PHYSICAL REVIEW B VOLUME 52, NUMBER 4 15 JULY 1995-II

Time-resolved nonlinear luminescence of biexcitons in ZnSe-$Zn_xMg_{1-x}S_ySe_{1-y}$ single quantum wells

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(Received 28 April 1995)

Nonlinear optical properties of dense excitonic systems in ZnSe-$Zn_xMg_{1-x}S_ySe_{1-y}$ single quantum wells have been studied by means of time-resolved nonlinear luminescence spectroscopy, based on an excitation correlation technique. The enhancement in luminescence efficiency of biexcitons was clearly observed in a time-correlation trace of nonlinear biexciton luminescence. The origin of the enhancement was attributed to the stimulation of biexciton luminescence.

In highly excited semiconductors, a dense excitonic system has the unique properties that are caused by the interaction between two or more excitons. These properties are characterized by the formation of biexcitons (excitonic molecules), the inelastic scattering of excitons, and so forth. So far, such characteristic phenomena have been studied through their nonlinear optical properties. Especially in wide-band-gap II-VI compound semiconductors, excitons have relatively larger binding energies as well as smaller Bohr radii compared with those in III-V compound semiconductors, so that the excitons in II-VI compound semiconductors exist stably at higher densities than those in III-V compound semiconductors. As a result, the above phenomena are remarkably observed in the dense excitonic systems of wide-band-gap II-VI compound semiconductors. From the point of view of device applications as well as basic physics, it is important to study the nonlinear optical properties of dense excitonic systems in wide-band-gap II-VI compound semiconductors, especially in their quantum-well structures, because it has been pointed out to date that excitons contribute to the formation of optical gain, that is, the lasing process.[1–8]

In this paper, we study nonlinear optical properties of dense excitonic systems in a high-quality ZnSe-based single quantum-well (SQW) structure by means of time-resolved nonlinear luminescence spectroscopy, based on an excitation correlation technique. The time-resolved nonlinear luminescence spectroscopy, so-called population mixing, is one of the powerful tools for studying optical nonlinearities in semiconductor materials.[9–13] Particularly, we present evidence for stimulation of biexciton luminescence in the SQW structure with a binary ZnSe quantum-well layer.

The sample used in the present work was prepared by metalorganic-molecular-beam epitaxy.[14] The SQW structure was grown on a (100)-oriented GaAs substrate, following the deposition of a 25-nm-thick ZnSe buffer layer. The structure consisted of a 10.5-ML (3-nm-thick) ZnSe well layer sandwiched between 150- and 50-nm-thick $Zn_{0.90}Mg_{0.10}S_{0.18}Se_{0.82}$ barrier layers. A 1-nm-thick ZnSe cap layer was formed on top of the SQW structure. This structure is coherently grown on the GaAs substrate, hence the ZnSe well layer is under biaxial compressive strain due to a lattice constant mismatch of 0.25%.

The experiments were performed using a mode-locked titanium sapphire laser and a titanium sapphire regenerative amplifier, both of which were pumped by a cw Ar^+ laser. The repetition rate and the pulse width of the amplified laser output were 250 kHz and 200 fs, respectively. The wavelength of the amplified laser output can be tuned from 745 to 875 nm. The second-harmonic light of the amplified laser output was used as an excitation source.

Figure 1 shows the time-integrated luminescence spectra at 2 K taken from the SQW sample mentioned above under excitation energy densities of (a) 0.02, (b) 0.08, (c) 0.21, (d) 0.84, and (e) 2.80 $\mu J/cm^2$. The excitation wavelength was 400 nm, which corresponded to band-to-band excitation. At the excitation energy density as low as 0.02 $\mu J/cm^2$, the luminescence spectrum is dominated by the radiative recombination of $n=1$ heavy-hole excitons (denoted by X), which shows the peak at 432.5 nm (2.866 eV). The luminescence

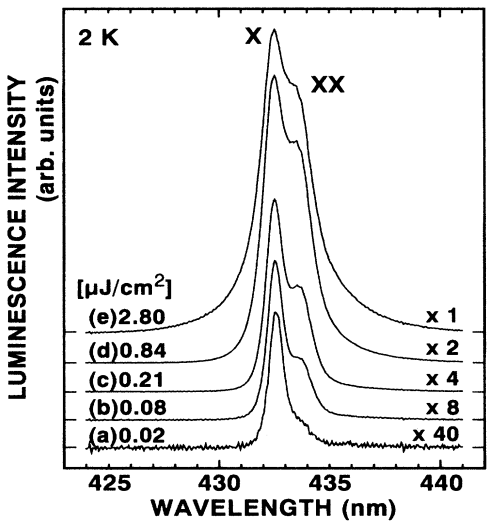

FIG. 1. Time-integrated luminescence spectra at 2 K taken from a ZnSe-$Zn_{0.90}Mg_{0.10}S_{0.18}Se_{0.82}$ SQW under excitation energy densities of (a) 0.02, (b) 0.08, (c) 0.21, (d) 0.84, and (e) 2.80 $\mu J/cm^2$.

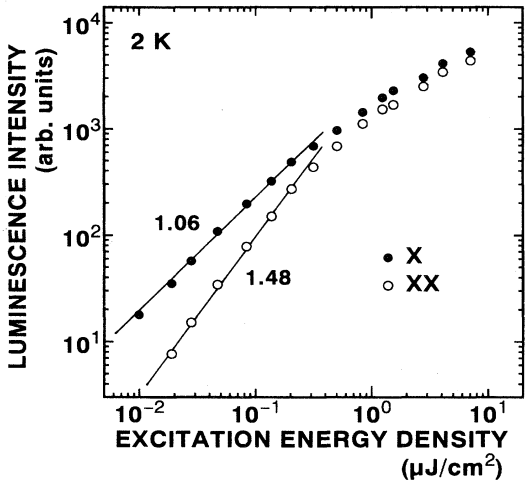

FIG. 2. The variation of exciton (X, solid circles) and biexciton (XX, open circles) luminescence intensity with excitation energy density at 2 K.

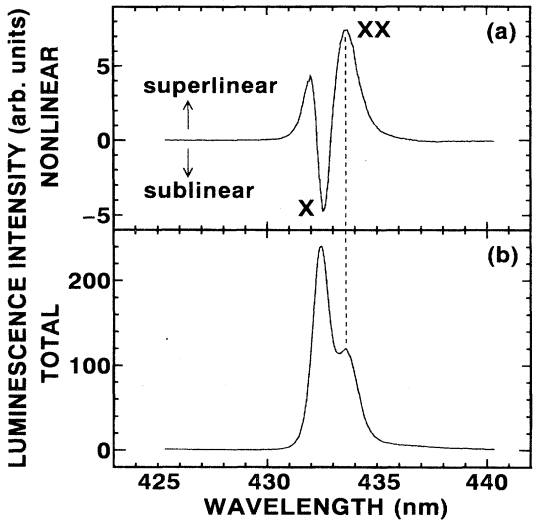

FIG. 3. Nonlinear luminescence spectrum in (a) and total luminescence spectrum in (b) obtained at 2 K under excitation energy density of 0.39 μJ/cm^2. The nonlinear luminescence spectrum was obtained at no time delay between two excitation pulses.

linewidth of the $n=1$ heavy-hole excitons is as small as 5 meV, which shows the high quality of the SQW structure. It is noted here that a shoulder (denoted by XX) on the low-energy side of the $n=1$ heavy-hole exciton line grows more rapidly than the exciton line and becomes prominent with increasing excitation energy density. The peak position of the line XX is located at about 433.6 nm (2.859 eV). Then, the energy difference between the line X and the line XX is approximately 7 meV.

The luminescence intensity of both the line X and the line XX as a function of excitation energy density is shown in Fig. 2 as solid and open circles, respectively. As the excitation energy density (I_P) is increased up to about 0.4 μJ/cm^2, the luminescence intensity of line X grows almost linearly ($I_X \propto I_P^{1.06}$), while that of line XX grows superlinearly ($I_{XX} \propto I_P^{1.48}$). Such a feature has also been observed under a cw He-Cd laser (325 nm) excitation condition.[14] Above 1 μJ/cm^2, the luminescence intensity of both line X and line XX shows sublinear dependence on the excitation energy density. On the basis of the spectral position as well as the superlinear dependence on the excitation energy density, the line XX is attributed to the radiative recombination of biexcitons (excitonic molecules). The dependence of the biexciton intensity on the exciton intensity for our result gives approximately $I_{XX} \propto I_X^{1.4}$. This result indicates that the biexciton density does not vary as the square of the exciton density. Such a reduction in the exponent from 2 has also been observed in the case of GaAs-based quantum-well structures.[15–19] One of the reasons for the reduction was explained by considering the short recombination time of excitons and biexcitons in such direct-band-gap materials.[19] Specifically, owing to the shorter radiative lifetime of biexcitons than that of excitons, it was considered that the biexciton density varied less strongly than quadratically as the exciton density was increased.

From the experimental results mentioned above, the binding energy of biexcitons in our ZnSe SQW is estimated to be about 7 meV. This value is two times as large as that in bulk ZnSe (3.5 meV). The increase in the binding energy is clearly due to the effect of quantum confinement on the biexciton in the quantum well. However, it seems that the enhancement in the binding energy of biexcitons in our ZnSe SQW is relatively smaller than those reported previously.[20,21] This is probably due to the weak confinement of carriers because of the small band offsets for both conduction and valence bands in the ZnSe-$Zn_{0.90}Mg_{0.10}S_{0.18}Se_{0.82}$ heterointerface.

In order to study the high-density effect of excitons further, time-resolved nonlinear luminescence of excitons and biexcitons has also been measured in the same SQW sample. The experimental procedure for time-resolved nonlinear luminescence measurement is as follows: The excitation beam was divided into two beams of equal intensity by a beam splitter. One of them was modulated at a frequency Ω_1 (=1000 Hz), and the other was modulated at a frequency Ω_2 (=831 Hz) by an optical chopper. Both of the two beams were focused at the same spot on the sample with a time delay τ between the two pulses. The sum-frequency component ($\Omega_1+\Omega_2=1831$ Hz) of the luminescence signal was detected by a lock-in technique in order to select the nonlinear component of the luminescence.

Figure 3(a) shows the nonlinear luminescence spectrum at 2 K taken from the SQW sample under excitation energy density of 0.39 μJ/cm^2. The upward direction (positive value) on the vertical axis represents superlinear dependence on the excitation energy density and the downward direction (negative value) represents sublinear dependence on the excitation energy density. This nonlinear luminescence spectrum was obtained at no time delay between the two excitation pulses. The total luminescence spectrum obtained at the same excitation condition is shown in Fig. 3(b). It can clearly be seen from this figure that the nonlinear luminescence spectrum shows a positive signal at the luminescence line of biexcitons (XX), whereas it shows a negative signal at the luminescence line of excitons (X). In addition, another posi-

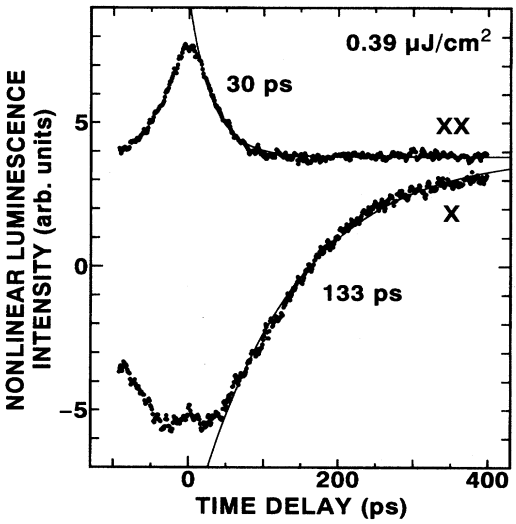

FIG. 4. Time-correlation traces of nonlinear luminescence for both the exciton (X) and the biexciton (XX) at 2 K under excitation energy density of 0.39 μJ/cm^2. The solid lines are due to least-squares fits to the experimental data.

tive signal is observable at about 432.0 nm. This signal is located at the higher-energy side of the total exciton luminescence line. The origin of these optical nonlinearities will be discussed later.

The time-correlation traces of the nonlinear luminescence at both the positive peak of biexcitons (XX) and the negative peak of excitons (X) in Fig. 3(a) are shown as dots in Fig. 4. The time-correlation traces are symmetric as against the time delay $\tau=0$. It is found from this figure that both of the time-correlation traces have a superlinear (positive) base, that is, a much slower decay component compared with the time range in the present measurement. The origin is probably due to the saturation of nonradiative centers.[12] Then, the experimental results were approximately analyzed by taking account of a constant base in addition to an exponential decay. The solid lines shown in Fig. 4 are the results obtained by means of least-squares fits to the experimental data. As a result, the decay-time constants were obtained to be 30 and 133 ps for the time-correlation traces of the biexciton and the exciton, respectively.

Now we examine the temporal behavior of the nonlinear luminescence. First of all, we consider that the sublinear (negative) signal in the nonlinear luminescence of the exciton mainly originates from the phase-space-filling effect of exciton states. In such a case, it is reasonable to understand that the decay-time constant of 133 ps for the time-correlation trace of the exciton can simply be attributed to the radiative lifetime of the exciton. In fact, the radiative lifetime of excitons has also been measured by means of our separate time-resolved luminescence experiments using a synchroscan streak camera, and was obtained to be about 140 ps. This value approximately agrees with the decay-time constant for the time-correlation trace of the exciton.

Next, we consider the superlinear (positive) signal in the nonlinear luminescence of the biexciton. It is noted again that the upward direction (positive value) on the vertical axis in the nonlinear luminescence [Figs. 3(a) and 4] represents the superlinear dependence on the excitation density, in other words, the increase in the luminescence efficiency. Therefore, the result of the time-correlation trace for the biexciton indicates that the luminescence efficiency of biexcitons is considerably enhanced when the time delay between the two excitation pulses is within a certain time range, which is characterized by a decay-time constant of about 30 ps in the time-correlation trace. This enhancement originates from the higher-order nonlinearity with respect to the density of biexcitons. One probable process is the stimulation of biexciton luminescence. Namely, the stimulation of biexciton luminescence occurs when the biexciton formation by the second excitation pulse is achieved before the annihilation of the biexcitons created by the first excitation pulse. In this case, the decay-time constant of 30 ps for the time-correlation trace of the biexciton can be attributed to the radiative lifetime of biexcitons. This result strongly suggests the possibility of biexciton lasing, that is, the population inversion between biexciton and exciton states in this SQW structure with the binary quantum-well layer. Parallel to the appearance of the fast-decay component of the nonlinear biexciton luminescence, an anticorrelation appears in the time-correlation trace of the nonlinear exciton luminescence. Such an anticorrelation trace has also been observed in the case of GaAs-based quantum wells and was explained by considering the finite rise time of the exciton population.[12] The origin of the anticorrelation may also be due to the increase in the density of excitons as a result of the radiative annihilation of biexcitons.

As has already been mentioned above, the nonlinear luminescence signal has a superlinear (positive) base which is caused by the saturation of nonradiative centers. Therefore we consider that the origin of the superlinear peak observed at 432 nm is mainly due to the saturation of nonradiative centers. However, part of the signal may reflect the distribution of excitons with excess kinetic energies because of the saturation of exciton ground states.

In conclusion, we have studied the nonlinear optical properties of dense excitonic systems in the ZnSe-$Zn_{0.90}Mg_{0.10}S_{0.18}Se_{0.82}$ SQW structure by means of the time-resolved nonlinear luminescence spectroscopy. The enhancement in the luminescence efficiency of biexcitons was clearly observed in the time-correlation trace of the nonlinear biexciton luminescence. The origin of the enhancement was considered to be due to the stimulation of biexciton luminescence. Our experimental results strongly suggest that the biexciton luminescence, that is, the optical transition from biexciton to exciton states contributes to the formation of optical gain and related laser emission in high-quality II-VI semiconductor quantum-well structures with binary quantum-well layers.

The authors would like to thank Professor Tsunemasa Taguchi of Yamaguchi University for valuable discussions. This work was partly supported by the Iketani Science and Technology Foundation and by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture of Japan.

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