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Lattice Matched Epitaxial Growth of ZnSSe on GaAs by MOCVD

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Lattice disordering and surface morphology were studied for heteroepitaxial systems of ZnSe and ZnSSe grown on GaAs by MOCVD. Strain due to lattice mismatch between ZnSe and GaAs is sustained up to an epi-layer thickness of about 2000Å. Lattice disordering and crystallinity deterioration occur in a growth thicker than 2000A. Mirror surface morphology was obtained by using organic compounds as source materials for Se and S. Marked improvement in crystallinity has been revealed to occur for lattice matched mirror surface ZnSSe grown on GaAs.

1 Introduction

Wide band-gap II-VI compound semiconductors, ZnSe and ZnS, have attracted much attention as suitable materials for blue light emitting devices, because of their direct wide band-gap above 2.6eV. Metal organic chemical vapor deposition (MOCVD), a successful epitaxial growth technique for III-V materials, is also valid for the epitaxial growth of these II-VI compound semiconductors on III-V semiconductor substrates [1]. This heteroepitaxial MOCVD growth is expected to be a suitable technique for mass-production of wide-gap II-VI semiconductor devices. It has been reported by many authors that single crystals of ZnSe and ZnS can be grown on GaAs or GaP substrate[2-6]. However, device quality epi-layers have not been achieved as yet. In order to apply these heteroepitaxial systems to optoelectronic devices, defect free epitaxial layers with a good crystallinity are essential.

In the present work, lattice deformation and lattice disordering in the MOCVD grown ZnSe and ZnSSe heteroepitaxial layers grown on (100) GaAs have been studied. Lattice parameters and full width at half maximum (FWHM) from X-ray diffraction pattern of grown layers have been measured. An excellent mirror smooth surface was achieved by using organic materials as group VI sources[7].

2 Experimental

2-1 MOCVD growth

The growth system used in the present work is applicable to a wide prossure range from 50 mTorr to atmospheric pressure. A vertical quartz reactor is used. A substrate on a SiC coated carbon susceptor is heated by IR-radiant heaters. Dimethylzinc (DMZ) was used as a zinc source. Hydrogenselenide (H_2Se) or dimethylselenide (DMSe) was used as a selenium source. For ZnSSe growth, diethylsulfide (DES) was used as a sulfur source. High purity grade (7N) hydrogen was used as a carrier gas. For growth using H_2Se, DMZ and H_2Se are introduced separately just above the substrate under about 0.1 Torr pressure in order to prevent premature reactions resulting from high reactivity of H_2Se. For growth using DMZ and DMSe, free from undesirable premature reactions, these gases were pre-mixed and introduced into the reactor under atmospheric pressure.

Typical growth parameters are listed in Table 1. Before growth, the substrate was pre-heated under a hydrogen atmosphere at 600°C for 15 minutes.

2-2 SEM and X-ray measurements

Surface morphology and thickness for grown layers were observed by using a scanning electron microscope (SEM).

Lattice prameters ($a_\perp$) perpendicular to the surface plane and FWHM for the diffraction pattern were measured from (400) diffraction by Cu $K_{\alpha 1}$ line (λ=1.5405A). For more precise evaluation of crystal quality, double crystal X-ray measurement was carried out.

3 Results and discussions

3-1 Mirror surface growth

Figure 1 shows SEM photographs of as-grown and cleaved cross-section of epitaxial ZnSe layers on (100) GaAs substrates grown under typical conditions. When H_2Se was used as Se source, a rough surface was obtained, as shown in Fig.1(a). On the other hand, when DMSe is used as Se source, an excellent mirror smooth surface was achieved, as shown in Fig.1(b). This marked difference in surface morphology between the two systems is probably due to the difference in chemical reactivity and thermal stability for H_2Se and DMSe.

Achieving a mirror smooth surface will accelerate device applications for heteroepitaxial systems.

Table 1 Typical Growth Conditions

	ZnSe		ZnSSe
	DMZ+H_2Se	DMZ+DMSe	DMZ+DMSe+DMS
[Zn] (mol/min)	2.59×10^{-5}	3.19×10^{-5}	3.19×10^{-5}
[Se] (mol/min)	1.33×10^{-4}	6.25×10^{-5}	3.46×10^{-5}
[S] (mol/min)	-	-	2.30×10^{-5}
VI/II	5.1	2.0	1.8
Tg (°C)	320	500	500
Pg (Torr)	<0.1	760	760

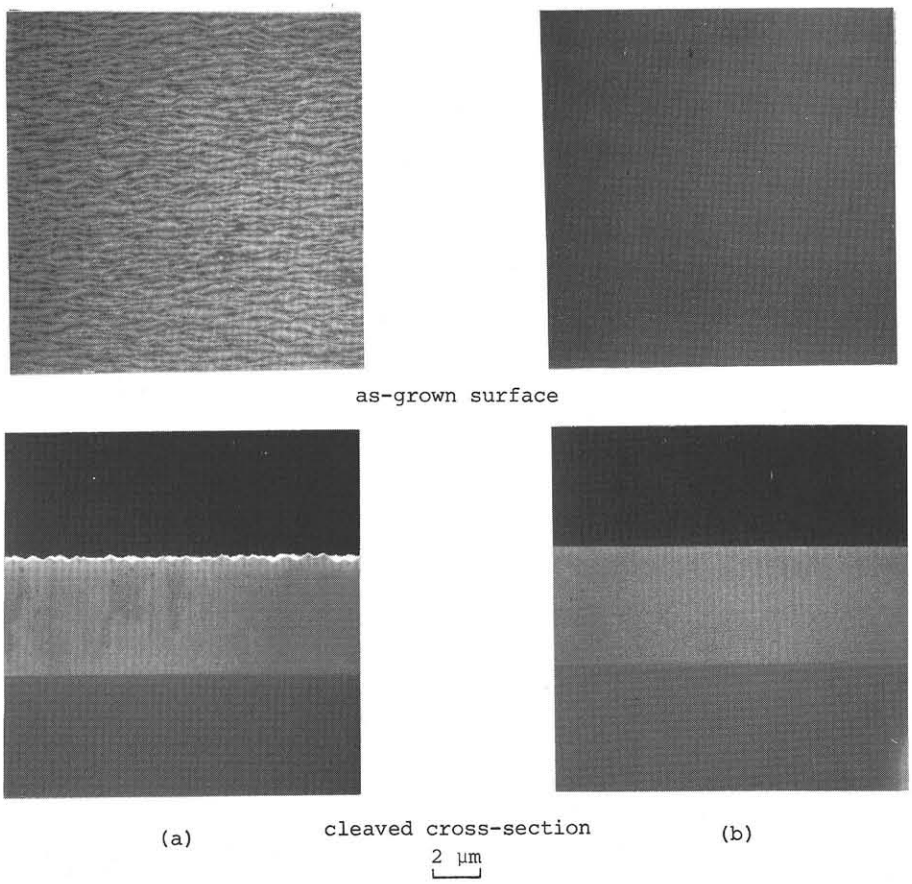

Fig.1 SEM photographs showing the surface morphology and cleaved cross-section of ZnSe/GaAs grown from DMZ and H_2Se (a), and from DMZ and DMSe (b).

3-2 Lattice mismatch and disordering

Figure 2 shows changes in lattice parameter ($a_\perp$) and FWHM for the X-ray diffraction pattern versus thickness of ZnSe layers grown from DMZ and H_2Se. Figure 3 shows changes for the layer grown from DMZ and DMSe. In spite of the difference in source material combinations and growth parameters, $a_\perp$ and FWHM shows similar tendencies in both figures. ZnSe grows to 2000A thickness with a deformed lattice parameter ($a_\perp$) rather than with the inherent lattice constant (a_{ZnSe}), and FWHM decreases with layer thickness increase (region 1). At about 2000A thickness, $a_\perp$ begins to approach a_{ZnSe}. Simultaneously FWHM increases drastically (region 2). As the layer thickness increases further, $a_\perp$ approaches a_{ZnSe} gradually and FWHM becomes narrower again (region 3).

The ZnSe lattice constant is larger than that for GaAs by 0.25% at room temperature. ZnSe lattice matched to GaAs grows with its lattice stretching in the growing direction, because of the compressive stress in a direction parallel to the substrate surface. As a result, an observed lattice parameter for ZnSe on GaAs, measured by X-ray diffraction, is larger than a_{ZnSe}. Neglecting the heteroepitaxial wafer curvature, the strained ZnSe lattice parameter, perpendicular to the substrate, is calculated by the following equation;

$$(a_\perp)_{cal} = a_{ZnSe} + \nu(a_{ZnSe} - a_{GaAs}),$$

where ν is Poisson's ratio for ZnSe: ν=1.20, a_{ZnSe} =5.6676, a_{GaAs}=5.6533.

From this equation, $(a_\perp)_{cal}$ for epitaxial ZnSe on GaAs is calculated to be 5.6848Å, which is about 0.3% larger than a_{ZnSe}. Experimental data, shown in region 1, agree well with the calculated value, which means that ZnSe is grown epitaxially on the GaAs substrate when the layer thickness is less than 2000Å.

FWHM for the X-ray diffraction pattern is a good index of representing crystallinity.

In region 1, FWHM for the X-ray diffraction pattern decreases, and epitaxially grown ZnSe layer crystallinity is improved with thickness increase. In region 2, FWHM increases drastically, corresponding to the layer thickness increases. This phenomenon is explained as follows.

In region 1, ZnSe is epitaxially grown on the GaAs substrate within a limit of the internal stress, in spite of the as much as 0.25% lattice mismatch between ZnSe and GaAs. The epitaxially grown ZnSe on GaAs is compressed in a plane parallel to the substrate surface. This lateral stress increases with thickness increase. In region 2, at a certain thickness, the stress increase causes epi-layer lattice disordering. This corresponds to increase in FWHM for the X-ray diffraction pattern.

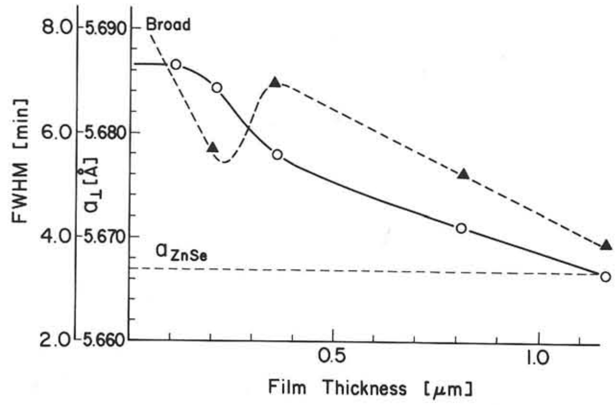

Fig.2 Lattice constant ($a_\perp$) and full width at half maximum (FWHM) of X-ray diffraction pattern against the epi-layer thickness of ZnSe grown from DMZ and H_2Se.

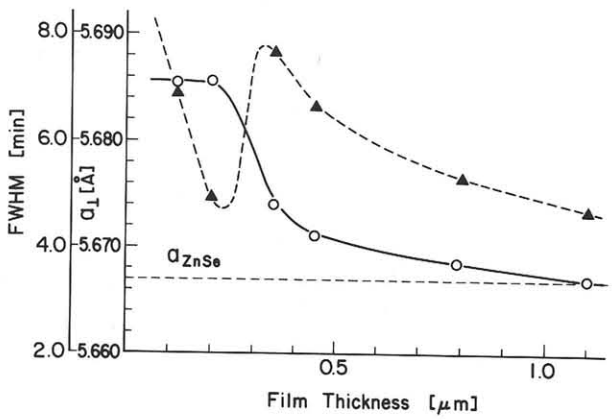

Fig.3 $a_\perp$ and FWHM of ZnSe grown from DMZ and DMSe.

Once the lattice disordering occurs, the epi-layer releases the stress by the lattice disordering and the layer on the disordered region is grown with the inherent lattice constant (region 2 and 3). Because of the subsequent stress free growth, FWHM becomes narrower with the thickness increase. These phenomena are also confirmed by double-crystal X-ray measurement, as shown in Fig.4.

Figure 4 shows that FWHM for the double-crystal X-ray diffraction pattern of lattice matched ZnSSe decreases monotonically with layer thickness increase, without drastic increase observed in ZnSe on GaAs. ZnSSe crystallinity is improved with layer thickness increase. For an about 4μm thickness, FWHM as narrow as 40 seconds was obtained, which is much narrower than that for ZnSe on GaAs.

These results confirmed that lattice matched ZnSSe, grown on GaAs, is essential to achieve defect free crystal growth. In addition to the lattice matching, mirror smooth surface MOCVD growth, using organic compounds as group VI element source is also a key to device quality epi-layers.

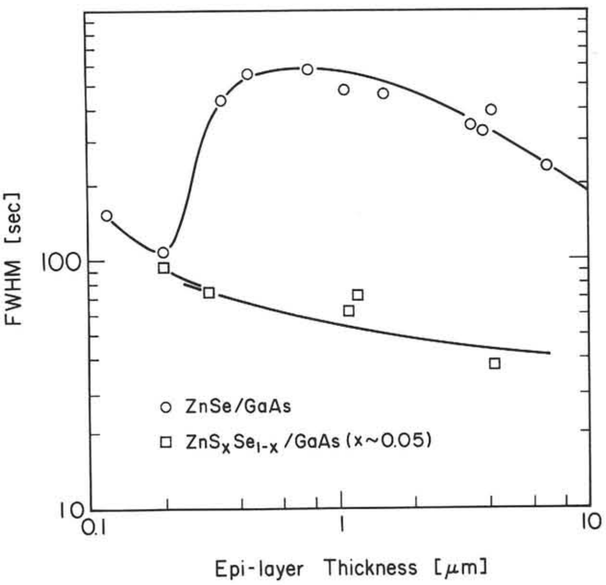

Fig.4 FWHM against the epi-layer thickness measured by double-crystal X-ray diffraction for ZnSe/GaAs (a), and ZnSSe/GaAs (b).

4 Summary

Lattice deformation and lattice disordering tendencies in ZnSe and ZnSSe heteroepitaxial layers grown on GaAs have been revealed. A marked difference in surface morphology exists between two MOCVD material systems. Smooth mirror surface morphology has been obtained using organic compounds as an element for the Se and S sources. However, lattice disordering occurs for the ZnSe growth on GaAs when the epitaxial layer thickness increases over 2000Å, notwithstanding the source material difference. Marked improvement in crystallinity has been revealed to occur for the lattice matched ZnSSe grown on GaAs. Lattice matched MOCVD, using group VI organic compound, will increase an importance for fabrication of II-VI compound devices grown on III-V substrate.

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