from He-Cd laser (12 mW). The strong free exciton emission line at 3.79 eV appeared as well as deep center emissions at 2.65 eV, 2.96 eV and the shallow center emissions with a zero phonon line at 3.64 eV. The presence of free exciton emission shows that the grown single crystals are of high quality.

3.2 Homoepitaxial Growth by MBE

The growth rate was about 1.4±0.3 μm/hr at a substrate temperature of 260°C.

Figure 5 shows RHEED patterns of the MBE grown homoepitaxial ZnS with film thickness of about 5 µm. The pattern of the (100) epitaxial

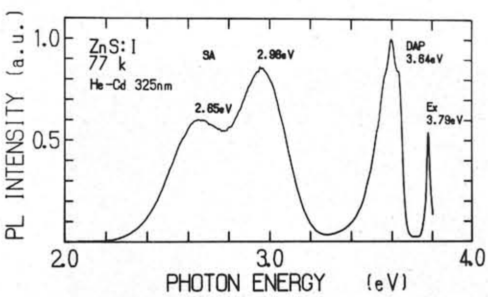


Fig.4 PL spectrum at 77 k. (111) Zn surface.

layer is a superposition of the (100) oriented one, the <111> rotation twin,and the doubly <111> rotated twin. The layer grown on the (110) substrate includes a small amount of the <111> rotation twin. The layers grown on the (111)A and the (111)B substrates show patterns composed of the <111> rotation twin and the rings superimposed on the (111) single pattern. Judging from the RHEED patterns, the layer grown on the (110) substrate is superior to the layers grown on the other substrates.

Figure 6 shows the surface morphologies. the layer grown on the (100) substrate showed rough and irregular islands as well as the pattern peculiar to the (100) surface. On the other hand, the layer on the (110) substrate showed well-defined surface troughs which may be inherent in this plane. The (110) surface with high quality is consistent with the RHEED patterns containing a small amount of the twin pattern.

Figure 7 shows PL spectra of the layers grown on the substrates with different orientations. In the present measurement, the epitaxial layers of about 5 µm thick were used. Therefore, the PL emission is due to only the grown layer. Both the layers grown on the (100) and (110) substrates exhibited strong and dominant free exciton emission at 3.79 eV. The deep center emissions around 2.8 eV were greatly reduced. Thus, the layers on the (100) and (110) substrates have excellent quality.

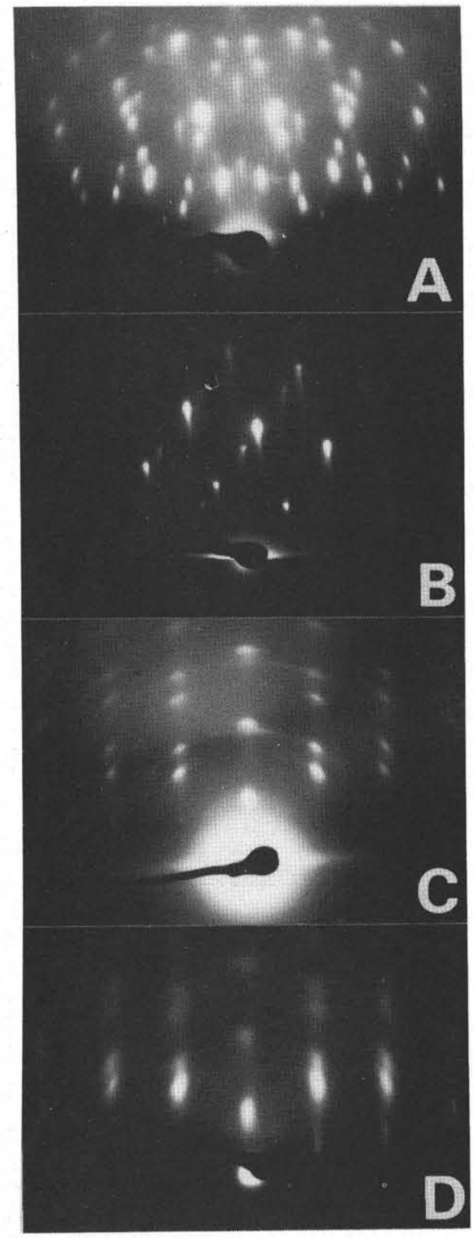


Fig. 5 RHEED patterns. A:(100), B:(110), C:(111)A, D:(111)B.

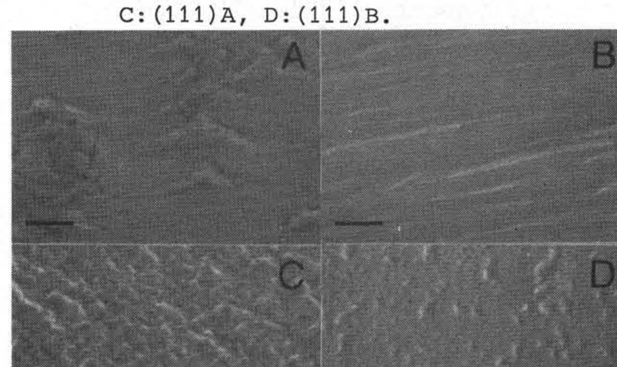


Fig. 6 Surface morphology. A:(100), B:(110), C:(111)A, D:(111)B. —— : 2 µm.

On the other hand, the layers grown on the (111)A and (111)B substrates showed only the deep center emissions.

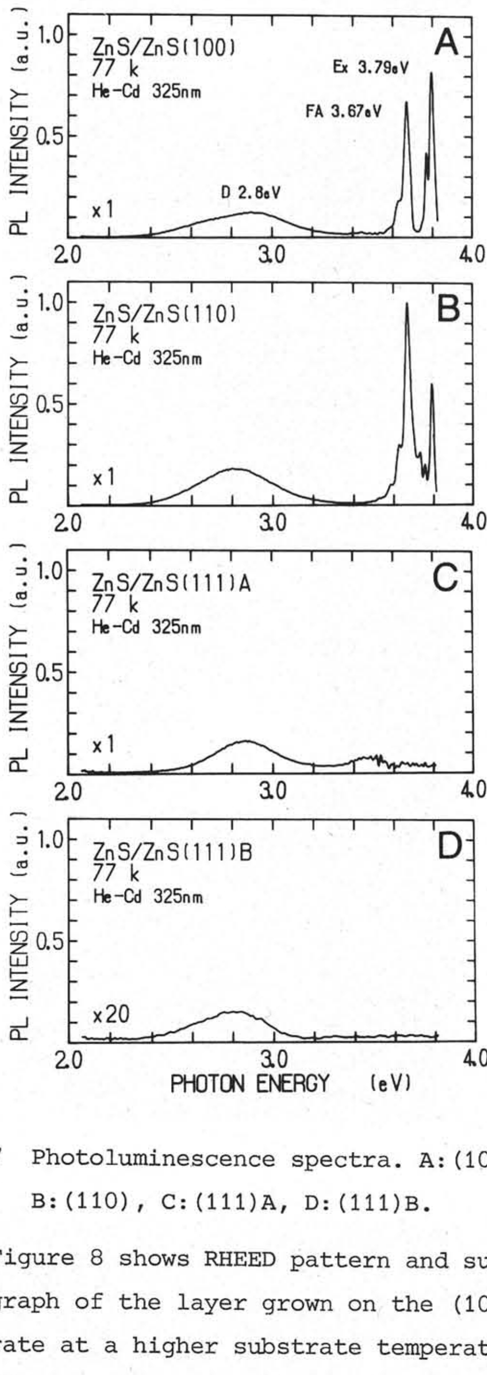
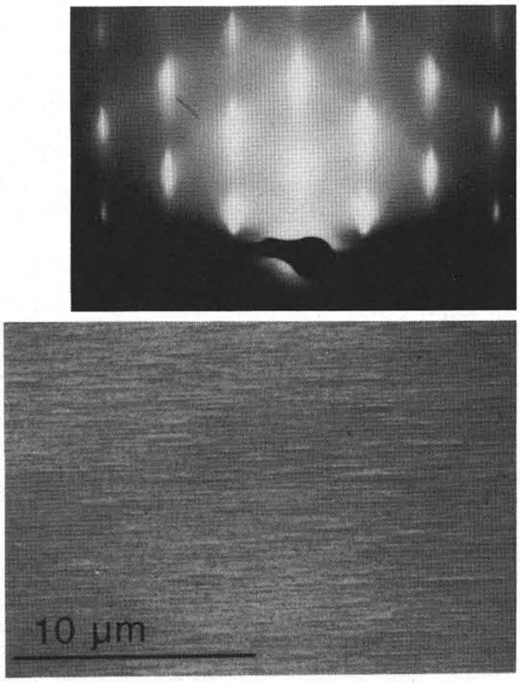


Fig. 7 Photoluminescence spectra. A:(100), B:(110), C:(111)A, D:(111)B.

Figure 8 shows RHEED pattern and surface photograph of the layer grown on the (100) substrate at a higher substrate temperature of 300°C. The layer has higher crystalline perfection and more smooth surface than the layers grown at 260°C. The growth rate at 300°C was about 0.1 µm/hr.

4. CONCLUSION

ZnS bulk single crystals larger than $1x1x1\ cm^3$ in size with the etch pit density of less than $2x10^4\ cm^{-2}$ were grown by the iodine chemical vapor transport method using a novel two temperature technique.



(a)

(b)

Fig.8 RHEED pattern (a) and surface morphology (b) of the (100) homoepitaxial layer grown at 300°C.

Homoepitaxial growth of ZnS by MBE was described for the first time and the substrate orientation dependence was shown. The (100) and (110) orientations are superior to the (111)A and (111)B orientations from the characterization by RHEED, morphology and photoluminescence. Pure single crystal was obtained by MBE homoepitaxy at a substrate temperature of 300°C.

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