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Excitonic transition of (ZnSe–ZnS)/CaF_2 strained-layer superlattices under lower excitation

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A photoluminescence (PL) study of ZnSe–ZnS strained-layer superlattice (SLS) on a transparent substrate, CaF_2, grown by atmospheric pressure metalorganic chemical vapour deposition (AP-MOCVD) is presented. Two absorption bands and three emission bands in the SLS were observed for the first time under low excitation. The origin of some bands might be ascribed to the excitonic transition of $n = 1$ heavy and light hole.

1. Introduction

ZnSe is a direct-gap semiconductor with a zincblende crystal structure and a relatively large band-gap energy of 2.7 eV at 300 K. Excitons in ZnSe are relatively strongly bound with a binding energy of ~20 meV. Recently, attention has been paid to the strained-layer superlattice (SLS) using a ZnSe layer as the well material, which promises the possibility of being able to obtain excitonic emission [1] and optical bistability (OB) [2,3]. In the case of ZnSe/GaAs and ZnSe/CaF_2 systems, the lattice mismatches are about 0.27% and 3.6%, respectively. A few reports on the GaAs crystal as a substrate material in early heteroepitaxial growth have been published [4,5]. But in the excitonic emission region of a ZnSe crystal, the GaAs substrate is not transparent, which is inconvenient for the study of the absorption and optical bistability of the ZnSe epilayer or the superlattices with ZnSe wells. Although we can now selectively etch ZnSe/GaAs structure [6], it is difficult to obtain a larger pass-light area with a thinner epilayer ($d < 1$ μm). An appropriate transparent substrate is still a direct and efficient method for studying the optical properties of the ZnSe epilayer.

2. Experimental procedure

The ZnSe–ZnS SLSs were grown on (111) CaF_2 substrates by atmospheric-pressure MOCVD using dimethylzinc (DMZ), H_2Se and H_2S as source marterials for Zn, Se and S, respectively [7]. The optimization of reactor design and growth conditions have been restrained [8,9]. The satellite peaks were observed by X-ray diffraction measurement indicating ZnSe–ZnS with superlattice structure. From the PL measurement, the quantum size effect was evidenced by the relationship between the ZnSe well layer thickness and the peak energy shift of excitonic emission. The 3650 Å line of a Hg lamp was used as the excitation source. To obtain temperature-dependence measurements, the samples were mounted on a cold finger of the He refrigerator which could cool the sample temperature down to about 10 K. The epilayers were grown on a fresh natural cleavage face of a CaF_2 single crystal. After flushing with hydrogen, the substrates were heated at 600°C for 10 min prior to growth in order to desorb volatile species from the surface, then the temperature was reduced to the substrate temperature (350–450°C). To avoid effects of lattice mismatch and of thermal stress, the

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substrate temperature was reduced slowly after the growth.

3. Results and discussion

3.1. Structure analysis

Comparing the ZnSe/GaAs heterostructure with ZnSe/CaF$_2$, the latter has many unfavourable growth factors. The larger lattice mismatch leads to more misfit defects in the epilayer. The main problem in the ZnSe/CaF$_2$ system is the disparity of the linear coefficient of expansion for those two materials ($a_1 = 19.7 \times 10^{-6}$ °C^{-1} for CaF$_2$, and $a_2 = 8.5 \times 10^{-6}$ °C^{-1} for ZnSe). By taking the transparent CaF$_2$ material as the ZnSe–ZnS SLS substrate and controlling the thickness of each layer, we can also obtain the samples of (ZnSe–ZnS)/CaF$_2$ SLSs with higher quality than that of (ZnSe–ZnS)/GaAs SLSs. As a result, the average lattice constant (a'') [10] of SLS parallel to the interface is given by

$$a'' = a_{\mathrm{ZnSe}}\left(1 - \frac{fG_{\mathrm{ZnS}}}{G_{\mathrm{ZnSe}}h + G_{\mathrm{ZnS}}}\right),$$

where $f = (a_{\mathrm{ZnSe}} - a_{\mathrm{ZnS}})/a_{\mathrm{ZnSe}}$ is the misfit between stress-free lattice constants. G_{ZnSe} and G_{ZnS} are the shear moduli constants [11]. $h = L_{\mathrm{ZnSe}}/L_{\mathrm{ZnS}}$ is the ratio of two layer thicknesses.

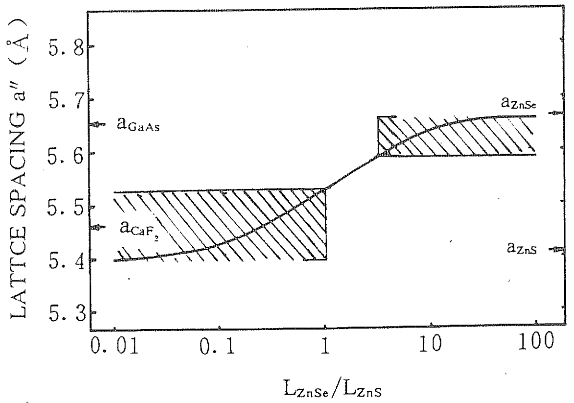

Fig. 1. Variation of a'' as a function of $L_{\mathrm{ZnSe}}/L_{\mathrm{ZnS}}$ in ZnSe–ZnS SLS.

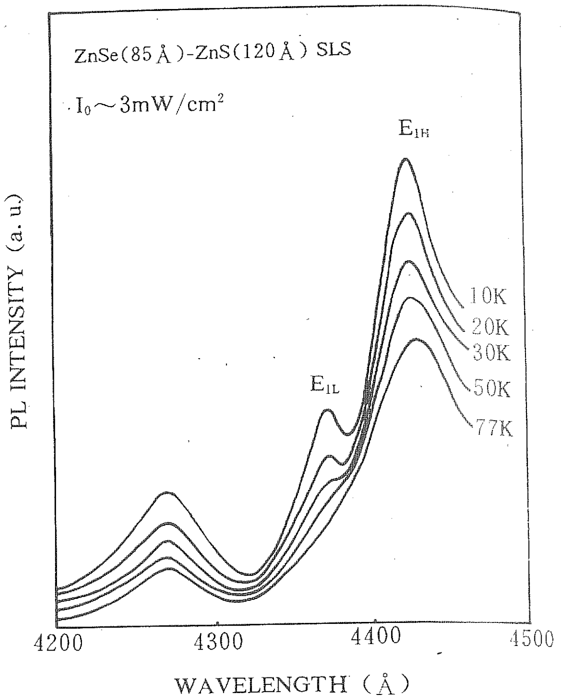

Fig. 2. PL spectra measured at various temperatures for the ZnSe–ZnS/CaF$_2$ SLS under $I_0 \sim 3$ mW/cm^2.

Fig. 1 represents the calculated curves of a'' as a function of h. The lattice constants of a_{GaAs}, $a_{\mathrm{CaF_2}}$, a_{ZnSe} and a_{ZnS} are also given in this figure. As can be seen, for $h < 1$, a'' is close to the lattice constant of the CaF$_2$ substrate and the mismatch is below 1%. But for the (ZnSe–ZnS)/GaAs SLS structre, only for $h > 3$ the mismatch is smaller than 1%. For the ZnSe–ZnS SLS or MQWs, the optical properties mainly rely on the ZnSe well thickness, and the quantum size effect and the larger binding energy are a function of the well thickness. Thus, the GaAs substrate is not suitable for the ZnSe–ZnS MQWs structure. This is why it is not difficult to observe subband transition in a (ZnSe–ZnS)/CaF$_2$ SLS structure. Here, we focus on a particular superlattice sample with 100 periods of 85 Å thick ZnSe layers and 120 Å thick ZnS layers.

3.2. PL spectra

Fig. 2 shows the emission spectra in the temperature region of 10–77 K, using the 3650 Å line of a Hg lamp as an excitation source. At 10 K, there are three peaks located at 2.801, 2.835 and 2.904 eV, respectively. The allowed subbands in ZnSe–ZnS SLS can be calculated from Kronig–Penney band model [12], assuming a one-dimensional periodic square well potential [13] and the light hole exciton calculated by "internal biaxial stress". The values calculated are $E_{1H} = 2.796$ eV and $E_{1L} = 2.847$ eV. From the viewpoint of peak energy position, the peaks at 2.801 and 2.835 eV might be ascribed to the emission of $n = 1$ heavy and light hole excitons, respectively. The origin of the peak at 2.904 eV is not understood. It should be noticed that the high energy tail of $n = 1$ heavy hole excitonic peak broadens and the relative intensity of the light hole excitonic peak decreases with increasing temperature and disappears at temperatures higher than 50 K. One reason might be that the excitonic binding energy of the light hole is smaller than that of the heavy hole. Another cause may also be that the hot electron density in subbands increases as the temperature increasing due to the Boltzmann distribution exp $(-\Delta E/kT)$, and the half-width of the heavy hole excitonic band broadens and covers the emission of light hole exciton.

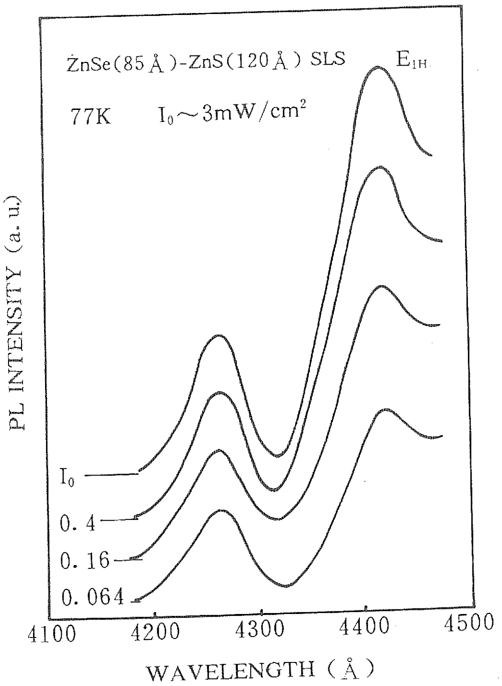

Fig. 3. Excitation intensity dependence of the excitonic emission at 77 K.

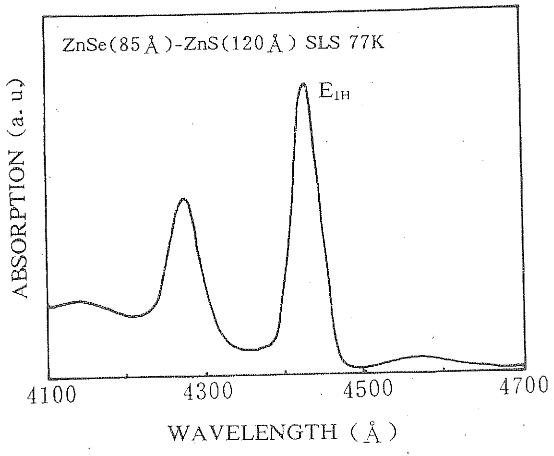

Fig. 4. Absorption spectrum of the ZnSe–ZnS/CaF$_2$ SLS at 77 K.

Fig. 3 shows the 77 K PL spectrum of the (ZnSe–ZnS)/CaF$_2$ SLS under different excitation intensities. At the same temperature, the excitonic energies hardly change under the region of excitation from 0.16 I_0 to I_0 ($I_0 \sim 3$ mW/cm^2), indicating that the process of photoheating is small at this region. Fig. 4 shows the absorption spectrum of the (ZnSe–ZnS)/CaF$_2$ SLS at 77 K. It is found that there are two absorption bands peaked at 2.796 and 2.897 eV. The band E_{1H} at lower energy side is attributed to the absorption of $n = 1$ heavy hole free excitons, according to the calculation mentioned above. The band at higher energy side is not understood.

4. Conclusions

In conclusion, the optical properties of the (ZnSe–ZnS)/CaF$_2$ SLS were analysed by taking into account the strain effect and excitonic emission. Under lower excitation, two absorption bands peaked at 2.796 and 2.897 eV and three emission bands peaked at 2.801, 2.835 and 2.904 eV in the SLS were observed for the first time. The absorption band E_{1H} attributed to the absorption of $n = 1$ heavy hole free excitons and the emission bands at 2.801 and 2.835 eV might be ascribed to the recombination of $n = 1$ heavy and light hole free excitons, respectively.

Acknowledgements

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