Type conversion under hydrostatic pressure in ZnSe-ZnS strained-layer superlattices

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A conversion from type-I to type-II in a ZnSe-ZnS strained-layer superlattice under hydrostatic pressure is observed. The hydrostatic-pressure dependence of the integrated intensity and the linewidth of the $n=1$ heavy-hole exciton emission spectra is represented by a couple of straight lines with a clear kink at about 31 kbar. Moreover, the emission peaks appear below the band-gap energy of the ZnSe well layers above 31 kbar. All of these features are well explained by the type conversion associated with the Γ-Γ conduction-band crossover between the ZnSe well and ZnS barrier layers.

In recent years, there has been much work on the effects of the external modulations in semiconductor superlattices and multiple-quantum-well structures. Hydrostatic-pressure studies[1-3] and electric-field studies[4] have enabled us to understand the fundamental electronic structures in GaAs-based quantum-well structures through the interlayer Γ-X crossover. Magnetic-field studies have also clarified the band structures in diluted magnetic semiconductor quantum-well structures such as ZnSe-$Zn_{1-x}Fe_xSe$ (Ref. 5) and CdTe-$Cd_{1-x}Mn_xTe$ (Ref. 6) through the Zeeman splitting of the valence band.

We present here the first evidence of a conversion from type I to type II under hydrostatic pressure in wide-band-gap ZnSe-ZnS strained-layer superlattices (SLS's). This type conversion results from a Γ-point crossover of the ZnSe well and ZnS barrier conduction bands. One of the most characteristic aspects of this SLS is that the conduction-band offset is much smaller than the valence-band offset. This aspect has been suggested by the model-solid theory.[7] Our recent studies by photoluminescence excitation (PLE) spectroscopy have shown that type-I ZnSe-ZnS SLS's have no electron quantum state higher than $n=2$ in the conduction-band wells.[8] The conduction-band offset was estimated to be less than 150 meV on the basis of Kronig-Penney analysis. Judging from the differences in the conduction-band deformation-potential constant and the bulk modulus of ZnSe well and ZnS barrier layers, one can expect that a conduction-band crossover between these layers occurs at a moderate value of hydrostatic pressure. This article presents the evidence of the crossover. It is clearly observed in the changes in the integrated intensity, the linewidth, and the peak energy of the $n=1$ heavy-hole exciton emission spectra.

ZnSe-ZnS SLS's were grown on (100)-oriented GaAs substrates at 350 °C without buffer layers by a low-pressure metal-organic chemical-vapor deposition (MOCVD) method with all gaseous sources. The sample used in this study consists of 150 periods of 2.0-nm-thick ZnSe well layers separated by 4.0-nm-thick ZnS barrier layers. The GaAs substrate was thinned to about 50 μm. A small piece of the thinned sample was placed in a Merrill-Bassett diamond-anvil cell with liquid nitrogen as the pressure transmitting fluid. The energy shift of the R_1 luminescence line from a ruby crystal was used to calibrate the pressure. The cell was directly immersed in liquid nitrogen. Photoluminescence (PL) spectra were measured using a conventional lock-in detection technique in conjunction with a 75-cm single grating monochromator. The excitation source was a 350-nm line of a continuous-wave argon-ion laser.

Figure 1 shows the schematic hydrostatic-pressure dependence of the conduction-band edges for both ZnSe well and ZnS barrier layers in the ZnSe-ZnS SLS. In this calculation, we used -5.4 and -4.0 eV as a hydrostatic band-gap deformation-potential constant $(a_c - a_v)$ for ZnSe and ZnS, respectively.[9] Moreover, we divided the hydrostatic band-gap deformation-potential constant into a hydrostatic conduction-band deformation-potential constant (a_c) and a hydrostatic valence-band deformation-potential constant (a_v), using the calculated ratio (a_c/a_v) given by Camphausen, Connell, and Paul.[10] These values are listed in Table I. As a bulk modulus, we used 6.25×10^5 bar (Ref. 11) and 7.69×10^5 bar (Ref. 12) for ZnSe and ZnS, respectively. Therefore, we obtained the energy shift of the conduction-band edges under hydrostatic pressure by 5.84×10^{-3} P eV and 3.62×10^{-3} P eV for ZnSe and ZnS, respectively. Here P is the hydrostatic pressure in units of kbar. The conduction-band offset under no external hydrostatic pressure is shown as ΔE_c in this figure. The conduction-band edges for both ZnSe and ZnS layers shift toward higher energy with increasing hydrostatic pressure and cross at P_0, as shown in Fig. 1. In this way, our calculation suggests that the con-

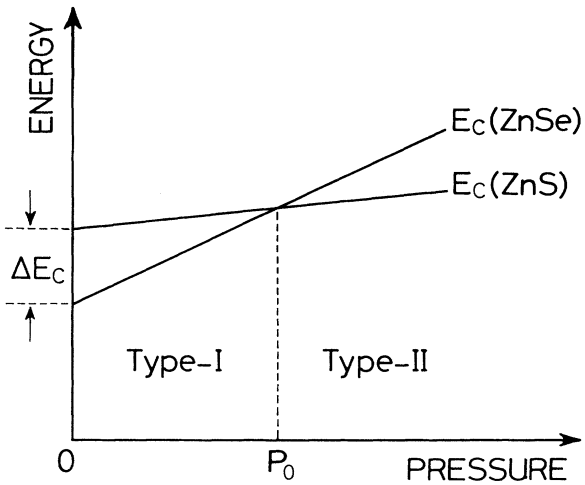

FIG. 1. Schematic changes in the conduction-band edges for both ZnSe well and ZnS barrier layers in a ZnSe-ZnS SLS as a function of hydrostatic pressure. In this figure, ΔE_c denotes the conduction-band offset at atmospheric pressure and P_0 denotes the crossover pressure.

version from type I ($P < P_0$) to type II ($P > P_0$) occurs in the ZnSe-ZnS SLS under hydrostatic pressure.

Figure 2 shows PL and absorption spectra of the ZnSe-ZnS SLS used in this study. Two peaks observed in the absorption spectrum correspond to $n=1$ heavy-hole (hh) and $n=1$ light-hole (lh) excitons. The PL peak appears by 28 meV lower-energy side of the $n=1$ heavy-hole exciton peak in the absorption spectrum, and is located at the tail part of the exciton absorption spectrum. This dominant PL peak, therefore, can be attributed to the intrinsic radiative recombination of the $n=1$ heavy-hole excitons. The Stokes shift is probably determined by the interface fluctuation. The fundamental optical properties of this SLS have already been reported.[13]

Photoluminescence spectra of the ZnSe-ZnS SLS under atmospheric and various hydrostatic pressures at 77 K are shown in Fig. 3. With the application of hydrostatic pressure, the PL peak position shifts toward higher energy and the linewidth broadening takes place. Especially, the linewidth obtained at 45.8 kbar is 3.3 times as broad as that obtained at atmospheric pressure. The line shape becomes much more asymmetric with increasing pressure because of the decrease of the intrinsic recombination relative to the lower-energy component of the spectrum. This lower-energy component can be attributed to the recombination of excitons localized more deeply. The origin of this component has not been understood clearly so far. It is probably ascribed to the recombination of excitons deeply localized at interface defects.

Figures 4(a) and 4(b) show the hydrostatic-pressure dependence of the integrated intensity and the linewidth (the full width at half maximum) of the $n=1$ heavy-hole exciton emission spectra at 77 K, respectively. In this

TABLE I. The hydrostatic band-gap deformation-potential constants $a_c - a_v$, and the conduction- and valence-band deformation potential constants, a_c and a_v. These values are written in units of eV.

	$a_c - a_v$	a_c	a_v
ZnSe	−5.4	−3.65	1.75
ZnS	−4.0	−2.78	1.22

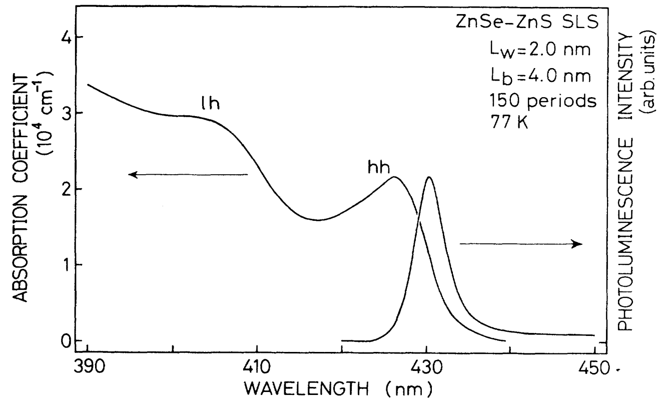

FIG. 2. Photoluminescence and absorption spectra of a ZnSe-ZnS SLS ($L_w = 2.0$ nm and $L_b = 4.0$ nm, 150 periods) at 77 K.

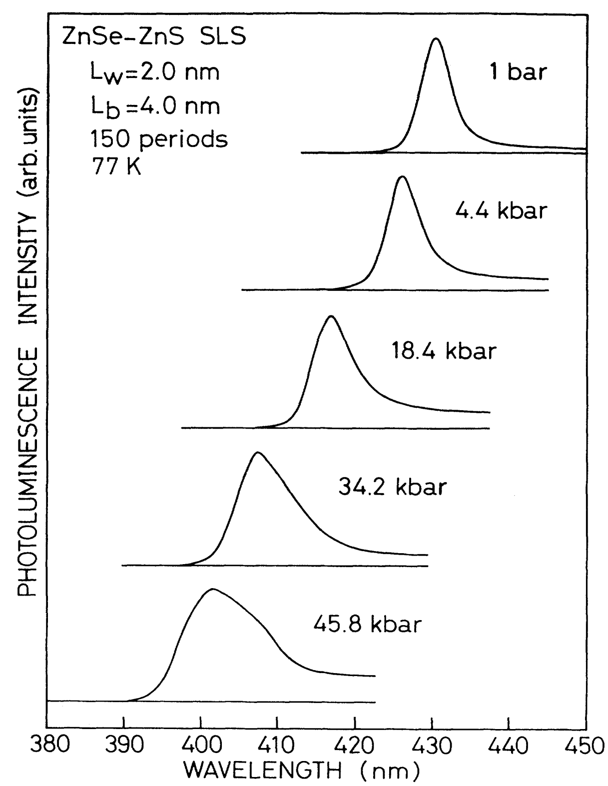

FIG. 3. Photoluminescence spectra of a ZnSe-ZnS SLS ($L_w = 2.0$ nm and $L_b = 4.0$ nm, 150 periods) under atmospheric and various hydrostatic pressures at 77 K. Each spectrum is normalized at the maximum of the peak height.

figure, solid lines are due to linear least-squares fits to the experimental data. The emission intensity in Fig. 4(a) gradually decreases with increasing hydrostatic pressure up to 31 kbar. With further increasing pressure the intensity decreases more rapidly. Therefore, the pressure dependence of the emission intensity is represented by a couple of straight lines with a kink. Parallel to these changes, the linewidth in Fig. 4(b) increases as the hydrostatic pressure increases, and the kink point in these changes appears at the same pressure of 31 kbar. These observations obtained in the changes in the integrated intensity and the linewidth can be explained by considering that the conduction-band edges of ZnSe and ZnS layers cross around 31 kbar and the conversion from type I to type II occurs at this pressure. Conduction electrons are confined to the ZnSe well layers below 31 kbar. However, electrons are confined to the ZnS barrier layers above 31 kbar. Then, the electrons and heavy holes are spatially separated and recombination takes place across the heterointerface. As a result, the intrinsic exciton luminescence intensity decreases. The emission intensity of the intrinsic component is more sensitive to the band structure than that of the lower-energy component of the spectrum, because the lower-energy component is due to excitons localized more deeply and is not sensitive to the change of band lineups from type I to type II. The overlap in the intrinsic and the lower-energy components may influence the linewidth and the PL peak position. However, as shown in Fig. 3, the emission intensity of the lower-energy component does not exceed that of the intrinsic one. Therefore, the influence of the overlap in the intrinsic and the lower-energy components is thought to be very small, especially on the emission intensity. Thus, the appearance of the clear kink point which was observed in the changes in the emission intensity and the linewidth can be explained only by the crossover to type II.

To support our identification, we estimated the luminescence quenching around the crossover. Using the envelope-function approximation, the square of the overlap integral between the $n=1$ electron wave function and the $n=1$ heavy-hole wave function at 50 kbar is about 17% of that at atmospheric pressure. In addition to the above value, we took account of the exciton effect, that is, the lateral spatial extension of the exciton Bohr radius in the direction parallel to the heterointerface.[14,15] As a result, we approximately obtained that the exciton oscilla-

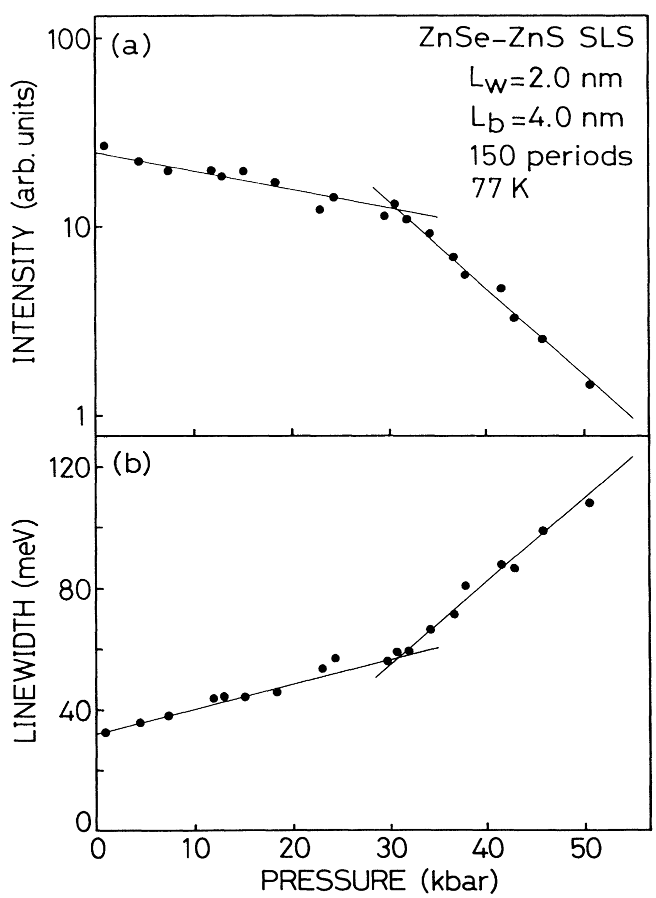

FIG. 4. (a) Hydrostatic pressure dependence of the integrated intensity and (b) the linewidth of the $n=1$ heavy-hole exciton luminescence of the ZnSe-ZnS SLS at 77 K. The solid lines are linear least-squares fits to the experimental data.

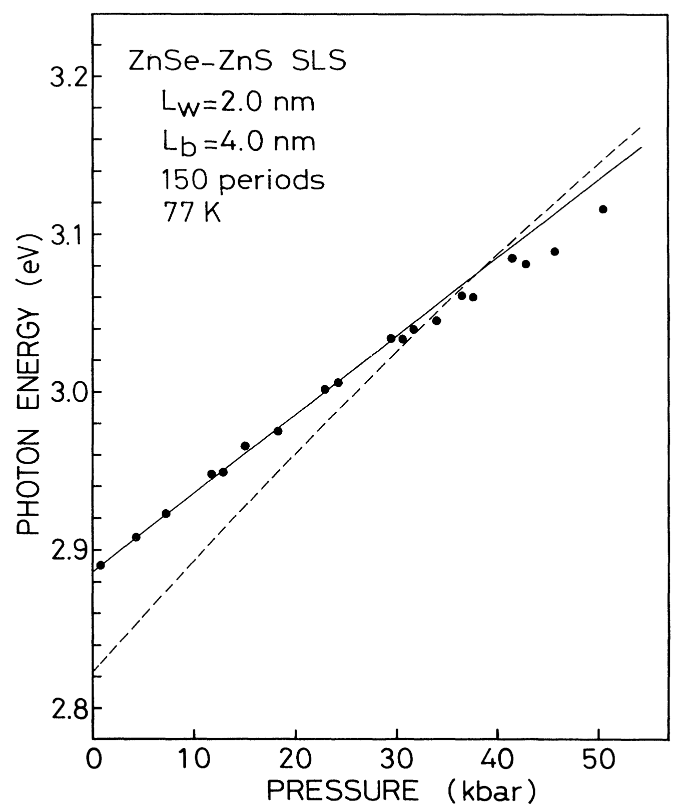

FIG. 5. Hydrostatic-pressure dependence of the peak energy of the $n=1$ heavy-hole exciton luminescence of the ZnSe-ZnS SLS at 77 K. The solid line is a linear least-squares fit to the experimental data below 30 kbar. The dashed line shows the hydrostatic-pressure dependence of the band-gap energy of the ZnSe well layers.

tor strength at 50 kbar decreased to about 4% of that at atmospheric pressure.[16] This calculated result supports the experimental luminescence quenching of about 7% shown in Fig. 4(a).

The pressure-dependent emission peak energies of the $n=1$ heavy-hole exciton at 77 K are shown in Fig. 5. The emission peak energy shifts toward higher energy with increasing hydrostatic pressure. The energy shift below 30 kbar is well fitted by a straight solid line shown in the figure. A dashed line shows the hydrostatic-pressure dependence of the band-gap energy of the ZnSe well layer at 77 K. We calculated it by taking account of the strain effect due to the lattice mismatch[8] and the experimental pressure coefficients of the band-gap energy.[17] Above 31 kbar, the peak energy deviates from the solid line and appears below the band-gap energy of the ZnSe well layer. This observation also supports that the conversion from type I to type II occurs around 31 kbar. Here, we do not take account of the $n=1$ heavy-hole quantum confinement energy and the binding energy of excitons, because these values are found to balance each other around the crossover.

The type conversion we observed is induced by the Γ-Γ conduction-band-edge crossover between ZnSe well and ZnS barrier layers. The crossover takes place because of the small conduction-band offset in this SLS and the difference in the energy shift of the conduction-band edges under hydrostatic pressure between these layers. The Γ-Γ type conversion may give unique characteristics to the system which is not observed in the Γ-X type conversion.

Finally, we consider the conduction-band offset. Recently, Shahzad, Olego, and Van de Walle have reported the empirical approach to derive the band offset in ZnSe-ZnS_xSe_{1-x} ($x<0.30$) SLS's.[18] They indicated that the conduction-band offsets are very small ($\Delta E_c \simeq 5$ meV), and that the experimental observations are in good agreement with the theoretical calculations based on the model-solid approach. On the basis of our hydrostatic-pressure measurements, we can obtain the conduction-band offset in ZnSe-ZnS SLS's shown as ΔE_c in Fig. 1 under no external hydrostatic pressure. Using the calculated energy shifts of both ZnSe and ZnS conduction-band edges as a function of hydrostatic pressure shown above and the crossover pressure obtained experimentally, we estimated the conduction-band offset ΔE_c to be 68.8 meV. If we use 820 meV as the valence-band offset on the basis of Harrison's linear combination of atomic orbitals theory, the conduction-band offset is estimated to be 198 meV without the effects of strain due to the lattice mismatch between ZnSe and ZnS layers. However, the effects of the strain must be considered in this SLS. In order to discuss the propriety of the obtained value of the conduction-band offset, we use the modified model-solid theory[8] as one of the theoretical approaches that can estimate the conduction-band offset. In this calculation, the biaxial strain due to the lattice mismatch can be divided into the uniaxial and the hydrostatic components and the effects of each component can be individually treated. As a result of these calculations, the conduction-band offset was estimated to be 74.7 meV. This calculated value of the conduction-band offset approximately agrees with the experimentally estimated value of 68.8 meV. Moreover, these two values are consistent with the result of Kronig-Penney's analysis of the PLE measurements.[8]

In conclusion, we have obtained direct observations of a conversion from type I to type II in a wide-band-gap ZnSe-ZnS strained-layer superlattice under hydrostatic pressure. This type conversion results from the Γ-Γ conduction-band crossover between ZnSe well and ZnS barrier layers and occurred around 31 kbar at 77 K. This phenomenon was clearly observed in the changes in the integrated intensity, the linewidth, and the peak energy of the $n=1$ heavy-hole exciton emission spectra. From our experimental results, we obtained the conduction-band offset at atmospheric pressure. It is $\Delta E_c = 68.8$ meV. This value is close to that obtained by the semiquantitative calculations, and is consistent with our experimental results of the PLE spectroscopy.

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