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Epitaxial growth of zinc-blende ZnSe/MgS superlattices on (001) GaAs

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We report the growth of zinc-blende ZnSe/MgS superlattices (SLs) on GaAs (001) substrates. The SLs were grown with metalorganic vapor phase epitaxy by selecting appropriate precursors for Mg and S. MgS naturally forms rocksalt structures, but zinc-blende MgS layers were grown. The lattice constant of MgS was estimated to be 5.59 Å. X-ray diffraction measurements show that the ZnSe/MgS SLs are grown coherently to the GaAs substrates up to the total thicknesses of ~3000 Å. © 1996 American Institute of Physics. [S0003-6951(96)04506-8]

Wide band gap II–VI semiconductor superlattices (SLs) have attracted much attention for realizing blue/green light emitting devices. It is well known that the band offset plays an important role in determining the characteristics of heterostructures. However, most of II–VI heterostructures proposed up to now have band offsets localized to either conduction or valence band edges. In the case of ZnSe/ZnSSe SLs, the band offset is localized to valence bands, while the conduction band discontinuity is very small.¹ For ZnMnSe/AnMnSe/ZnSe SLs, the heterojunctions exhibit very small valence band offsets.² Recently II–VI compound semiconductors containing group-IIA elements like Mg are expected to be the most promising materials to realize heterostructures.^{3–8} In particular, ZnMgSSe^{3–5,7} has been extensively studied since Zn(Cd)Se/ZnMgSSe heterostructures can confine both electrons and holes. Nakayama *et al.* demonstrated first continuous-wave operation of blue-green laser diodes using ZnMgSSe as the cladding layer.⁹

ZnMgSSe films of the zinc-blende structure can be grown on GaAs (001) substrates, and the band gap energies can be changed from 2.8 to 4 eV maintaining lattice matching to the GaAs substrates.³ However it is reported that the crystalline quality of ZnMgSSe layers tends to be worse with the increase of the Mg composition. For binary Mg chalcogenides of the zinc-blende structure, the lattice constants of 5.89 and 5.62 Å and the band gap energies of 3.6 and 4.5 eV are estimated for MgSe and MgS, respectively.³ However the binary compound MgS naturally forms the rocksalt structure, and the reported lattice constants and bandgap energies were extrapolated from the experimental data on the quaternary alloys.

Although the zinc-blende MgS has not previously been reported, the largest band gap among II–VI semiconductors is estimated in MgS. Therefore in the combination of ZnSe and MgS, the band offsets of the conduction band and the valence band are expected to be very large.¹⁰ This will offer large quantum confinement effects on both electrons and holes. In addition, ZnSe/MgS heterostructures will have small lattice mismatch of 0.87% and are reasonably lattice-matched to GaAs substrates. These attractive features motivate us to try to grow the zinc-blende MgS. In this letter, we report the first successful epitaxy of zinc-blende ZnSe/MgS SLs on GaAs (001) substrates.

The growth apparatus used in the present experiment was an atmospheric-pressure metalorganic vapor phase epitaxy (MOVPE) system. ZnSe/MgS SLs were grown on semi-insulating (S.I.) GaAs (001) substrates. The precursors used were diethylzinc (DEZn), diethylselenide (DESe), dimethylcyclopentadienyl-magnesium [(MeCp)₂Mg] and diisopropylsulfide (DiPS). The flow rates were controlled by mass flow controllers. The line of the Mg precursor was heated to about 70 °C, since the vapor pressure of (MeCp)₂Mg is low. Typical growth conditions are summarized in Table I.

The growth processes on the substrate surface were monitored by a He–Ne laser (6328 Å) using an optical multiple reflection in the films. This technique has been utilized to measure the film thickness and the growth rate. The fabricated ZnSe/MgS SLs were characterized by high-resolution x-ray diffraction (HRXRD) measurements utilizing a Cu K α_1 line ($\lambda=1.5406$ Å) and photoluminescence (PL) measurements at 12 K. The specimens were excited by a He–Cd laser (3250 Å).

The thick solid line shown in Fig. 1 is a typical (004) x-ray diffraction pattern measured on the ZnSe/MgS SL with 21 periods (sample a). Several orders of satellite peaks which reflect the periodicity in the SL are clearly observed. The 0th peak is observed at the higher angle position compared to the GaAs (004) diffraction peak. The average lattice constant perpendicular to the interface ($a_{\perp av}$) was calculated to be 5.607 Å.

We have examined the dependence of the 0th peak position on the rotation angle in the (001) surface plane during the HRXRD measurements. The variation of the corresponding $a_{\perp av}$ value by the rotation was within the accuracy of the apparatus, 0.001 Å. Therefore it is concluded that the SL (001) planes are almost completely parallel to the (001) plane of the GaAs substrate.

TABLE I. Typical growth conditions of ZnSe/MgS SLs.

Substrate temperature	490 °C
DEZn flow rate	2.1 $\mu\text{mol}/\text{min}$
DESe flow rate	1 $\mu\text{mol}/\text{min}$
(MeCp) ₂ Mg flow rate	0.37–0.56 $\mu\text{mol}/\text{min}$
DiPS flow rate	16 $\mu\text{mol}/\text{min}$
Growth rate of ZnSe	0.43–0.48 $\mu\text{m}/\text{h}$
Growth rate of MgS	0.26–0.30 $\mu\text{m}/\text{h}$

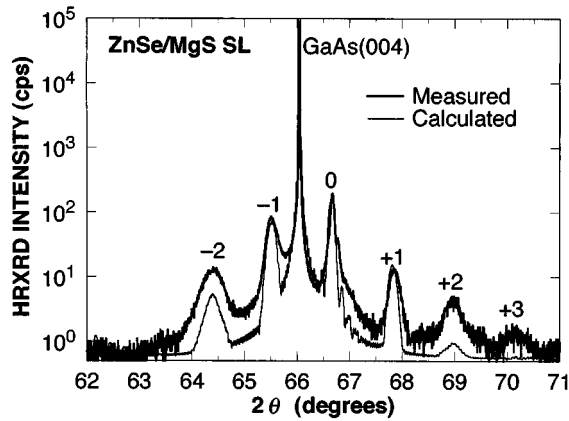


FIG. 1. X-ray diffraction pattern measured on a ZnSe/MgS SL with the 21 periods. Several orders of satellite peaks indicated by 0, ± 1 , ± 2 , and ± 3 were observed around the GaAs (004) peak. The thin solid line is the theoretical simulation calculated with the measured parameters.

The observed satellite peak positions were plotted in the form of $\sin\theta$ in Fig. 2. The linear relation to the order of the peaks shows the clear evidence that the observed peaks were diffracted from the SL structure. From this slope, the thickness in one period (L) was estimated to be 92.4 Å. These observations of the well-defined SL satellite peaks around the GaAs (004) peak demonstrate the successful growth of zinc-blende ZnSe/MgS SLs.

To determine the ZnSe well and MgS barrier layer widths from the HRXRD measurements, the precise knowledge of the lattice constants and the elastic constants is necessary to take into account the strain effects. However, these data are not available for the zinc-blende MgS at present. Therefore we have introduced another information on the layer widths from the *in situ* optical multiple reflection measurements. The reflection of the He-Ne laser light gives the maximum and the minimum depending on the film thicknesses. Near the average level of the reflections, the variation of the reflection with the film growth is almost proportional to the change of the optical path length induced by the increase of the film thickness. Therefore, the ratio of the reflection intensity change during the growth of the ZnSe (Δr_{ZnSe}) and MgS (Δr_{MgS}) layers is given by

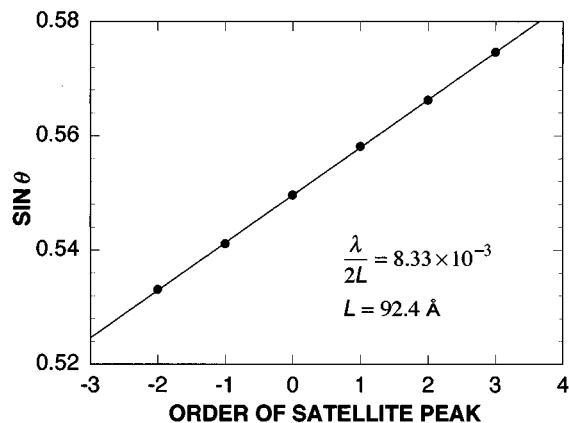


FIG. 2. The satellite peak positions observed in Fig. 1 were plotted in the form of $\sin\theta$. The thickness in one period L was estimated to be 92.4 Å from the slope.

TABLE II. Parameters measured on the samples a and b: average lattice constant perpendicular to the interface $a_{\perp\text{av}}$, thickness in one period L , ZnSe well width L_{ZnSe} , MgS barrier width L_{MgS} . M is the number of SL periods.

Sample	$a_{\perp\text{av}}$ (Å)	L (Å)	L_{ZnSe} (Å)	L_{MgS} (Å)	M
a	5.607	92.4	49.8	42.6	21
b	5.617	113.0	69.4	43.6	20

$\Delta r_{\text{ZnSe}} / \Delta r_{\text{MgS}} = n_{\text{ZnSe}} L_{\text{ZnSe}} / n_{\text{MgS}} L_{\text{MgS}}$, where n_{ZnSe} and n_{MgS} are the refractive indexes of ZnSe and MgS, respectively, and L_{ZnSe} and L_{MgS} are the ZnSe and MgS layer thicknesses, respectively. The one period in the SL is given by $L = L_{\text{ZnSe}} + L_{\text{MgS}}$. Therefore the ratio of the layer thicknesses, $L_{\text{ZnSe}} / L_{\text{MgS}}$, can be obtained with the knowledge of the refractive index values. In our experiments at the wavelength of 6328 Å, n_{ZnSe} of 2.578 and n_{MgS} of 2.206 were estimated using the modified single-effective-oscillator model.¹¹ From the measured ratio of $\Delta r_{\text{ZnSe}} / \Delta r_{\text{MgS}} = 1.37$ for this specimen together with $L = 92.4$ Å, L_{ZnSe} and L_{MgS} are calculated to be 49.8 and 42.6 Å, respectively. The measurements were performed on other SL samples following the same procedure, and the result for one more sample is added in Table II. Although the two samples shown in Table II have the MgS thicknesses less than 50 Å, the growth of the zinc-blende MgS layers was observed up to at least 100 Å.

Figure 3 shows the dependence of $a_{\perp\text{av}}$ on the total layer thickness for two series of samples with the fixed $L_{\text{ZnSe}} / L_{\text{MgS}}$ ratio and the fixed number of SL periods M with different layer thicknesses in one period L . The $L_{\text{ZnSe}} / L_{\text{MgS}}$ ratio is 1.17 and 1.59 for the closed circles and the closed triangles, respectively. $a_{\perp\text{av}}$ was kept almost constant at about 5.607 Å for $L_{\text{ZnSe}} / L_{\text{MgS}} = 1.17$ up to the thickness of 3200 Å and was kept at about 5.617 Å for $L_{\text{ZnSe}} / L_{\text{MgS}} = 1.59$ up to the thickness of 3000 Å. However, $a_{\perp\text{av}}$ was reduced when the film thickness increased further. This suggests the onset of the lattice relaxation of the films beyond the respective film thicknesses. This result indicates

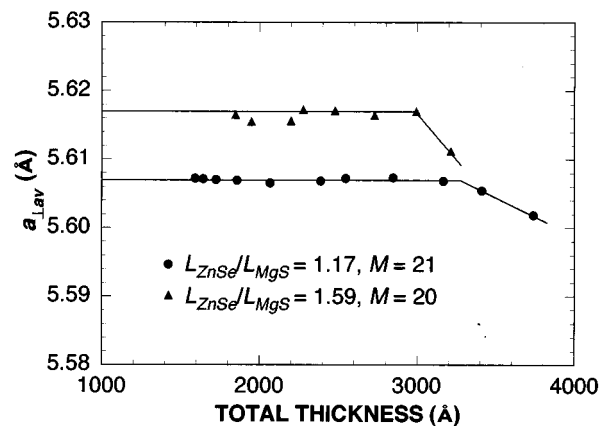


FIG. 3. Dependence of $a_{\perp\text{av}}$ on the total thickness for two series of samples with the fixed $L_{\text{ZnSe}} / L_{\text{MgS}}$ ratio and the fixed number of SL periods M , but with different layer thicknesses in one period L . $L_{\text{ZnSe}} / L_{\text{MgS}}$ and M were 1.17 and 21 for the closed circles and 1.59 and 20 for the closed triangles. $a_{\perp\text{av}}$ was kept almost constant up to the total thicknesses of 3200 Å for $L_{\text{ZnSe}} / L_{\text{MgS}} = 1.17$ and 3000 Å for $L_{\text{ZnSe}} / L_{\text{MgS}} = 1.59$. $a_{\perp\text{av}}$ was reduced as the film thickness increased further.

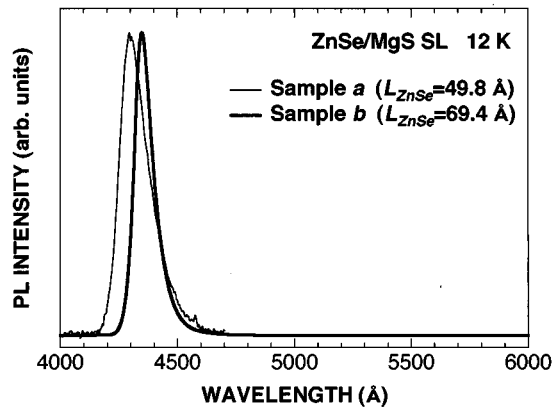


FIG. 4. PL spectra measured at 12 K on the ZnSe/MgS SLs of the samples a and b. The PL peaks were blue-shifted to the higher energy compared to that of bulk ZnSe.

that the ZnSe/MgS SL layers were grown coherently to the GaAs substrates up to the order of 3000 Å in total thickness.

Let us discuss the lattice constant of the binary MgS ($a_{0\text{MgS}}$). The lattice constants of ZnSe ($a_{\perp\text{ZnSe}}$) and MgS ($a_{\perp\text{MgS}}$) perpendicular to the interface are related to the above-determined quantities in the following equation: $L/a_{\perp\text{av}} = L_{\text{ZnSe}}/a_{\perp\text{ZnSe}} + L_{\text{MgS}}/a_{\perp\text{MgS}}$. In the ZnSe/MgS SL grown coherently on (001) GaAs, $a_{\perp\text{ZnSe}} = 5.688$ Å is estimated from the condition of the pseudomorphic deformation of ZnSe on GaAs using the elastic constants for ZnSe.¹ Employing the measured $a_{\perp\text{av}}$, L , L_{ZnSe} , and L_{MgS} values summarized for the two samples in Table II, the $a_{\perp\text{MgS}}$ was calculated to be 5.515 Å for the sample a and 5.508 Å for the sample b. Since the elastic constants for MgS is not available, we substitute those for ZnSe and ZnS.¹ The MgS lattice constant derived was 5.590 and 5.592 Å using the ZnSe and ZnS elastic constants, respectively, for the sample a. It was 5.587 and 5.589 Å using the ZnSe and ZnS elastic constants, respectively, for the sample b. From these results, the lattice constants of MgS was determined to be $a_{0\text{MgS}} = 5.59$ Å.

The credibility of the determined lattice constants and the layer thicknesses were examined by the theoretical simulation of the measured HRXRD pattern. The thin solid line in Fig. 1 shows the theoretical simulation calculated for the sample a. In this calculation, we take account of the thickness fluctuation for each layer to fit the broadening of the

satellite peaks assuming the fluctuation of ± 1 and ± 2 monolayers with the respective diffraction weighting of 0.73 and 0.32. The excellent fit of the simulation to the measured pattern shows that the determined $a_{0\text{MgS}}$ value is well reliable.

Figure 4 shows PL spectra measured at 12 K on the ZnSe/MgS SLs (samples a and b). The PL peaks were blue-shifted to the higher energy compared to free-excitons of bulk ZnSe and no midgap emission was observed. The blue shift of the PL peaks was observed with the decrease of the thickness of well layers in SLs, which suggests the quantum confinement effect in the fabricated ZnSe/MgS SLs.

In conclusion, we have demonstrated for the first time the successful growth of zinc-blende ZnSe/MgS SLs. The SLs were grown coherently to GaAs substrates up to the total thickness of ~ 3000 Å. The clear SL satellite peaks were observed in the HRXRD measurements and the lattice constant of MgS was estimated to be 5.59 Å.

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