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Generation Mechanism for Defects in ZnSe MOCVD Epi-Layers and Bulk Crystals

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High resolution cross-sectional transmission electron microscope observations were carried out for metal-organic chemical vapor deposition (MOCVD) ZnSe grown on (100) and (111) oriented GaAs substrates, lattice matched $ZnS_{0.09}Se_{0.91}$ grown on (100) GaAs, and ZnSe bulk crystals fabricated by the iodine transport procedure.

Large stacking fault densities were observed in the epitaxial ZnSe and lattice matched $ZnS_{0.09}Se_{0.91}$ layers on GaAs (100) substrates. A medium amount of these defects and a number of lamellar twins were observed in the epi-layers grown on (111) substrates. On the other hand, few stacking faults were observed in the ZnSe bulk crystals. These results suggest a model for the generation mechanism for defects in MOCVD ZnSe.

1. Introduction

ZnSe, ZnS and their mixed crystal ZnS_XSe_{1-X} are attractive as blue LED materials, because of their direct and wide bandgap. It has been reported that high quality epitaxial layers were prepared by the metalorganic chemical vapor deposition (MOCVD) technique and the molecular beam epitaxy (MBE) technique[1),2)].

In recent years, the crystal quality for ZnSe and ZnS_XSe_{1-X} on III-V semi-conductor substrates has been evaluated by means of X-ray diffraction and high-resolution transmission electron microscope (HRTEM) observation[3),4)]. It has been clarified that lattice matching between the epi-layers and substrates was necessary for improving crystal quality[4),5)], and that high concentration macro defects, such as stacking faults and twin boundaries, were serious problems[3),4)].

The main purpose of the present paper is to report the results of studies on these macro defect formations in MOCVD epi-layers and iodine chemical vapor transport bulk crystals using HRTEM. Cross-sectional lattice image observations for MOCVD ZnSe epitaxial layers grown on GaAs substrates, ZnS_XSe_{1-X} layers lattice matched to GaAs substrates, and bulk ZnSe single crystals have been compared for the first time.

2. Experimental

ZnSe and ZnS_XSe_{1-X} layers were grown by MOCVD in an rf-heated vertical reactor. The source materials were dimethylzinc (DMZn), dimethyl selenide (DMSe) and diethylsulfide (DES)[6)]. The substrates were (100) and (111) A oriented Cr-doped semi-insulating GaAs, etched with a solution of $H_2SO_4:H_2O_2:H_2O=4:1:1$ by volume.

The epitaxial growth was performed at 500 °C under atmospheric pressure. The DMZn transport rate was kept at 1.6×10^{-7} mol/min throughout this study. The DMSe and DES to DMZn mol ratio (VI/II) in the vapor phase was fixed at 2. The total hydrogen flow rate was 2 l/min. The growth rate under the above conditions was about 400 Å/min. The grown layers were about 2 μm thick.

ZnSe bulk single crystals were grown by a technique using iodine chemical vapor transport[7)]. A two zone furnace with controlled constant temperatures was used.

Iodine transport crystals were grown at 840 °C on ZnSe seed crystals under 850 °C source temperature. The growth time were about two weeks.

The authors studied the defect structure for ZnSe layers on (100) and (111) oriented GaAs substrates, lattice matched $ZnS_{0.09}Se_{0.91}$ layers on GaAs (100), and ZnSe bulk single crystals using HRTEM (JEM-2000EX). The specimens used were prepared by cutting out cross sections and thinning them to electron transparency by mechanical polishing and ion beam milling, using a technique similar to those reported earlier[3].

The grown ZnSe and ZnS_XSe_{1-X} layers and ZnSe bulk crystals were also characterized by X-ray diffraction and chemical etching study.

3. Results and Discussion

3-1. HRTEM observation

Figure 1 shows a multibeam lattice image for the ZnSe(100)/GaAs(100) interfaces. The lattice was viewed as a [110] projection. The faults in the ZnSe layer consisted, to a large extent, of interstitial Frank loops with about 100 Å diameters. These loops lie in the {111} planes and have a density of about $10^{18}cm^{-3}$, which vary little among the observed positions away from the epitaxial interface. These loops involved an extra {111} plane and were associated with an extrinsic stacking fault. Figure 2 shows a lattice image for the lattice matched $ZnS_{0.09}Se_{0.91}$-GaAs(100) interface. The faults in the $ZnS_{0.09}Se_{0.91}$ layer consisted of defects, which varied little from those in a mis-matched ZnSe-GaAs layer.

Figure 3 shows a lattice image of the ZnSe-GaAs (111) interface. High densities of lamellar twins and a medium amount of stacking faults are seen in the (111) growth layers. The structure of the ZnSe layers grown on GaAs (111) A substrates was quite different from that of the layers grown on (100) substrates.

Figure 4 shows a lattice image of the ZnSe bulk single crystals. Few faulted loops and few lamellar twins are seen. The structure of ZnSe bulk crystals without a twin boundary is quite different from that of layers grown on (100) and (111) layers.

3-2. X-ray observation

3-2-1. ZnS_XSe_{1-X} epitaxial layers lattice-matched to GaAs

Earlier papers by the authors described hetero-epitaxial lattice disordering[6),8)] and clarified that lattice matching was necessary for improving crystal quality[4),5)]. In the present experiments, the ZnS_XSe_{1-X} layers obtained were evaluated by the composition X and the line width, i.e. the full width at half maximum (FHWM), of the (400) CuKα, the reflection of the double crystal X-ray rocking curves. At a sulfur content of about 0.09, where the epilayer is closely lattice matched to the substrate lattice for growth temperature, the high crystalline quality of the layers is evident in Figure 5, which shows a minimum line width of about 13 arc sec. The wider lines, observed in the $X < 0.09$ range, can be ascribed to crystalline defects, like misfit dislocation or micro twins introduced in the layers[9)]. In the $X > 0.09$ range, on the other hand, the authors believe that the strains in the layers, due to tensile stress, cause the line broadening.

Many stacking faults were observed in the lattice matched $ZnS_{0.09}Se_{0.91}$ layers. These results may be attributed to the stacking faults not being introduced by strain relaxation from lattice mismatching.

3-2-2. Bulk single crystals

In the present experiments, the authors were able to grow single crystals, bounded by large (111) and (100) faces. The crystals were composed of two or more twinning parts, but the large single crystal

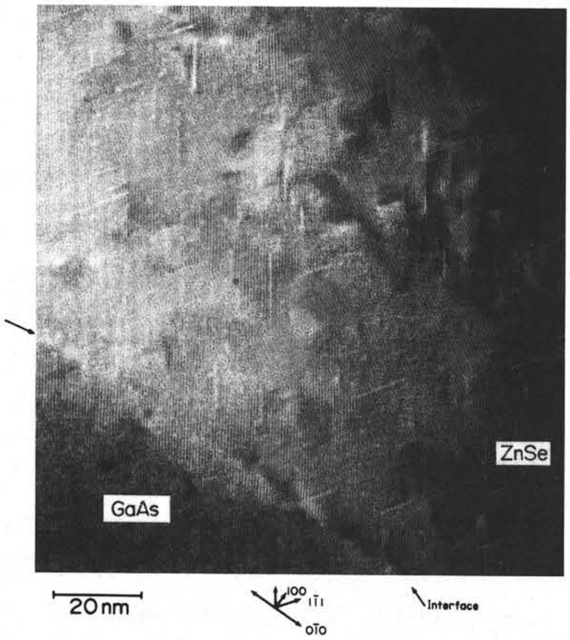

Fig.1. HRTEM photograph of ZnSe/GaAs(100) interface in [100] cross section

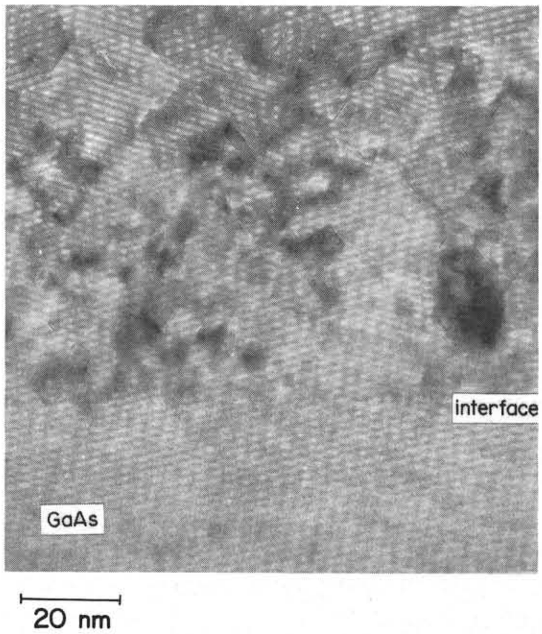

Fig.2. HRTEM photograph of $ZnS_{0.09}Se_{0.91}$/GaAs (100) interface in [100] cross section

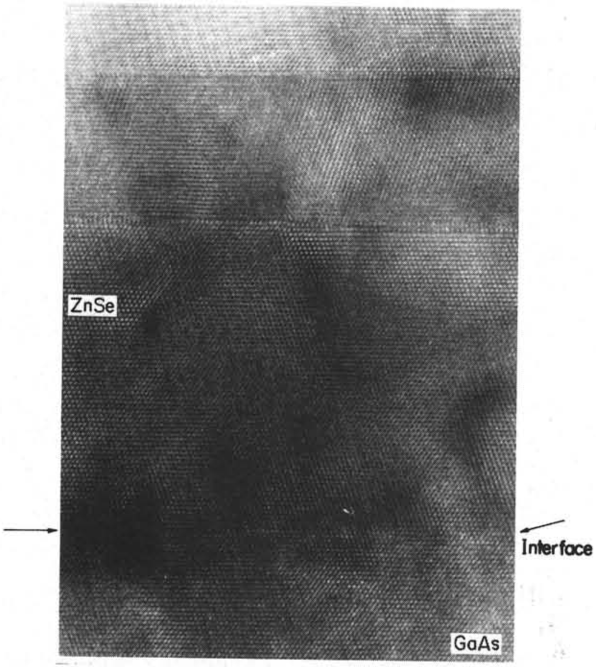

Fig.3. HRTEM photograph of ZnSe/GaAs(111)A interface in [100] cross section

Fig.4. HRTEM photograph of ZnSe single bulk crystal in[100] cross section.

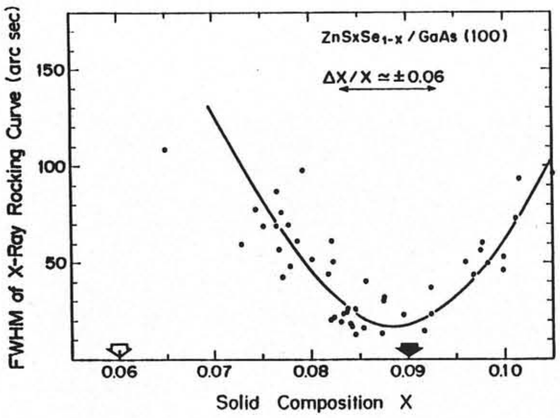

Fig.5. Line width (HWFM) of X-ray rocking curves as a function of composition X in ZnS_XSe_{1-X} epitaxal layers grown on GaAs (100)substrates.
▽: lattice-matched at room temperature.
▼: lattice-matched at growth temperature.

part extended without twin boundaries over a 50-100mm^3 volume.

Dislocation densities were determined from the counts of etch pits developed on the (111) surfaces, when etched by a solution of 30% NaOH solution in H_2O, boiled at 110 °C. In typical ZnSe plates, which were cut from single crystals, the dislocation densites were about $2x10^4 cm^{-2}$, with about 10 arc sec FHWM for the (400) CuKα reflection.

These results may be attributed to layer-by-layer growth which probably occurred on (111) facet growth in the bulk single crystals.

3-3. Defect formation models

There are two possible causes for the appearance of twins and stacking faults : (a) strain relaxation from lattice mismatching and (b) island growth. Table 1 shows the defects and their densities in this work. These results may be attributed to stacking faults introduced by island growth, and not to those caused by strain relaxation from lattice mismatching. A layer-by-layer growth has probably occurred in the case of the growth on (111) substrates, and the bulk crystal growth by the iodine transport. These results suggest that these defects may be controlled by layer-by-layer growth realized in MOCVD on a (100) substrate.

Table 1. Defect density observed by HRTEM

Sample \ Defect	Stacking fault	Twin boundary
a) ZnSe/GaAs (100)	++	-
b) $ZnS_{0.09}Se_{0.91}$/GaAs (100)	++	-
c) ZnSe/GaAs (111) A	+	++
d) ZnSe Bulk	-	+

++ ; many, + ; medium amount, - ; few.

4. Conclusions

ZnSe and ZnS_XSe_{1-X} crystals, grown by various procedures, were compared by lattice image observations for the first time. Many stacking faults were observed in the epitaxial ZnSe and lattice matched $ZnS_{0.09}Se_{0.91}$ layers by MOCVD. On the other hand, stacking faults were fewer in ZnSe layers grown on (111) GaAs substrates than in that grown on (100) GaAs substrates. Few stacking faults were observed in ZnSe crystals grown by the iodine transport procedure.

These result suggest that such defects may be caused by island growth in MOCVD, and the realization of layer by layer growth in MOCVD is important by the study of the growth conditions.

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