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Excitonic Properties in ZnSe/MgS Superlattices

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Optical properties of ZnSe/MgS superlattices (SL's) were studied by reflection and photoluminescence (PL) spectroscopies. The PL peaks were nicely coincident with the excitonic peaks in reflection spectra, and the origin of luminescence was indicated to be C1-HH1 and C1-LH1 excitons up to room temperature. The lineshape broadening due to longitudinal-optical(LO)-phonon scattering of excitons observed in reflection spectra was much decreased in this SL compared to bulk ZnSe. At low temperature below 50K, the localized exciton effect was clearly observed in the PL spectra.

1. Introduction

In wide-band-gap II-VI semiconductors, exciton binding energies are larger than those in III-V semiconductors, and there arises a possibility that the excitonic contribution improves the characteristics of blue semiconductor lasers. The excitonic effects are expected to be further enhanced by the quantum confinement in SL's. Among the II-VI semiconductors, ZnSe and MgS have the largest energy gap difference and are closely lattice-matched to GaAs substrates. We have proposed ZnSe/MgS SL's and succeeded to grow zincblende ZnSe/MgS SL's with MOVPE.[1,2] In comparison with ZnCdSe and ZnSSe wells, ZnSe wells are free from the alloy fluctuation. So we can discuss physical phenomena more definitely.

In this paper, the optical properties of this new type of SL's were studied with both reflectance and PL spectroscopies. Some structures caused by excitonic effects are clearly seen up to room temperature in the reflectance spectra. From the discussion on the exciton peak positions and linewidths, the origin of the luminescence is shown to be excitonic up to room temperature. The broadening of the exciton luminescence and absorption line shapes is much reduced in the SL's compared to bulk ZnSe due to the reduced exciton-LO phonon scattering with quantum confinements. At low temperature below 50K, the localized exciton effects are discussed concerning the PL spectra.

2. Sample preparation

ZnSe/MgS SL's were grown on semi-insulating GaAs (001) substrates by atmospheric-pressure MOVPE system. The used precursors were di-ethyl zinc (DEZn), tertiarybutyl isopropyl selenide (tBiPSe), bismethyl cyclopentadienyl magnesium ($(MeCp)_2Mg$), and di-isopropyl sulfide (DiPS). Since the growth of MgS was observed above 450°C, the growth temperature was set to 450°C. During the growth, the growth rate was monitored *in-situ* using a He-Ne laser by multiple reflection in the films. X-ray diffraction measurements were performed on the grown ZnSe/MgS SL's. Several orders of satellite peaks from the SL's were clearly observed around the GaAs (004) peak, which shows that the both ZnSe and MgS epilayers are grown in zincblende structure.

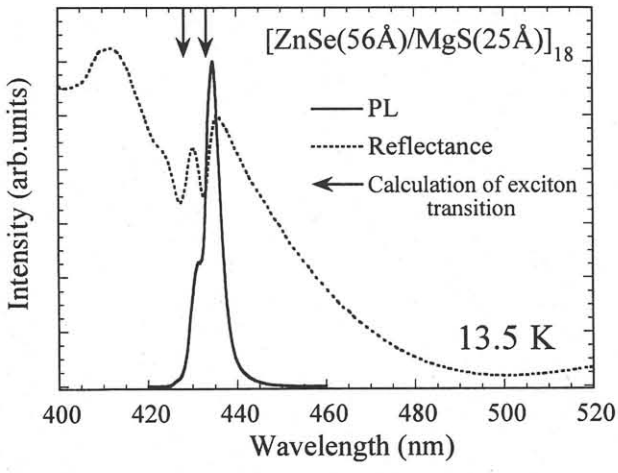

Fig. 1 PL & reflectance spectra of [ZnSe(56 Å) /MgS(25Å)]$_{18}$ SL measured at 13.5K. Two arrows show exciton absorption peaks and are very close to PL peaks.

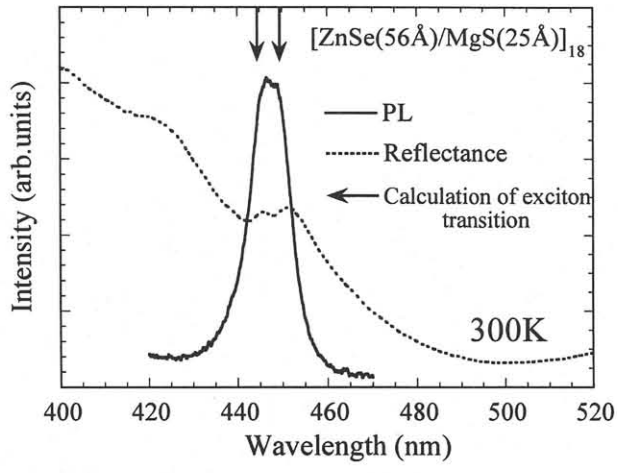

Fig. 2 PL & reflectance spectra of [ZnSe(56 Å) /MgS(25Å)]$_{18}$ SL measured at 300K.

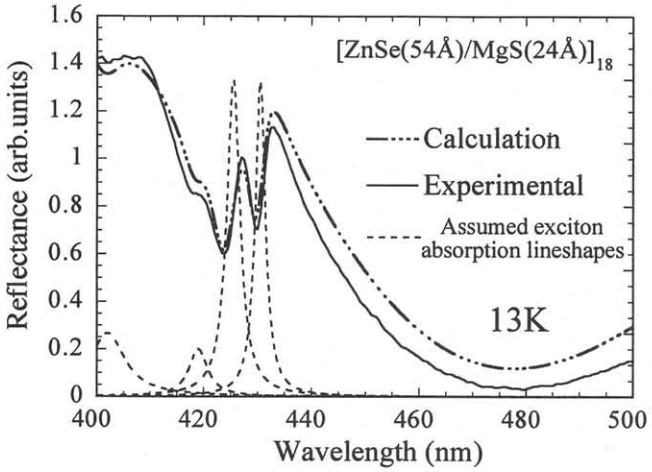

Fig. 3 Reflectance spectra and its fitting of [ZnSe(54 Å) /MgS(24 Å)]$_{18}$ SL. Dash and dot line is the calculated reflection spectrum and dotted lines are Lorentzian exciton absorption lineshapes assumed in the reflectance calculation.

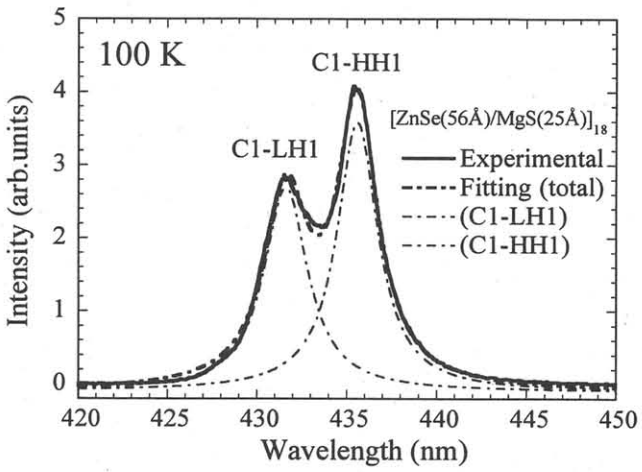

Fig. 4 PL spectrum and its fitting of [ZnSe(56 Å) /MgS(25Å)]$_{18}$ SL at 100K. Three dash and dot lines are the fitted spectra of total, C1-LH1, and C1-HH1 luminescence.

3. Results and discussion

PL and reflectance spectra of a ZnSe(56 Å)/MgS(25Å) SL with 18 periods were measured in the range of temperature between 13.5K and 300K. Figure 1 shows PL (solid line) and reflectance (dashed line) spectra measured at 13.5K. The clear excitonic contributions were observed in the reflection spectrum around 430nm superposed to the slowly-varying multiple reflection features. PL peaks very close to the excitonic peaks in the reflectance spectrum were almost in agreement with the calculated exciton transition wavelength. Exciton features were clearly observed at room temperature in the reflection spectra as shown by the dashed line in Fig. 2. The PL spectrum was also observed at room temperature, the position of which was in close agreement with the exciton peaks and the theoretically calculated ones.

At the temperature of 13.5K, the measured reflection spectrum was fitted with a theoretical model which includes excitonic effects and multiple reflections inside the whole epi-layer, where Lorentzian exciton absorption lineshapes were assumed. The exciton parameters such as the peak wavelength, the absorption coefficient and the linewidth were determined in order to reproduce the experimental spectra as shown in Fig. 3. The detailed analyses of reflectance spectrum are explained in another paper.[3] Figure 4 shows a PL spectrum and its fitting at 100K of the same sample. Three dash and dot lines are the fitted spectra of total, C1-LH1, and C1-HH1 luminescence. The total fitted spectrum well reproduces the measured spectrum.

Figure 5 shows temperature dependence of PL and exciton absorption peak energies. The exciton peak positions and the full width at half maximum (FWHM) of the line shapes were obtained by the theoretical fitting to reflection and PL spectra as discussed above. C1-HH1 peak energies of PL and excitons are almost coincident and are parallel with the ZnSe energy gap. Shifts of each peak energy to the lower energy for the higher temperature are due to the temperature dependence of the ZnSe energy gap. At low temperature below 50K, however, the C1-HH1 PL peak is located lower than the exciton absorption peak

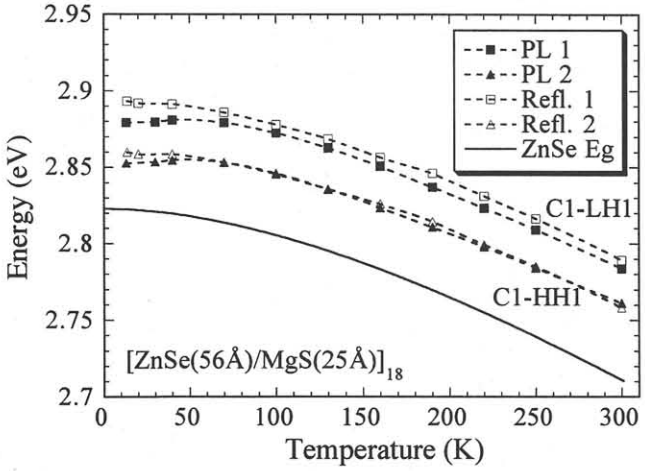

Fig. 5 Temperature dependence of PL & exciton absorption peak energies. Each peak energy is almost coincident and is parallel with the ZnSe energy gap.

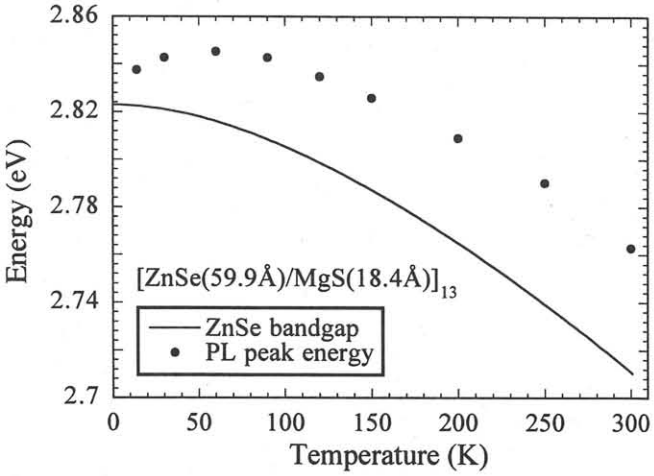

Fig. 6(a) Temperature dependence of PL peak energies of [ZnSe(59.9 Å)/MgS(18.4 Å)]$_{18}$ SL. At low temperature, PL peak energies show blue shift.

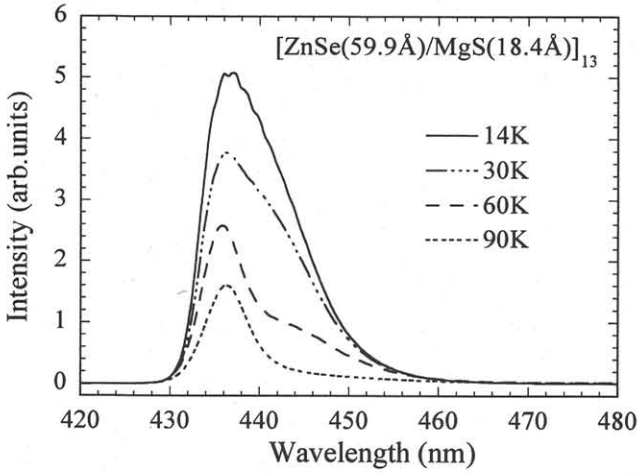

Fig. 6(b) Temperature dependence of PL spectra of $[ZnSe(59.9Å)/MgS(18.4Å)]_{18}$ SL. As the temperature rises, luminescence on the longer wavelength is quenched.

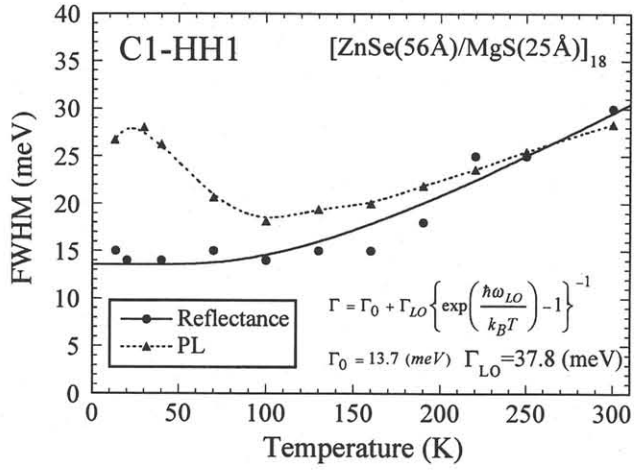

Fig. 7 Temperature dependence of FWHM of C1-HH1 excitonic absorption and PL. Solid line shows the fitting with LO phonon scattering. Γ_{LO} value is much reduced from the bulk value of 60meV.

energy. It is blue shifted for the higher temperature up to 50K. This phenomenon was more pronounced in a SL sample shown in Fig. 6(a). The corresponding PL spectra of this sample are shown in Fig. 6(b). As the temperature rises, luminescence on the longer wavelength is quenched. This will be due to the thermalization of localized excitons to free excitons.[4)]

The temperature dependence of FWHM of the exciton absorption line shapes and of the PL line shapes is shown in Fig. 7 for C1-HH1 transitions. The FWHM of the line width is written in the form:

$$\Gamma=\Gamma_0+\Gamma_{LO}\cdot(\exp^{\hbar\omega_{LO}/k_BT}-1)^{-1},$$

where Γ_0 is the inhomogeneous linewidth, and Γ_{LO} represents the homogeneous linewidth factor due to the LO phonon scattering, and ω_{LO} is the LO phonon frequency. The exciton-LO-phonon coupling constant Γ_{LO} derived from the fitting of the closed circles in Fig. 7 was 37.8 meV and was much reduced from the bulk value of 60 meV. The PL line shape is very close to the exciton line shape derived from the reflectance spectra, except for the low-temperature range where the PL peak was dominated with localized excitons. Except for the low temperature range for the C1-HH1 excitons, the very clear coincidence of the luminescence peak energy shown in Fig. 5 and the line shape shown in Fig. 7 was observed with the exciton absorption peaks up to room temperature. This demonstrates that the luminescence from the present ZnSe/MgS SL's is excitonic up to room temperature owing to the strong quantum confinement in this SL with the large band offsets.

4. Conclusions

Excitonic properties in ZnSe/MgS SL's were examined. Up to room temperature, excitonic structures were clearly observed in the reflectance spectra. This result indicates the enhancement of the exciton effects in ZnSe/MgS SL's. Excitonic parameters such as absorption peak energies and half widths obtained by the theoretical fits were very close to those of luminescence spectra, which demonstrates that the origin of luminescence is excitonic up to room temperature. Reduction of the exciton-LO-phonon coupling constant was clearly observed for C1-HH1 excitons in ZnSe/MgS SL's. At low temperature, the contribution of localized excitons was clearly observed.

Acknowledgements

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References

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