Acoustically driven bound exciton lifetimes in CdS crystals

O. A. Korotchenkov[a] and T. Goto
Department of Physics, Graduate School of Science, Tohoku University, Sendai 980, Japan

(Received 8 December 1997; accepted for publication 7 February 1998)

The exciton lifetime has been found to be repeatedly tuned by a MHz frequency acoustic driving without degradation of the optical properties of CdS crystals. The increase in the lifetime, up to 5%, followed by its ~20% decrease has been detected with increasing driving amplitude. The lifetime increase can now be understood as due to reduction in the electron-hole wave function overlap in electric fields generated by the driving. The decrease in the recombination lifetime is ascribed to a widening of the potential well trapping the exciton due to variations in the local-crystal environment at acoustic driving. © *1998 American Institute of Physics.* [S0003-6951(98)01614-3]

The bound exciton photoluminescence (PL) lines in III–V and II–VI semiconductors have been of interest for some decades and a variety of applications has been reported. Most of the attention has been given to impurity characterization and determination of grown crystal purity.[1] Novel applications of bound excitons have already been presented, e.g., the excitonic nature of optical gain and laser emission in II–VI semiconductor structures have been demonstrated.[2]

A key issue in optimizing such devices for optoelectronic applications concerns the oscillator strength/or lifetime of a radiative transition which is affected by external parameters such as an electric field.[3] A large increase in the recombination lifetime due to the field-induced polarization of electron-hole pairs has been observed in quantum wells. Most recently, the applications of strong piezoelectric fields generated by surface acoustic waves in a quantum well structure makes it possible to spatially separate photogenerated electron-hole pairs with a considerable increase in the radiative lifetimes.[4]

The present work attempts to test the basic idea of acoustic driving of bound exciton lifetimes in CdS crystals arising from the internal electric fields generated by the driving and accompanying lattice disturbances. The present results provide the first experimental evidence that the bound exciton lifetimes can be repeatedly tuned with acoustic driving. The simplicity and high performance of the effects observed on excitons bound to localized defect states in bulk material could be advantageous for their applications to other binding systems such as excitons in low-dimensional semiconductors. Accordingly, the concept of acoustic driving could imply optoelectronic applications in optically active media.

The samples were undoped CdS single-crystal platelets 300–700 μm thick with typical linear dimensions of about 5×7 mm^2 grown from the vapor phase. Their low-temperature PL spectra exhibited two dominant sharp lines designated as I_1 and I_2.[5] The data presented here were taken with the I_1 transition originating from decays of excitons bound to a neutral acceptor.[5] It was excited by a 4880 Å laser line which lies above in energy than the I_1 line (4888 Å) but well below the band gap of CdS (4802 Å at 4.2 K) thus considerably suppressing possible thermal effects originating from free carriers.

Acoustic driving in a piezoelectric CdS crystal 1 was accomplished by applying a rf voltage U to the stripe metal electrodes 2 deposited onto the edge of the opposite large surfaces, as shown in the inset of Fig. 1(a). Similar electrodes 3 were employed in order to detect the vibrational response. The data presented here were taken in the CdS platelet at a frequency of about 8 MHz which roughly corresponded to the fifth thickness eigenmode of the plate. The sample was mounted to a copper bar and cooled in a liquid helium bath cryostat. No detectable heating of the sample was observed in the chosen driving range by means of a calibrated carbon-glass resistor that was coupled to the bar close to the sample surface.

Polarized PL and Raman scattering measurements were carried out using a T64000 Jobin–Yvon monochromator

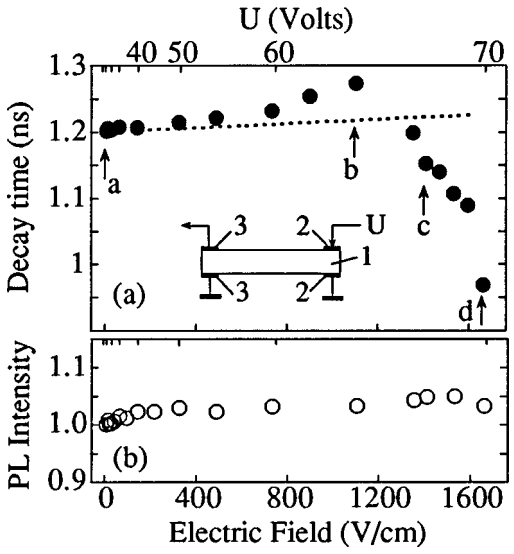

FIG. 1. (a) Lifetime dependence of the I_1 emission line for various driving amplitudes. The dotted line approximates theoretical calculations (Ref. 9) adjusted at zero driving amplitude. (b) The integrated emission intensity in the I_1 lines as a function of the driving amplitude. Inset in panel (a): schematic of the experimental setup, showing CdS platelet (1) and metal electrodes (2, 3).

[a]Permanent address: Faculty of Physics, Kiev University, Kiev 252022, Ukraine; electronic mail: olegk@mail.cc.tohoku.ac.jp

with a CCD detector and an argon laser. In order to estimate internal electric fields in the platelets and to define the field scale, a shift of the absorption edge to a lower energy upon increasing U was detected with a SpectraPro-500 monochromator and a tungsten lamp. The shift was then treated within the framework of Franz–Keldysh effect. For the emission decay measurements, picosecond laser pulses were obtained from a tunable Ar^+ pumped Ti:sapphire laser equipped with a $LiIO_3$ nonlinear crystal. A subtractive double monochromator with a reciprocal dispersion of 0.7 nm/mm and a Hamamatsu C-5680 streak camera were employed in this measurement. The I_1 luminescence transients have been found to exhibit an exponential decay typical of excitonic transitions. The laser power density was set at 0.15 W/cm^2 for the cw excitation and at 0.05 W/cm^2 in average for the pulse excitation.

Figure 1(a) displays the decay time of the I_1 exciton PL line as a function of acoustic driving amplitude. It is seen that the PL decay time initially increases upon the U increase in the range marked by arrows a and b in Fig. 1(a). On further increase in the driving amplitude in the region marked by arrows b and d, a pronounced decrease in the decay time appears. As evidenced by Fig. 1(b), the luminescence intensity does not change appreciably in the chosen driving range. We therefore conclude that the influence of nonradiative processes on the exciton lifetimes presented in Fig. 1(a) is small. It also should be emphasized that the lifetime of the bound excitons, contrary to those of the free excitons, is expected to be independent of temperature and only the luminescence intensity decrease is anticipated with increasing temperature because of ionization of the bound excitons. No such PL intensity decrease is seen in Fig. 1(b) thus providing additional proof against possible thermal effects accompanying the driving.

It should be mentioned that CdS platelets have been shown to be subject to acoustically induced changes of the net charge at crystal defects.[6] The net charge depends on the driving amplitude, and the generated electric field F is not generally proportional to the driving amplitude as is the case experimentally in Fig. 1. For the purposes of the present study, we distinguish between the long-range electric fields generated by the driving and the short-range interatomic forces modified by externally driven lattice vibrations. When it comes to investigating the absorption edge shift, the fitting to Franz–Keldysh effect bears significance to the long-range fields. The short-range forces, however, are also likely involved to produce the observed lifetime changes, as will be demonstrated in the following.

The bound exciton lifetime τ is[7,8]

$$\tau = C/\Delta E \lambda^3 |\varphi_0|^2, \tag{1}$$

where C is a constant of proportionality, ΔE is the transition energy, λ denotes the range of the local potential binding the exciton, and $|\varphi_0|^2$ is the electron-hole wave function overlap. The experimentally measured decay time of low-temperature PL is generally assumed to be the true lifetime of the bound exciton. The increase in the PL decay time observed in Fig. 1(a), a–b is therefore suggestive of the decreased electron-hole overlap $|\varphi_0|^2$ in the electric field generated by acoustic driving.

By applying the results of Blossey[9] to the range of F attained in our studies, we have obtained the field dependence of τ presented by the dotted curve in Fig. 1(a). It is seen that the enhanced lifetimes may at best be reasonably explained by $|\varphi_0|^2$ decrease below ≈400 V/cm whereas remarkable deviations from the predicted behavior appear at higher driving amplitudes.

Therefore we interpret our data as showing that the local field strength at the luminescent center most likely considerably exceeds those presented in Fig. 1 thus accounting for the enhanced lifetimes above ≈400 V/cm compared to that expected. There exist experimental results which argue this possibility. Available studies of deep donors in silicon at acoustic driving[10] acknowledge the evidence that changes in the equilibrium positions of defects in a low frequency vibrating lattice would vary the local-crystal environment and disturb the short-range interatomic forces at the bound exciton site.

If that is the case, enhanced local electric fields would then widen the exciton trapping potential well λ. A qualitative way to see how this arises is to assume that excitons are trapped in the Coulomb potential of impurity states. The electric field is known to lower one side of the Coulomb well.[9] Therefore, a slight widening of the well and movement of the exciton state down in the well are anticipated due to the asymmetry of the electric field potential.

We hence conclude that the reduced exciton lifetimes in Fig. 1(a), b–d, likely arise from the λ increase in Eq. (1). Obviously, both the decrease in electron-hole wave function overlap $|\varphi_0|^2$ and the λ increase occur. Hence an increase in the lifetime is observed when acoustic driving is applied, and this is followed by a pronounced decrease in the lifetime with increasing the driving amplitude as seen in Fig. 1(a). In our model, we suggest that enhanced local electric fields do account for the prolonged lifetimes observed in the driving range from ≈400 to 1100 V/cm in Fig. 1. However, the possibility that there may exist an unknown underlying mechanism responsible for this elongation cannot be entirely precluded.

It is known that resonance of the incident photon energy with the I_1 bound exciton in CdS crystals leads to a large increase in the Raman cross section[11] and the Raman efficiency can be related to the volume occupied by the exciton in the trapping potential.[7] Hence, the resonant Raman scattering technique can likely provide a distinguishing proof for the model suggesting a widening of the exciton trapping potential. Furthermore, it has been documented that small amounts of crystal damage or a small number of crystal defects changes the momentum conservation law so that enhancement of Raman intensities or even normally Raman inactive phonons have been observed.[12] Therefore, it may be anticipated that the variation of the local-crystal environment suggested above would modify the group theoretical selection rules and, thus, considerably change appropriate resonant Raman spectra.

In the $x(yy)\bar{x}$ scattering geometry employed, only an E_1 LO phonon[13] is predicted by the momentum conservation law, $\mathbf{q}=\mathbf{k_i}-\mathbf{k_s}$, with $\mathbf{q}$ the phonon wave vector, and $\mathbf{k_i}$ and $\mathbf{k_s}$ the wave vectors of the incident and scattered photons, respectively. As a consequence, only an E_1 LO phonon is

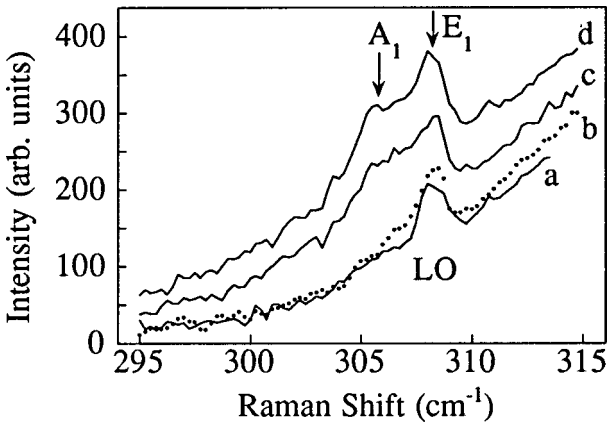

FIG. 2. LO phonon Raman line at different driving amplitudes. Curves a–d are taken at the amplitudes denoted by appropriate arrows in Fig. 1(a).

detected in spectrum a of Fig. 2. The scattering is weakly influenced by acoustic driving with amplitudes below the limit marked by arrow b in Fig. 1(a) as seen in spectrum b of Fig. 2. Dramatic changes are observed above this limit, in the range of the lifetime decrease observed in Fig. 1(a), b–d. As evidenced by curves c and d in Fig. 2, the E_1 phonon line is enhanced by a factor of 2 for the peak intensity. This increase is likely to be predominantly due to the broadening of the excitonic state discussed above. Indeed, the rough approximations lead to the Raman cross section of the form[14]

$$\sigma \sim [(\hbar\omega_\alpha + \hbar\omega_0 - \hbar\omega_i)^2 + \Gamma^2]^{-1}[(\hbar\omega_\alpha - \hbar\omega_i)^2 + \Gamma^2]^{-1}, \quad (2)$$

where α refers to the I_1bound exciton state with energy $\hbar\omega_\alpha$ involved into the scattering process, $\hbar\omega_0$ is the frequency of the created phonon, $\hbar\omega_i$ is the energy of the incident laser light, and Γ is the broadening parameter of the exciton state. It is seen that the LO phonon line should increase with the broadening because of increased coupling of the incident light $\hbar\omega_i$ to the Γ-broadened exciton state $\hbar\omega_\alpha$ in the second determinator in Eq. (2).

A far more striking feature of the data in Fig. 2, c and d is the appearance of an A_1 phonon polarized in the z direction.[13] This appearance must be contrasted with the momentum conservation law and conclusively confirms the variation of the local-crystal environment at the exciton site thus providing compelling evidence of the picture for the lifetime decrease.

In conclusion, the experimental evidence is presented that the bound exciton lifetime can be tuned by acoustic driving. The I_1 exciton recombination lifetime in CdS platelets shows an enhancement followed by a region of reduced lifetimes with increasing the driving amplitude. It has to be realized that the amount of the effect may vary from sample to sample. However, the effect on the lifetime has been repeatedly observed in the same sample without degradation of the optical properties of the CdS platelet.

One of the authors (O.A.K.) acknowledges the financial support from the Japan Society for the Promotion of Science and thanks Dr. M. Y. Shen for his help in measurement techniques. The work was supported in part by the Ministry of Education, Science and Culture of Japan.

[1] See, e.g., Z. H. Lu, M. C. Hanna, D. M. Szmud, E. G. Oh, and A. Majerfild, Appl. Phys. Lett. **56**, 177 (1990); P. J. Dean, Prog. Cryst. Growth Charact. **5**, 89 (1982); D. C. Reynolds, D. C. Look, D. N. Talwar, G. L. McCoy, and K. R. Evans, Phys. Rev. B **51**, 2572 (1995).
[2] J. Ding, H. Jeon, T. Ishihara, M. Hagerott, A. V. Nurmikko, H. Luo, N. Samarth, and J. Furdyna, Phys. Rev. Lett. **69**, 1707 (1992).
[3] H.-J. Polland, L. Schultheis, J. Kuhl, E. O. Göbel, and C. W. Tu, Phys. Rev. Lett. **55**, 2610 (1985); G. Bastard, E. E. Mendez, L. L. Chang, and L. Esaki, Phys. Rev. B **28**, 3241 (1983), and references therein.
[4] C. Rocke, S. Zimmermann, A. Wixforth, J. P. Kotthaus, G. Böhm, and G. Weimann, Phys. Rev. Lett. **78**, 4099 (1997).
[5] D. G. Thomas and J. J. Hopfield, Phys. Rev. **128**, 2135 (1962).
[6] I. V. Ostrovskii and A. Kh. Rozhko, Sov. Phys. Solid State **26**, 2241 (1985).
[7] E. I. Rashba and G. E. Gurgenishvili, Sov. Phys. Solid State **4**, 759 (1962).
[8] C. H. Henry and K. Nassau, Phys. Rev. B **1**, 1628 (1970).
[9] D. F. Blossey, Phys. Rev. B **2**, 3976 (1970); **3**, 1382 (1971).
[10] O. A. Korotchenkov and H. G. Grimmeiss, Phys. Rev. B **52**, 14598 (1995).
[11] T. C. Damen and J. Shah, Phys. Rev. Lett. **27**, 1506 (1971).
[12] D. Powell, A. Compaan, J. R. Macdonald, and R. A. Forman, Phys. Rev. B **12**, 20 (1975); S. Permogorov and A. Reznitsky, Solid State Commun. **18**, 781 (1976).
[13] C. A. Arguello, D. L. Rousseau, and S. P. S. Porto, Phys. Rev. **181**, 1351 (1969).
[14] R. Loudon, Proc. R. Soc. London, Ser. A **275**, 218 (1963).