PHYSICAL REVIEW B VOLUME 34, NUMBER 6 15 SEPTEMBER 1986

Quasi-two-dimensional excitons in a strongly localized regime in CdTe-ZnTe superlattices

Y. Hefetz, D. Lee, and A. V. Nurmikko
Division of Engineering and Department of Physics, Brown University, Providence, Rhode Island 02912

S. Sivananthan, X. Chu, and J.-P. Faurie
Department of Physics, University of Illinois, Chicago, Illinois 60680

(Received 23 June 1986)

Transient luminescence spectroscopy reveals that recombining excitons in a new, highly strained II-VI compound semiconductor superlattice CdTe-ZnTe are strongly localized at low lattice temperatures. We argue that such behavior is expected in a superlattice system with small valence-band offset under large lattice-mismatch strain when the influence of monolayer thickness variations (finite interface roughness) is considered.

The CdTe-ZnTe superlattice is a new II-VI compound semiconductor structure in which very large lattice-mismatch strain ($\Delta a/a \cong 0.06$) can be elastically accommodated.[1] Initial x-ray diffraction[1] and photoluminescence[2] data on the molecular-beam epitaxially (MBE) grown superlattices indicate that they are of good structural quality if proper care is exercised in their "strain design" by using sufficiently thin constituent and suitable buffer layers to minimize misfit dislocations. In this Communication we present experimental work where excitonic properties in the CdTe-ZnTe superlattice have been studied by picosecond time-resolved luminescence spectroscopy at low lattice temperatures. From the results we argue that not only is the uniform component of lattice-mismatch strain significant in perturbing the interband electronic transitions (in excess of 100 meV as shown recently[2]), but specifically, that local fluctuations in the strain lead to unusually strong localization effects for the quasi-two-dimensional (2D) excitons. These originate from random thickness fluctuations on a monolayer scale and modulate the band-edge energies through variations in the local strain. Conditions for such behavior are enhanced with the small valence-band offset expected in this superlattice.

Several structures were studied in this work which were grown by molecular-beam epitaxial methods at the University of Illinois (Chicago) on (100)-oriented GaAs substrates. Because of similarities in the exciton characteristics of these samples which had relatively small differences in dimensions, we will focus here on a particular superlattice structure consisting of 200 periods of 21-Å-thick CdTe layers and 30-Å ZnTe layers. [We use the term "superlattice" here to denote the structural aspects of the samples; the connection to multiple-quantum-well (MQW) structures will be discussed below.] This superlattice was separated from the substrate by a 2.1-μm-thick buffer layer of $Zn_{0.50}Cd_{0.50}Te$. Continuous-wave luminescence from the same series of samples has been recently used to argue[2] that such a highly strained superlattice is essentially free standing, i.e., that the actual strain distribution and the parallel lattice constant of the superlattice are independent of the buffer layer and the substrate. The uniaxial component of the lattice-mismatch strain splits the valence-band degeneracy in such a way that the lowest interband transition (predominantly within the CdTe layers) is heavy-hole-like.

Our time-resolved luminescence experiments employed a model-locked continuous-wave dye laser whose output was attenuated to prevent nonlinear effects from occurring (average power of ~ 1 mW weakly focused on the samples). Transient photoluminescence was collected by a monochromator–streak-camera combination, specially configured for optimum spectral and temporal resolution of approximately 5 Å and 15 psec even for weak signals.[3] Figure 1 summarizes results for the CdTe-ZnTe superlattice introduced above for which the cw luminescence spectra at $T = 2$ K are displayed, together with transient spectra following excitation by a picosecond laser pulse at time $t = 0$ psec and at photon energy $\hbar\omega = 1.95$ eV (lower panel). The transient spectra reached a maximum ampli-

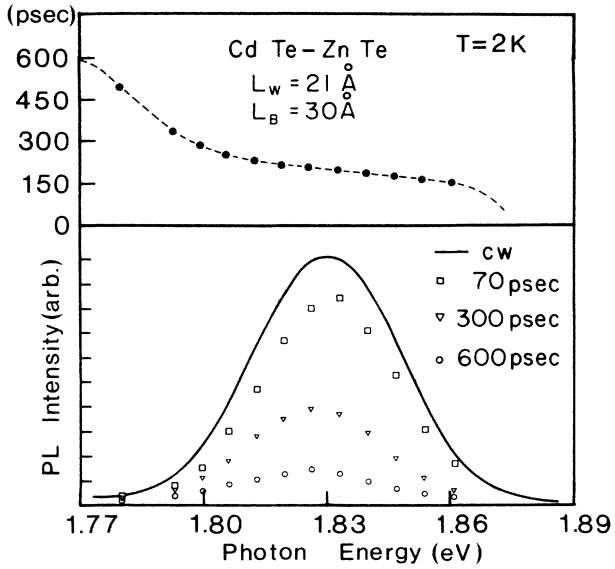

FIG. 1. Continuous-wave and time-resolved exciton recombination spectra from the CdTe-ZnTe superlattice discussed in text (lower panel). The upper panel shows the exciton lifetime in the range of localized states.

tude very quickly following the excitation; its rise time was essentially limited by the time resolution of our instrumentation. The upper panel shows the exciton lifetime obtained from the nearly single exponential decays at different photon energies of emission. Increasing the temperature up to 60 K produced little change in the spectral or temporal features in Fig. 1 apart from a small band-gap-related shift; a pronounced decrease in the luminescence efficiency occurred at further higher temperatures. Whereas Fig. 1 was obtained by photoexcitation well above the exciton ground state, experiments were also performed under nearly resonant conditions. Figure 2 shows the emission spectrum with excitation at 1.865 eV; while laser scatter through the double monochromator limited our ability to get arbitrarily close to the excitation energy, it was clear that the increase in the signal intensity at $\hbar\omega > 1.855$ eV corresponded to contribution by resonance luminescence. At lower photon energies, two clear sidebands are seen, separated from the resonance luminescence peak by 24 meV. Time-dependent emission under these excitation conditions showed that the resonance peak and the sidebands decayed synchronously with approximate lifetimes following that for primary peak as indicated in Fig. 1.

The general range of photon energies of emission in Figs. 1 and 2 clearly contains contributions from quantum confinement effects in the superlattice when compared with the ground-state exciton energy in bulk CdTe at 1.595 eV. Recent work on several related wide-gap II-VI compound semiconductor superlattices indicates[4] that in these systems most of the band-gap difference between the superlattice constituents is taken up as a conduction-band discontinuity. For the CdTe-ZnTe heterojunction, $\Delta E_g = 0.78$ eV in the absence of strain. In the limit of $\Delta E_v = 0$, excitons in such a superlattice with layer dimensions considered here would be modified from those usually considered in an isolated quantum-well case (or a sufficiently spaced multiple-quantum-well structure). However, Kronig-Penny calculations show that the electron confinement in the CdTe layers is quite strong with relatively little interwell coupling ($< 20\%$). Therefore, in the absence of any other effects, the quasi-two-dimensional excitons of the superlattice would approximate a quantum-well-confined electron with a heavy-hole Coulomb bound to it (the binding energy in bulk CdTe is approximately 10 meV). On the other hand, our experimental observations summarized above immediately suggest that the exciton recombination spectra do not originate from free quasi-two-dimensional excitons but are connected instead with localized excitons. The wide spectral width ($\gtrsim 30$ meV) and the lack of significant spectral diffusion (Fig. 1) as well as the absence of temperature-dependent spectral shifts further imply that such localization is quite effective in producing spatial immobility for the excitons. The spectra under resonant excitation indicate the presence at most of only small amounts of spectral diffusion within an inhomogeneously broadened transition. The sideband energies are in the general range for optical phonons and will be discussed below.

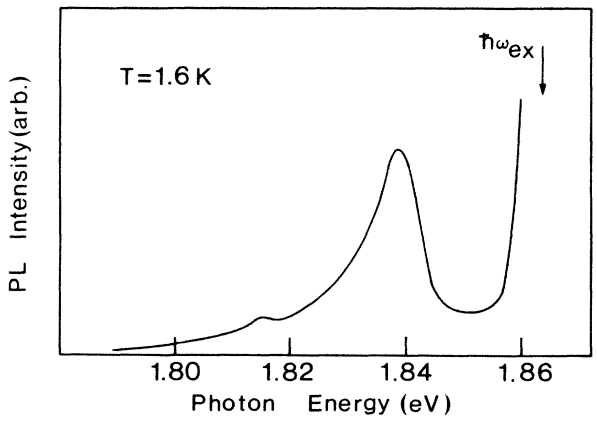

FIG. 2. Luminescence from the CdTe-ZnTe superlattice sample under photoexcitation directly into the localized states (at $\hbar\omega_{ex} = 1.865$ eV). The sidebands are due to optical-phonon-assisted processes.

Recent $\mathbf{k}\cdot\mathbf{p}$ band-structure calculations[2] for the CdTe-ZnTe superlattice (assuming $\Delta E_v = 0$) and correlation with optical data suggests that the strain energies are minimized if the superlattice is essentially free standing; i.e., that the lattice constant parallel to the layer planes is independent of the buffer layer or substrate. While these calculations pertain to the case of a uniform strain (where the unit cells of CdTe and ZnTe undergo tetragonal distortion), they can also provide a lower limit for an estimate of the influence of random strain fluctuations as follows. As a first approximation to small but finite interface roughness in the superlattice (which is characteristic in many MBE-grown material systems), consider layer-thickness fluctuations on a monolayer scale (~ 3.2 Å for CdTe). Estimate of the effects of such fluctuations in the spirit of the superlattice relaxed model of Ref. 2 then shows that random potential wells on the order of 20 meV are generated for the excitons. For localization of the entire quasiparticle, the characteristic extent of the fluctuations in the layer plane should be of the order of the exciton Bohr radius (~ 60 Å for bulk CdTe). However, a considerably more effective mechanism for localization is obtained if strain variations from the monolayer fluctuations (islands) are considered directly in local context only (i.e., unrelaxed throughout the superlattice), a situation which is likely to be physically approximated in MBE-grown strained layer structures. Then our estimates (which include uncertainties about the valence-band deformation potential constants) show that random potential wells in excess of 30 meV for the heavy-hole band alone will occur. Instead of the whole exciton, efficient localization of the heavy hole can readily take place. Furthermore, the heavy-hole Bohr radius is small enough (~ 13 Å in CdTe) so that efficient localization can be expected in the context of a distribution of traps along a single (2D) CdTe-ZnTe interface. In this view, the electron Coulomb attraction preserves the exciton;[5] a small reduction in the Coulomb energy is expected since the large conduction-band confinement energy tends to keep the electron wave function centered within the CdTe quantum wells.[6] The localization and associated exciton spatial immobility which is experimentally measured is thus mainly indicated by a

broadening into a low-energy tail of the density of states for the heavy hole. We emphasize that the 2D character of the problem significantly enhances the effectiveness of the localization; we have simulated this in a 2D random-walk problem.[7] Luminescence excitation spectra (as well as the linewidths in Fig. 1) show that the extent of the localized states is on the order of 50 meV for the CdTe-ZnTe superlattice discussed here. This value is significantly in excess of the exciton Coulomb energy and the localization is thus appropriately referred to as taking place in a strongly localized regime. We note that the concept of a well-defined mobility edge seems inappropriate here given the nonthermal nonequilibrium character of the problem[8] in terms of the very rapid trapping of the excitons (fast rise time of transient luminescence) and the relatively short exciton lifetime (with a component from nonradiative processes at defects). The physical origin of the increase in lifetime on the low-energy tail of the luminescence is not entirely clear although it appears likely that it reflects a decrease in the nonradiative contribution for more tightly localized excitons.

Finally, we comment on the spectral sidebands which are seen in Fig. 2 and are most likely connected with optical-phonon-assisted radiative recombination. A Raman process can be ruled out since the time dependence of the sidebands follows the luminescence, not the excitation. (Another possibility is phonon-assisted tunneling within the localized exciton states; however, given the very small amount of spectral diffusion this is not expected to generate such pronounced sidebands.) Exciton–LO-phonon coupling is a relatively strong process in both CdTe and ZnTe and the localized quasi-two-dimensional character may well enhance it further. Assuming a free standing CdTe-ZnTe superlattice, we have estimated the effects of the hydrostatic (dominant) strain on the $q=0$ optical-phonon energies by using experimentally reported values of the Grüneisen constant for wide-gap II-VI semiconductors. With $\gamma \sim 1.2$ to 1.8 in ZnTe and comparable values for CdTe,[9] we estimate that the bulk LO phonon of CdTe in the superlattice is increased from approximately 21 to 24 meV while that in the ZnTe layers decrease from about 28 to 24 meV. This coincidence (within the approximate nature of the estimate) makes the interpretation of the phonon sidebands somewhat ambiguous as to the spatial region of the superlattice from which their interaction originates (although the CdTe layers appear most likely because of the large degree of electron confinement). The spectral width of the sidebands (7–8 meV) indicates broadening which may be associated with the influence of local strain variations on the phonon spectrum or reflect some local lattice relaxation. Clearly, Raman scattering experiments would be useful to study the effects of strain-induced phonon energy shifts further; the excitonic case discussed here is somewhat complicated also because of the possible participation of interface-related phonons of the superlattice.

In conclusion, we have reported results of time-dependent optical studies in a new compound semiconductor superlattice CdTe-ZnTe. The excitonic recombination at low lattice temperatures shows characteristics of strong localization. Such spatial immobility in a quasi-two-dimensional system is expected in a highly strained superlattice or quantum-well system where small valence-band offsets and finite (although small) interface roughness are present.

This research was supported by the U.S. Defense Advanced Research Projects Agency Contracts No. N00014-86K-0377 (Brown) and No. MDA903-85K-0030 (Illinois). The authors also acknowledge the many technical contributions of W. C. Goltsos.

[1]G. Monfroy, S. Sivanathan, X. Chu, and J.-P. Faurie, R. D. Knox, and J. L. Staudenmann, Appl. Phys. Lett. **49**, 152 (1986).

[2]R. Miles, G. Wu, M. Johnson, T. McGill, J.-P. Faurie, and S. Sivanathan, Appl. Phys. Lett. **48**, 1383 (1986).

[3]Y. Hefetz, W. Goltsos, A. V. Nurmikko, L. A. Kolodziejski, and R. L. Gunshor, Appl. Phys. Lett. **48**, 372 (1986).

[4]For review, see, e.g., A. V. Nurmikko, R. L. Gunshor, and L. A. Kolodziesjski, IEEE J. Quantum Electron. (to be published).

[5]S. Permogorov, A. Reznitsky, S. Verbin, and V. Lysenko, Solid State Commun. **47**, 5 (1983).

[6]J.-W. Wu, A. V. Nurmikko, and J. J. Quinn, Phys. Rev. B **34**, 1080 (1986).

[7]Y. Hefetz and A. V. Nurmikko (unpublished).

[8]E. Cohen and M. D. Sturge, Phys. Rev. B **25**, 3828 (1982).

[9]For example, B. A. Weinstein and R. Zallen, in *Light Scattering in Solids IV,* edited by M. Cardona and G. Guntherodt, Topics in Applied Physics, Vol. 54 (Springer-Verlag, Berlin, 1984), p. 372.