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Excitonic properties of zinc-blende ZnSe/MgS superlattices studied by reflection spectroscopy

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Excitonic properties of newly developed zinc-blende ZnSe/MgS superlattices (SL’s) were measured by reflection spectroscopy. The modification of the excitonic peaks by the multiple reflection in the SL films was treated theoretically and a fitting method to estimate the exciton absorption peak positions and exciton linewidths was developed. Although zinc-blende MgS did not exist before, excellent optical properties were observed in the ZnSe/MgS SL’s. Excitonic structures were clearly observed from 13 K up to the measured room temperature. In spite of strong ionicity of MgS barrier layers in the ZnSe/MgS SL’s, the reduction of exciton–LO-phonon coupling was clearly observed in narrower wells. This indicates that the quantum confinement effect on excitons is large due to the large band offsets and it overcomes the enhancement of exciton–LO-phonon scattering due to high ionicity in barrier layers. [S0163-1829(97)03307-9]

I. INTRODUCTION

There has been a great deal of interest recently in wide-band-gap II-VI semiconductors because of its attraction for basic physics as well as their potential to realize blue/green light-emitting devices. Exciton binding energies are larger than those in III-V semiconductors mainly because of larger electron and hole effective masses, and further enhancement of excitonic effects is expected by introducing the quantum confinement in quantum well (QW) and superlattice (SL) structures. In blue/green range, Zn$_x$Cd$_{1-x}$Se/ZnS, 6 and ZnSe/Zn$_x$S, 1–3 the band offsets are increased with higher Cd sharing of band offsets among conduction and valence bands operate in pure blue regions or shorter wavelengths, proper quantum confinement in SL’s and related devices that will confine both electrons and holes to the ZnSe well layer. Furthermore, using the lattice constant of 5.59 Å recently determined for the zinc-blende MgS, relatively small lattice mismatch (~1.4%) between ZnSe wells and MgS barriers is possible in this heterostructure. Therefore, from a viewpoint of crystalline quality of grown SL’s and carrier confinement to well layers, ZnSe/MgS SL’s will be a promising material for investigating excitonic properties. In comparison to...
Zn, Cd$_1$$_x$Se and Zn, Cd$_1$$_x$S wells. ZnSe wells are free from alloy broadening. This will make the discussion on physical phenomena more straightforward.

In this paper, a detailed study on optical properties of ZnSe/MgS SL’s is reported. In order to investigate the excitonic properties in these SL’s, reflection spectroscopy was used. The advantage of reflection spectroscopy is that reflectance is independent of nonradiative recombinations, therefore the measurements are possible in a wider temperature range in comparison to photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy, which are based on radiative recombination processes. Furthermore, reflectance measurements do not require the etching process of GaAs substrates, which is usually necessary for measuring absorption spectra. A theoretical fitting method to the measured reflection spectra was developed considering the multiple reflection in the transparent SL films. The exciton absorption peak positions and exciton linewidths were estimated with good accuracy. The prepared ZnSe/MgS SL’s showed clear excitonic enhancement and excitonic peaks were clearly observed from 13 K to the measured room temperature. The blueshift of the exciton peaks by the quantum confinement in the ZnSe/MgS SL’s is compared with the theoretical calculation. The temperature dependence of the exciton linewidth is also discussed. Since MgS in the barrier layers has higher ionnity than Zn$_x$Se$_{1-x}$, the exciton–LO-phonon coupling in this SL may be enhanced if the wave function is penetrated into the barrier layers for narrow wells and the resultant scattering is enhanced through the Fröhlich interaction in the barrier layers. On the other hand, the exciton–LO-phonon coupling will be reduced if the quantum confinement effect in narrow wells dominate as is observed in other SL’s. The present measurements show that the latter effect of the quantum confinement dominates in the ZnSe/MgS SL’s, and the exciton–LO-phonon coupling is reduced for narrower wells.

II. SAMPLE PREPARATION

ZnSe/MgS strained SL’s were grown on semi-insulating GaAs(001) substrates with atmospheric-pressure (AP) MOVPE. For the growth of MgS, bismethyl cyclopentadienyl-magnesium [(MeCp)$_2$Mg] and di-isopropyl sulfide (DiPS) were selected as precursors. For the growth of ZnSe, di-ethyl zinc (DEZn) and tertiarybutyl isopropyl selenide (tBiPSe) were used. Since the growth of MgS was observed above 450 °C, the growth temperature was set to 450 °C. For the straightforward analysis of the reflection spectra, SL structures were grown directly on GaAs substrates without buffer layers starting from the ZnSe layer. The sample surfaces were terminated with the ZnSe layer for preventing MgS layers from being oxidized. During the growth, the growth rate was monitored in situ by an optical multiple reflection in the films with a He-Ne laser (632.8 nm). From this monitoring, the ratio of the ZnSe/MgS layer thickness was measured. Therefore together with the SL period calculated from the SL satellite peaks in x-ray diffraction measurements, the thickness of ZnSe and MgS layers in SL’s were determined. Characterization of SL’s was carried out with optical reflectance and PL measurements. In reflectance measurements, a halogen lamp was used as a light source, and throughout this work, measurements were performed with incident light propagating along the normal to the SL surfaces.

III. CALCULATION OF REFLECTION SPECTRA

To obtain excitonic properties such as absorption peak positions, absorption intensities, and half-widths of absorption peaks from reflection spectra, measured reflection spectra were fitted by a theoretical calculation. In this calculation, exciton absorptions were treated as Lorentzian functions, which is appropriate for the weak exciton-phonon coupling case. The criteria to distinguish the weak and strong coupling cases were fully discussed by Rudin, Reinecke, and Segall and they showed that the most III-V and II-VI materials satisfy the criterion for the weak coupling case. The measured reflection spectra were highly modified by the multiple reflection from all of the epitaxial layers and the optical interference between the lights reflected from the sample surface and from the heterointerface to the GaAs substrate were taken into account. Power reflectivity from the sample surface in the normal incidence arrangement is expressed as follows:

$$R = \frac{(r + r')^2 - 4rr' \sin^2(\delta/2)}{(1 + rr')^2 - 4rr' \sin^2(\delta/2)},$$

where $r$ is the amplitude reflectivity from the sample surface to the air, $r'$ is the one from the GaAs heterointerface to the film, $\alpha$ is the absorption coefficient in the film, and $\delta$ is the optical path length in the film, which is given by $\delta = 4\pi n_{\text{SL}} L/\lambda_0$. $n_{\text{SL}}$ is the refractive index of the SL, $L$ is the total epitaxial layer thickness, and $\lambda_0$ is the wavelength of the incident light.

When excitonic contributions to the refractive index and the absorption coefficient are given explicitly, $n_{\text{SL}}$ and $\alpha$ are given by the following equations:

$$n_{\text{SL}} = n_0 - \sum_i \sum_j \frac{2}{\pi \nu} \frac{\Delta \Gamma_j}{4\Delta_i^2 + \Gamma_j^2},$$

$$\alpha = \alpha_0 + \sum_i \sum_j \frac{\Gamma_j^2}{4\Delta_i^2 + \Gamma_j^2}.$$
mon in the four cases are caused by multiple reflection. Fitting to this multiple reflection spectrum gives us the total epitaxial layer thickness with the knowledge of the refractive index. The sharp structures superimposed on the multiple reflection spectra are the excitonic contributions. It is much different depending on the exciton peak positions. When the exciton peak is located near the top or bottom of the multiple reflection spectra, a single peak appeared as shown in Figs. 2a and 2c. These exciton spectra are similar to the results derived with the single-path reflection model,\textsuperscript{16,17} where only the interference between the reflection from the surface and the single-path reflection from multiple quantum wells (MQW) was considered. Following this model, the exciton spectra reflect the real or imaginary part of the exciton dielectric constants depending on the phase shift by the path length between the surface and the MQW layers. In the present case, the phase shifts at the maximum and minimum multiple reflections select the imaginary part of the exciton dielectric constant as shown in Figs. 2a and 2c. In the two cases, the polarity of the excitonic contribution is opposite depending on the phase shift of the multiple reflection. At the middle level of the multiple reflections, the real part of the exciton dielectric constant dominates in the reflection spectra as shown in Figs. 2b and 2d, by the phase shift from the multiple reflection similar to the above cases of Figs. 2a and 2c. Since the real part of the excitonic refractive index is antisymmetric, the excitonic contribution in Figs. 2b and 2d are also asymmetric.

In the actual calculation, which will be discussed in the next section, the reflections at the sample surface and the interface to the GaAs substrate were taken into account, but the smaller reflections at the SL heterointerfaces were neglected for simplicity. The refractive index dispersion relations of ZnSe and MgS were obtained by a modified single effective oscillator model.\textsuperscript{17–20} The average refractive index of the SL layer $n_0$ was approximated by the mean value of the two layers weighted with the respective thicknesses.

**IV. RESULTS AND DISCUSSIONS**

The experimentally measured reflection spectrum (solid line) was compared with the result of theoretical calculation (dot-dashed line) in Fig. 3. The sample structure measured is the SL with 18 periods of 54Å-thick ZnSe well layers and 24Å-thick MgS barrier layers. Measurements were carried out at 13 K. The slowly varying feature in the measured spectrum is due to the multiple reflection. The clear structures around 430 nm due to excitonic effects are evident. The measured reflection spectrum was nicely reproduced by the theoretical fitting shown by the dotted-dashed line in Fig. 3. The accuracy of this fitting method depends on the sharpness of the excitonic features and the sharpness was good enough even at room temperature. For this fitting, we had to include
four excitonic peaks that are clear in the measured reflection spectrum in the 400–440-nm range from the deviation from the normal multiple reflection spectrum. The dashed lines are the assumed exciton absorption peaks with the Lorentzian shape fitted for the major two peaks are 100,000 cm⁻¹ at 13 K in Fig. 3. To identify the origin of each exciton peak, the peak positions determined from the fitting were compared with the calculated transition wavelength.

Figure 4 shows the theoretical calculation of the transition wavelength between subbands. The excitonic absorption peak positions determined in Fig. 3 are shown by the solid circles. The energy separations of the two peaks shown by the open and closed squares are in reasonable agreement with the calculation.

TABLE I. Parameters used in subband transition calculation. Parameters for ZnSe were taken from Ref. 4. Effective masses for zinc-blende MgS are not yet known and were assumed to be the same as ZnS. (Effective masses are in the unit of m₀, Cᵢⱼ’s are 10⁶ kg cm⁻²)

<table>
<thead>
<tr>
<th>Material</th>
<th>α₀ (Å)</th>
<th>E₀ (eV)</th>
<th>m*(C)</th>
<th>m*(HH)</th>
<th>m*(LH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnSe</td>
<td>5.669</td>
<td>2.82</td>
<td>0.147</td>
<td>0.6</td>
<td>0.31</td>
</tr>
<tr>
<td>MgS</td>
<td>5.59</td>
<td>4.5</td>
<td>0.27</td>
<td>0.47</td>
<td>0.49</td>
</tr>
<tr>
<td>C₁₁</td>
<td></td>
<td></td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₁₂</td>
<td></td>
<td></td>
<td>0.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnSe</td>
<td>0.826</td>
<td>0.498</td>
<td>5.40</td>
<td>1.2</td>
<td></td>
</tr>
</tbody>
</table>

From the comparison of the measured exciton peak positions and the calculated transition energies, the two major exciton peaks in Fig. 3 were identified as the C₁-HH1 and C₁-LH1 exciton transitions. The third small exciton contribution is close to the C₁-HH2 transition. The transition between the C₁ and HH2 subbands is normally forbidden because of the parity selection rule. The observation of the weak C₁-HH2 transition suggests that there remains slight asymmetry in the grown SL. The most probable factor will be tailing of the grown ZnSe/MgS heterointerfaces due to the inadequate gas exchange during the MOVPE growth. The fourth exciton peak in the shorter wavelength is most probably the contribution from the C₂-HH2 transition, but the additional contribution from the C₂-LH2 transition may be superimposed. In Fig. 3, intensity of the C₁-LH1 exciton absorption peak is comparable to that of the C₁-HH1 peak. In the present reflectance measurements, the electric field of the incident light is polarized parallel to the well layers. The observed large contribution of the C₁-LH1 exciton is different from the normally predicted oscillator strength ratio of 3 to 1 for C-HH and C-LH transitions, respectively. Detailed discussion on this point needs further experimental studies.
FIG. 5. Temperature dependence of reflection spectra measured on a ZnSe/MgS SL. The C1-HH1 and C1-LH1 excitonic structures around 440 nm were clearly visible up to room temperature.

The well-width dependence of the absorption peak wavelengths extracted from the reflection spectra on other SL’s is also shown in Fig. 4. In this figure, the measured exciton peaks related to C1-HH1 and C1-LH1 were plotted with open and closed squares, respectively. Some samples showed only one peak in the corresponding range as shown by closed triangles, maybe because of poor interface properties. The blueshift of the measured exciton peaks for the narrower well widths is in accordance with the calculated transition wavelength. Although the measured exciton peaks show the tendency to shift to shorter wavelengths than the calculated ones, the separations of the two exciton peaks are very close to the calculated HH1-LH1 separations. The tendency that the measured transition wavelengths are slightly shifted to shorter wavelength than the calculated ones is not due to the theoretical fitting method but is due to the problem remaining in the growth of the superlattices. Especially, there remains the problem of extra MgSe layer formation with the thickness of less than 1 ML at the interfaces depending on how the interfaces were grown. Clear excitonic features are not observed in these SL’s with the extra MgSe layers and the details are under study.

In order to investigate the excitonic effects in the ZnSe/MgS SL’s at the higher temperature, the temperature dependence of the reflection spectrum was measured as shown in Fig. 5. The measured sample is the SL with 18 periods of ZnSe(56 Å)/MgS(25 Å). It is noted that the C1-HH1 and C1-LH1 excitonic structures around 440 nm remain clearly visible up to room temperature. This will demonstrate the enhanced excitonic effect due to the quantum confinement in this SL. From these measurements, the temperature dependence of the FWHM of the exciton absorption line shape can be discussed. It is interesting to investigate the exciton–LO-phonon coupling in the ZnSe/MgS system from the measured exciton linewidth. The reduction of the exciton–LO-phonon coupling was reported on ZnSe quantum wells and MgS quantum well system with bulk excitons. In this work, the exciton–LO-phonon coupling parameter $\Gamma_{LO}$ was estimated to be 34 meV for the SL with the 56-Å well. For the SL with the 87-Å well, the measured FWHM value showed the higher temperature dependence in the low-temperature range than that of the SL with the 56-Å well. Therefore the acoustic-phonon scattering term was included and the nice fitting shown with the solid line was obtained with the fitting parameters given in Fig. 6. The $\Gamma_{LO}$ value of 46 meV thus determined in Fig. 6, however, will have the uncertainty of ±3 meV because of the increased fitting parameters.
The value of about 60 meV in ZnSe. All the measured values in Fig. 7 were smaller than the bulk increases for this range of well widths that is less than the well width less than 60 Å will be interesting from two point of view. First, the penetration of the exciton–LO-phonon coupling compared to other II-VI SL’s. The other point is that the penetration of the wave functions will increase for the narrow well region that may increase the LO-phonon coupling. At present, the inhomogeneous broadening in the narrow well region is too large to accurately estimate the exciton linewidth. Further improvement of the heterointerfaces in the grown ZnSe/MgS is necessary and the study is under progress.

V. CONCLUSIONS

Excitonic properties in the ZnSe/MgS SL’s were examined. We showed that reflectance measurement is a useful method to investigate optical properties by employing the fitting with the developed simulation. It is free from substrate removal and the optical properties at room temperature can be easily studied. Excitonic parameters such as absorption peak positions, absorption intensities, and half widths were obtained by employing the Lorentzian exciton line-shape function assumed in the theoretical simulation. The exciton absorption peak positions determined from the reflection spectra agreed well with the subband transition wavelength calculated. Up to room temperature, excitonic structures were clearly observed. This result strongly indicates the enhancement of the exciton effects in ZnSe/MgS SL’s. Reduction of the exciton–LO-phonon coupling constant was clearly observed for excitons in narrower wells.

ACKNOWLEDGMENTS

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given in Ref. 19 are given in Ref. 18 for ZnSe. The parameters for MgS were given as follows: $E_0 = 7.5 \text{ eV}$ (extrapolated from the energy gap dependence in other II-VI semiconductors), $E_g = 4.5 \text{ eV}$ (energy gap of MgS) and $E_d = 27 \text{ eV}$ (almost the common value among the similar II-VI semiconductors).
