PHYSICAL REVIEW B VOLUME 38, NUMBER 5 15 AUGUST 1988-I

# Optical investigation of biexcitons and bound excitons in GaAs quantum wells

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(Received 26 February 1988)

The photoluminescence spectra from a number of high-quality GaAs single-quantum-well samples grown by molecular-beam epitaxy reveal a doublet emission having an energy separation of $\sim 1.25$ meV. A similar doublet was observed in a sample for which the interrupted growth technique was used. Using excitation-intensity-dependent luminescence and time-resolved spectroscopy, we will show that the lower-energy components of these doublets have different origins in different samples and can be attributed either to biexcitons or to impurity-bound excitons.

Using low-temperature photoluminescence (PL) from a number of high-quality GaAs multiple-quantum-well samples grown by molecular-beam epitaxy (MBE), Miller and co-workers[1,2] first reported a double peak whose splitting was $\sim 1$ meV. The high-energy peak was attributed to the $n=1$ heavy-hole–free-exciton transition. Based on the excitation intensity, temperature, and polarization dependencies of the lower-energy peak, they concluded that this transition was due to biexcitons with a binding energy of about $B_{\text{biex}}=1$ meV. These results were also supported by Kleinman[3] who, using the six-parameter wave function of Brinkman, Rice, and Bell,[4] calculated variationally the binding energy of the biexcitons and the bound excitons in GaAs quantum wells (QW) for various well thicknesses ($L_z$). This calculation contained no adjustable parameters other than the variational parameters and yields a value of $B_{\text{biex}}=0.13$ meV for bulk GaAs.[4] For the GaAs QW it was found that the calculated biexciton binding energy obeyed Haynes's rule[5,6] and that in the two-dimensional (2D) limit the ratio of the biexciton binding energy over the exciton binding energy was 3–4 times larger than the corresponding quantity in the three-dimensional (3D) case. The calculated value of $B_{\text{biex}}$ was found to be in good agreement with the 1 meV splitting mentioned above for wells narrower than 25 nm ($L_z < 25.0$ nm). The fit was found not to be as good for the wider wells ($L_z > 25.0$ nm).

It has recently been proposed that interrupting the molecular-beam epitaxial growth momentarily when changing from one type of semiconductor layer to another leads to smoother interfaces.[7] The low-temperature PL spectra of QW structures prepared with interrupted growth showed multiple peaks which have been interpreted as originating from within different smooth regions in the QW layer which differ in width by exactly one monolayer.[7] However, it must be remembered that fine structure in low-temperature PL spectra may have other causes such as impurity transitions. Using this interrupted growth technique, one would expect the concentrations of residual impurities to increase at the interface which could give rise to additional structure in the low-temperature PL. Kleinman[3] has also estimated the binding energy of excitons bound to neutral donors for the GaAs QW. These values are slightly larger than $B_{\text{biex}}$ and are also found to obey Haynes's rule. Nomura, Shimozaki, and Ishiki[8] used PL measurements to study single quantum wells inhomogeneously doped with Si. They identified the low-energy peak as being due to excitons bound to donors localized at the center of the well. The experimental data of the binding-energy dependence on the well width agreed with the theoretical results obtained by Kleinman[3] for the well widths ranging from 7.4 to 15.4 nm. In this paper we will show that low-temperature PL can be misleading and care must be taken in the interpretation of the results. The excitation density dependence of the luminescence intensity and time-resolved PL measurements were used in the investigation of a luminescent peak located $\sim 1$ meV below the $n=1$ heavy-hole–free-exciton transition on two different QW samples, one grown using the interrupted growth technique and the other grown with conventional, uninterrupted growth.

The excitation source used in this experiment was a mode-locked Ar-ion laser synchronously pumping a cavity dumped dye laser. The excitation wavelength was 800 nm at an average power density of $I_0=1.0$ W/cm$^2$. The pulse width was less than 30 ps and the repetition rate was 80 MHz. The samples were mounted in a strain-free manner and immersed in 1.8-K superfluid He. The luminescence was dispersed by a double $\frac{3}{4}$-m spectrometer coupled to a fast photomultiplier tube (ITT-F4128F). The lifetimes were obtained in the usual way by timing the interval between the laser pulses, detected by a fast Si avalanche photodiode, and the luminescence photon pulses using a time-to-amplitude converter (TAC). The output of the TAC was then processed by a microcomputer based pulse-height analyzer. This tube has an exponential decay time constant of 70 ps when used in conjunction with our photon counting electronics. Both GaAs/$Al_xGa_{1-x}As$ QW samples were grown at GTE Laboratories in a Riber 2300 MBE system. Growth conditions were optimized us-

 

ing reflection high-energy electron diffraction (RHEED) intensity recovery and oscillation studies. For sample 1, grown continuously, the undoped substrate temperature was 650 °C and the growth rate was 0.9 $\mu$m/h. The narrowness of the low-temperature PL peaks from the QW attested to the high quality of this sample.[9] For sample 2 epitaxial layers were grown, using growth interruption, on (100) silicon doped GaAs at a substrate temperature of 600 °C at a growth rate of 0.6 $\mu$m/h. A superlattice buffer layer was grown on the substrates to provide a smoother and cleaner starting surface followed by a series of undoped single quantum wells of different widths. Growth interruption was accomplished at each interface by shuttering the ovens producing the group-III elements for 60 sec while maintaining an arsenic overpressure.

The excitation-intensity-dependent PL spectra for both QW samples are represented in Fig. 1. Curves (a), (b), and (c), whose energy scale is indicated at the top of the figure, were obtained from sample 1 having a well thickness $L_z$ of 14.2 nm. The two peaks labeled EX and BIEX are clearly seen for the three excitation intensities with a separation of 1.25 meV. At the lowest value of excitation intensity, curve (c), the exciton peak dominates the spectrum. As the laser intensity increases [curves (b) and (a)], the lower energy peak becomes dominant. If the intensities of these two peaks are plotted as a function of excitation power density ($I_p$), one obtains an approximately linear dependence $(I_p)^{0.98}$ for the exciton peak while the lower energy biexciton peak exhibits a superlinear dependence and grows approximately as $(I_p)^{1.25}$. Such linear dependence is expected for free excitons whereas a superlinear behavior is characteristic of biexcitons.[10] In order to confirm the intensity dependent results, we have measured the transient luminescence decays of both exciton and biexciton peaks at the three power densities used in Fig. 1. The results are shown in Fig. 2. One common feature of these decay curves, independent of the intensity of excitation used, is the shorter lifetime of the biexciton peak as compared to that of the higher-energy exciton line (EX) (approximately 1.7 times faster). This is again what would be expected if the lower energy transition was due to the biexciton. In fact, the apparent decay rate of the biexciton is predicted to be two times faster than that of the free exciton for quasiequilibrium.[10]

The same sets of experiments were done on a 18.0 nm wide QW in sample 2 which was grown using the interrupted growth technique. In this same sample, the dou-

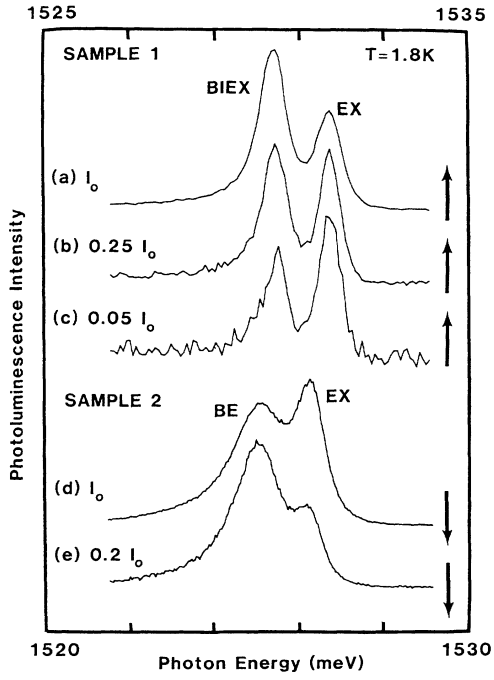


FIG. 1. Low-temperature (1.8 K) PL spectra at different excitation powers. Curves (a), (b), and (c) correspond to a sample (1) which was grown with no growth interruption. The well thickness is $L_z = 14.2$ nm and the energy scale for the luminescence from this QW is located at the top of the figure. Curves (d) and (e) represent the PL spectra of sample 2 which was grown using the interruption growth technique. The well thickness is $L_0 = 18.0$ nm and its photoluminescence energy scale is located at the bottom of the figure. For all the spectra collected, the laser wavelength was 800 nm at a maximum power density $I_0 = 1.0$ W/cm$^2$.

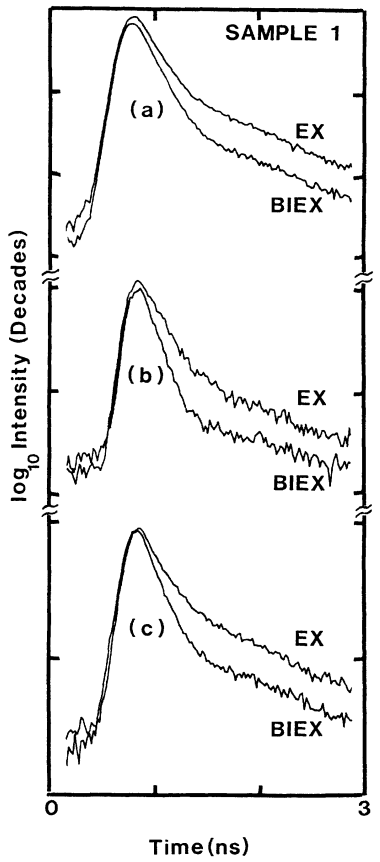


FIG. 2. The luminescence decay of the lines EX and BIEX for sample 1 corresponding to the conditions of excitation of Fig. 1, curves (a), (b), and (c), respectively. Each of the tick marks on the vertical scale represents one decade of intensity. The decay curves represent exponential decays having time constants of (a) $\tau_{ex} = 211$ ps, $\tau_{biex} = 178$ ps; (b) $\tau_{ex} = 246$ ps, $\tau_{biex} = 163$ ps; (c) $\tau_{ex} = 281$ ps, $\tau_{biex} = 187$ ps.

blets observed in the PL spectra of narrow QW was attributed to free exciton and impurity-related bound exciton (BE) emission, although higher-lying structure due to large island formation could be distinguished using PL excitation spectroscopy, temperature-dependent PL, and time-resolved PL spectra.[7] For wider QW, this structure is unresolvable. The different thicknesses of the QW's studied in this work ($L_z = 18.0$ nm for sample 2 compared to $L_z = 14.2$ nm for sample 1) is responsible for the different energy scale for use with Fig. 1, curves (d) and (e). Again a doublet is observed with about the same energy spacing. However, when the intensity of excitation is decreased, the low-energy component of the doublet becomes stronger relative to its high-energy counterpart. This is the opposite of what was observed for sample 1, but exactly what is expected for an extrinsic (BE) process which saturates at higher excitation levels. As before, the decay curve of each peak was recorded for the different intensities of excitation and are shown in Fig. 3. The decay of the free-exciton luminescence (labeled EX) was exponential and faster than that of the BE peak for both of the power densities used. Surprisingly, the lifetimes of the free-exciton and bound-exciton lines were found to depend on the pump intensity. A saturation of the extrinsic recombination channels might be at the origin of the lengthening of the lifetimes with increasing pump power. The important point here, however, is that the decay time of the lower energy peak BE of this sample follows very closely but always exceeds the decay time of the free-exciton line, in contrast to what was found in sample 1 for the biexciton and exciton peaks.

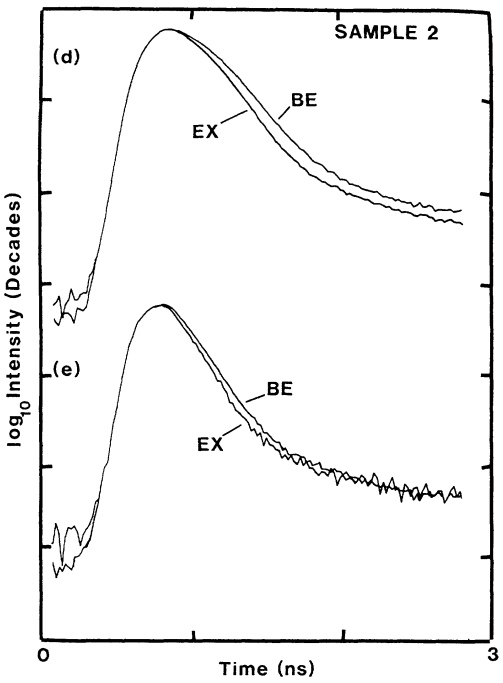


FIG. 3. The luminescence decay of the lines EX and BE of sample 2 for the two excitation conditions shown in Fig. 1, curves (d) and (e). The decay curves represent exponential decays having time constants of (d) $\tau_{BE} = 232$ ps, $\tau_{ex} = 203$ ps; (e) $\tau_{BE} = 179$ ps, $\tau_{ex} = 171$ ps.

On the basis of these results obtained from the excitation density dependence of the PL intensity and the transient behavior, it is clear that the low-energy components of the doublets, i.e., biexciton for sample 1 and BE for sample 2, originate from very different recombination mechanisms. As discussed previously, one would expect the concentrations of residual impurities to be increased at the interface for samples grown under the interrupted growth technique (e.g., sample 2). Both sets of results for this sample (excitation density dependence of the PL and the transient behavior) are in good agreement with the attribution of peak BE to an exciton bound to an impurity (probably donor) within the well. The saturation of the donor bound-exciton line with increasing excitation intensity is due to the finite concentration of impurities. This saturation effect was also observed by Nomura *et al.*[8] for their donor bound-exciton peak in doped QW's. Furthermore, since the bound excitons are fed by the free excitons, the bound-exciton line can never decay more rapidly than the free exciton, in agreement with our results. The theoretical calculation of Kleinman[3] for the binding energy of the donor bound exciton as a function of well thickness leads to a value of 1.4 meV for a 18.0-nm well. However, one should keep in mind the predicted systematic shift of the binding energy as the impurity's core becomes closer to the edge of the QW which, for the interrupted growth conditions, has to be taken into consideration.[11] In sample 1, however, the behavior of the lower energy peak is clearly that of a biexciton.

In summary, we have studied experimentally the dependence of the double peak on excitation intensity and its transient behavior. We have shown that care must be taken in the assignment of the low-energy component of the doublet. The low-energy component may be due either to the biexciton or an impurity bound exciton (or both) depending on the growth technique and quality of the quantum wells, and also on the excitation conditions.

The authors would like to acknowledge Richard Florian of ITT for the loan of the photomultiplier tube. This work was supported by the Natural Sciences and Engineering Research Council of Canada. We would like to thank J. Powers and W. Menzi for technical assistance during the growth of these samples.

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