

# Free exciton emission and optical nonlinearity of ZnSe-ZnS/CaF<sub>2</sub> superlattices under high excitation density

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(Received 19 November 1990; revised 29 March 1991)

Chin J. Semicond. **12**(12), 763-766 (December 1991)

The free exciton emission and optical nonlinearity in ZnSe-ZnS grown by MOCVD on CaF<sub>2</sub> substrates have been studied under different excitation densities at 77 K. We report the first observation of the new emission band due to Ex - Ex interaction, exciton saturating absorption and exciton optical bistability in ZnSe-ZnS/CaF<sub>2</sub> superlattices. The dominant exciton optical nonlinear mechanism for ZnSe-ZnS/CaF<sub>2</sub> superlattices under high excitation density is the combination of phase-space filling of exciton state and exciton band broadening.

## I. INTRODUCTION

ZnSe is the Groups II-VI wide-gap semiconductor material, which possesses a relatively large exciton binding energy and somewhat strong optical nonlinearity. The first characteristic has been used to detect the blue color after excitation<sup>2</sup>, and optical bistability.<sup>3</sup> When ZnSe is used as the superlattice-well material based on the magnitude of the quantum effect, the optical excitation characteristics of the material are greatly refined. It is possible to use it as a high-gain blue laser and fast-laser bistable device. Anderson *et al.*<sup>4</sup> studied the laser-absorption at saturation of ZnSe-ZnMnSe superlattices with the pump probe technique. They believed that for the laser of a narrow well the exciton-saturated absorption should be derived from the combination of the phase-space filling of the exciton state and the exciton Coulomb screening. Fu *et al.*<sup>5</sup> studied the characteristics of the exciton emission of the ZnSe/(Zn,Mn)Se multiple quantum wells at 10 K and first observed the exciton-molecular emission. In this paper, we studied the absorption characteristics of the ZnSe-ZnS/CaF<sub>2</sub> exciton emission at 77 K under varying excitation intensities. We first observed the scattered emission of the free exciton-free exciton interaction of ZnSe-ZnS superlattices and intend to present our preliminary discussion on the physical mechanism related to the emission.

## II. EXPERIMENTAL

The samples were ZnSe-ZnS superlattices grown by MOCVD on the CaF<sub>2</sub> substrate. The well width and pile width were 4 nm and 6nm, respectively, and the period was 100. The emission was excited by a pulse at 337.1 nm of the UV-24 type N<sub>2</sub> laser. The spectrum was analyzed with a Spex 1404 double-grating monochromator and then sampled and systematically integrated with a C31034 type photomultiplier and a 4400 type Boxcar. The absorption of the nonlinear portion of the laser was examined with the customarily used pump-probe technique. The light pump at the 337.1 nm pulse line was obtained from a N<sub>2</sub> laser with a continuous pulsing time of only 10 ns and a multiple frequency of 30 Hz. The detecting beam was from the laser pump of 440 coumarin producing a synchronized pulsing output. After the emission was reduced, the light intensity was lowered before the start of the probe. The apparatus for the measurement is shown in Fig. 1.

The measurement of bistability was carried out with a nitrogen laser pump containing 440 coumarin strong blue-laser synchronized emission. After it was modulated at the position of a

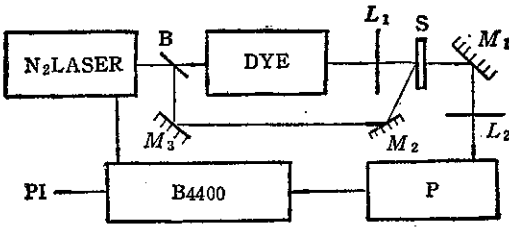


FIG. 1. Apparatus for the measurement of the optical exciton nonlinearity of ZnSe-ZnS superlattices: B: beam splitter; S: sample;  $L_{1,2}$ : lens;  $M_{1,2,3}$ : reflectors; P: photomultiplier; B4400: 4440-type integrated system; PI: printer;  $N_2$ :  $N_2$  laser, and Dye: tunable laser.

relatively large nonlinear refractive index, the measurement was started. The entire response time for the receptor was 2 ns.

### III. RESULTS AND DISCUSSION

#### 1. Free exciton emission

Figure 2 is the spectrum of the emission by ZnSe-ZnS/CaF<sub>2</sub> at 77 K varying excitation intensities. From Fig. 2, we can see that a relatively low excitation density, there is one emission peak at 440 nm, which is very close to the exciton absorption peak of 439.5 nm. Thus, at low excitation density, the major emission is derived from the free exciton of ZnSe-ZnS/CaF<sub>2</sub> superlattices. As a excitation intensity increases, there appears a new peak close to the lower energy end, and this peak rapidly increases with an increase in the excitation intensity. This phenomenon resembles the  $E_x$ - $E_x$ <sup>6,7</sup> scattered emission from a single crystal of ZnSe and ZnS<sub>x</sub>Se<sub>1-x</sub>. Since it occurs on the high intensity side, we can fundamentally rule out the possibilities of scattering due to contamination or the exciton-electron or phonon interactions. Thus, it is possible that it was due to  $E_x$ - $E_x$  scattering or exciton-molecular emission. In order to differentiate between these two possibilities, we prepared a selective excitation spectrum. Actually, we did not observe a double-photon absorption at the energy level where the  $E_x$ - $E_x$  scattering occurred. Thus, we finally ruled out the possibility of the exciton-molecular interaction, and the source must definitely have been the  $E_x$ - $E_x$  scattering. For a further study of the emission characteristics of ZnSe-ZnS/CaF<sub>2</sub> superlattices at high excitation density, we obtained another spectrum by increasing the excitation intensity as shown in Fig. 3. Here, we find an interesting phenomenon. As the intensity increases, the  $E_x$ - $E_x$  scattering intensifies and is accompanied by a distinct blue shift. Possibly this may be related to the phase-space filling of the

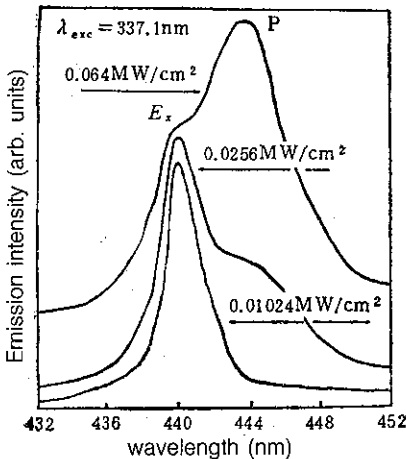


FIG. 2. Free exciton emission spectra of ZnSe-ZnS/CaF<sub>2</sub> superlattices under varying excitation density.

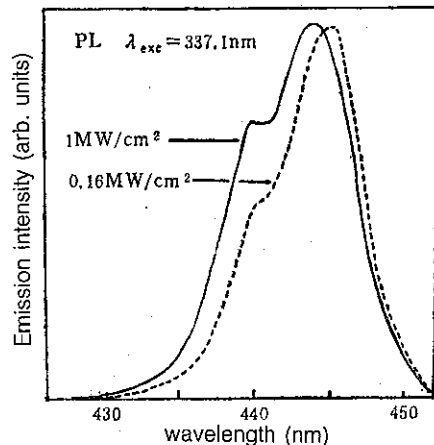


FIG. 3. Free exciton emission spectra of ZnSe-ZnS/CaF<sub>2</sub> superlattices under high excitation density.

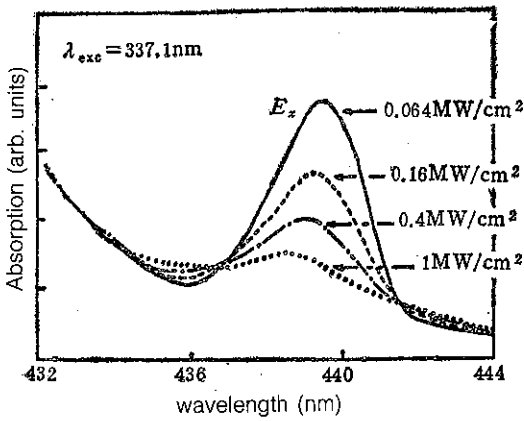


FIG. 4. Exciton absorption of ZnSe-ZnS/CaF<sub>2</sub> superlattices under varying light pump intensity.

exciton state because according to the Pauli exclusion principle, at high excitation intensity, the low-energy exciton states have been filled and new excitons can only occupy high-energy states. Hence, the exciton emission is accompanied by a blue shift.

### 2. Nonlinear exciton absorption

Figure 4 is the exciton absorption spectrum obtained under varying pumping intensities. From Fig. 4, we can see that as the pumping intensity increases, the exciton absorption peak gradually reaches saturation, and the blue shift broadens. According to several mechanisms of the principal exciton nonlinearity,<sup>3,4</sup> it is possible that the occurrence of nonlinearity is due to the combination of the phase-space filling of the exciton state and the broadening of the exciton band. The former is due to the Pauli exclusion principle, and the net result is the blue shift; the latter is due to the exciton-exciton ( $E_x$ - $E_x$ ) interaction that causes the band broadening, and the net result is the band saturation and broadening. These are the results that we obtained for ZnSe-ZnS/CaF<sub>2</sub> superlattices to give a strong  $E_x$ - $E_x$  scattering and the blue-shift. This further confirms our analyses to be rather accurate.

### 3. Optical bistability of laser

The exciton saturation and its absorption characteristics of ZnSe-ZnS/CaF<sub>2</sub> superlattices were detected at 77 K; we then selected a wavelength which showed a large variation in nonlinearity at 440.5 pulse-laser output. After we measured ZnSe-ZnS/CaF<sub>2</sub> superlattices at 77 K, the instantaneous variation of the incident beam and the transmitted beam intensities with time, and the bistability of the double-loop for the variation of these two beams with time (Fig. 5). In Fig. 5(a), we saw that the intensities of the transmitted light and the incident beam varied differently with time. This evidently demonstrates the appearance of optical nonlinearity. In Fig. 5(b), we can clearly see the bistability phenomenon again. For the forward-reverse feeding

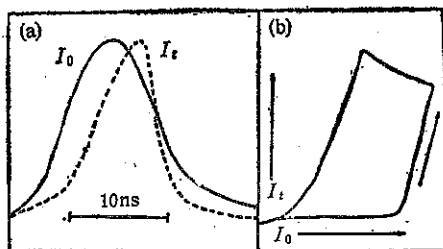


FIG. 5. Excitonic optical bistability of ZnSe-ZnS/CaF<sub>2</sub> superlattices

mechanism, we think that it is derived chiefly from the simple F-P cavity of the two surfaces of ZnSe-ZnS superlattices because on the sample surface, the refractive index  $R$  is close to 0.3. At the exciton saturation, the F-P cavity precision  $F$  was estimated to be greater than 2.4; therefore possibly the forward-reverse feeding mechanism could have taken place.

#### IV. CONCLUSION

To summarize, we first observed the  $E_x$ - $E_x$  scattering emission for ZnSe-ZnS/CaF<sub>2</sub> superlattices under varying pumping intensities. We also observed clearly the exciton saturation characteristics. We first applied a monochromator laser pulse to observe the optical bistability of ZnSe-ZnS/CaF<sub>2</sub>. The experimental results indicate that at high excitation density, the principal mechanism of ZnSe-ZnS/CaF<sub>2</sub> superlattices is the phase-space filling of the exciton states and the exciton band broadening due to exciton-exciton collisions.

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Translated by Lieng-Huang Lee

Edited by G. M. Temmer