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Photocurrent spectroscopy of $GaAs/Al_xGa_{1-x}As$ quantum wells in an electric field

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A photocurrent spectroscopy study has been made of *p-i-n* photodiodes in which the intrinsic regions were composed of $GaAs/Al_xGa_{1-x}As$ quantum wells. A sequence of distinct exciton absorption peaks was observed in the photocurrent spectra. Biasing the diodes allowed the effects of electric fields on the excitons to be examined. A comparison was made of the shifts of the energies of the excitons with applied field (Stark shifts). Changes in the relative amplitudes of the exciton peaks with bias were also noted. The Stark shifts for excitons in quantum wells with AlAs barriers were smaller than for wells with $Al_{0.3}Ga_{0.7}As$ barriers. Explanations for these observations are given.

Optical transitions between conduction- and valence-band subbands in semiconductor superlattices and quantum wells have been studied extensively. The most commonly used techniques in these studies are optical measurements such as photoluminescence, excitation spectroscopy, and optical absorption. Recently, these techniques have been applied to the investigation of the effects of electric fields on excitonic transitions in $GaAs/Al_xGa_{1-x}As$ quantum wells.[1-6] These studies have dealt primarily with changes in the lifetimes and energies (Stark shifts) of the lowest-energy heavy-hole (h_1) and light-hole (l_1) exciton resonances when an electric field is applied perpendicular to the wells. In the past, photocurrent spectroscopy (PCS) has also been used to study the electronic properties of semiconductor quantum wells.[7] Recent work suggests that PCS can provide information equivalent to that obtained using the above-mentioned purely optical techniques.[6,8]

In this paper we present a PCS study of the effects of electric fields on excitons in multiple quantum well devices. The devices used in these measurements were *p-i-n* photodiodes in which the intrinsic regions were composed of $GaAs/Al_xGa_{1-x}As$ multiple quantum wells. The electric fields were applied perpendicular to the wells. We observe a sequence of heavy- and light-hole exciton resonances (up to 8) in spectra which closely resemble the absorption spectra of quantum wells. Shifts in the energies of the exciton peaks (Stark shifts) were observed as the applied field was varied. We find that some of the higher-energy excitonic transitions show a very small Stark shift in comparison to the h_1 and l_1 excitons. This is the first study of the effects of electric fields on the energies of the higher-lying excitons. We also observe increases in the amplitudes of some of the exciton peaks as the electric field is increased, and we find that when the quantum well barrier is composed of AlAs, the Stark shift for a given electric field is smaller than in a quantum well of comparable width with an $Al_{0.3}Ga_{0.7}As$ barrier. Explanations for these observations based on calculations of the exciton energies are presented.

The two samples which will be discussed were grown by molecular-beam epitaxy (MBE). An n^+ layer of GaAs doped with Si at approximately 2×10^{18} cm^{-3} was grown on an n^+ GaAs substrate. Following this, 10 undoped quantum wells were grown. In the first sample (sample 1) they were composed of 10 layers of GaAs and 11 layers of $Al_{0.3}Ga_{0.7}As$. In the second sample (sample 2) pure AlAs was used instead of $Al_{0.3}Ga_{0.7}As$. One or two additional layers of GaAs and of the barrier material ($Al_{0.3}Ga_{0.7}As$ or AlAs) which were doped p^+ with Be at 2×10^{18} cm^{-3} were grown on top of the quantum wells, followed by a p^+ GaAs cap layer approximately 100 Å thick. Comparisons of the energies of the exciton lines to envelope function calculations[9] of the energies suggest that the width of the GaAs wells was between 80 and 85 Å (depending upon which masses and offsets were used) in both samples, although there is some question about which barrier height and what boundary condition to use in the calculation for sample 2 since the AlAs barriers were indirect.[10] Γ-point offsets were used in these calculations. The AlAs and $Al_{0.3}Ga_{0.7}As$ layer widths were estimated from growth rates to be 110 Å.

Each sample was contacted on the top and bottom faces and mounted in a variable temperature cryostat. Light from a grating monochromator with a tungsten lamp source was focused onto the p^+ surface of the sample. A dc bias was applied to the sample, and the current passing through the sample was recorded as a function of the wavelength of the incident light. The resultant spectra were not normalized to take into account the wavelength dependence of the intensity of the light source, but this dependence was smooth and fairly flat throughout the wavelengths of interest. The resolution of the monochromator was typically 8 Å. At 10 K (the temperature used in the measurements reported here) and for reverse bias voltages between −0.5 and 2.0 V in sample 1 and −0.5 and 4.0 V in sample 2, dark currents were less than 10 pA. For frequencies less than 50 Hz, ac and dc measurements of the photocurrent were in good agreement.

Figure 1 presents photocurrent spectra for sample 1 at different bias voltages. Eight peaks, labeled 1–8, are present in the spectra. Figure 2 shows similar spectra for sample 2. Seven peaks are observed and are labeled 1′–7′. Figures 3 and 4 are plots of the energies of the exciton peaks as a function of bias voltage for samples 1 and 2, respectively. In Figs. 1–4 voltages corresponding to reverse bias are positive. The peak positions were located by visual inspection or by fitting them to a Gaussian peak with a linear background when a large background was present. Some peaks

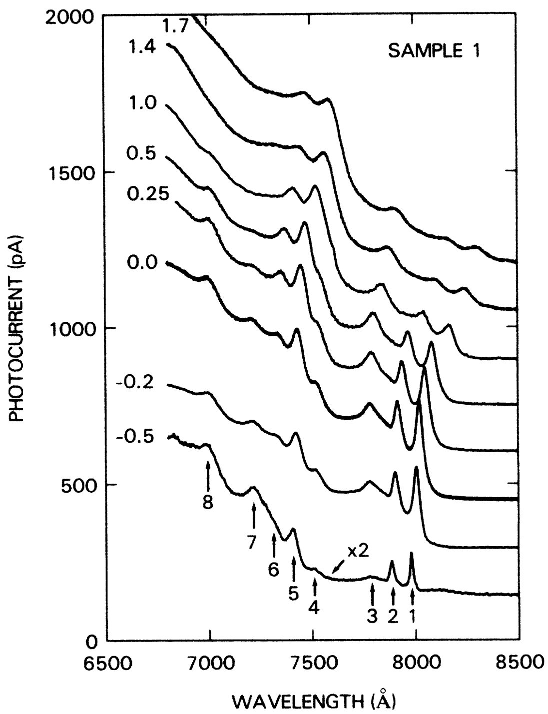

FIG. 1. Photocurrent spectra for sample 1 at different bias voltages. The bias voltage for each spectrum is given to the left of the spectrum. Reverse bias is positive. The base line for each spectrum has been offset by 150 pA relative to the spectrum at the next lowest voltage. There is also a 150 pA offset in the −0.5 V spectrum. The exciton peaks have been labeled (1–8) in the figure. Measurements were made at 10 K.

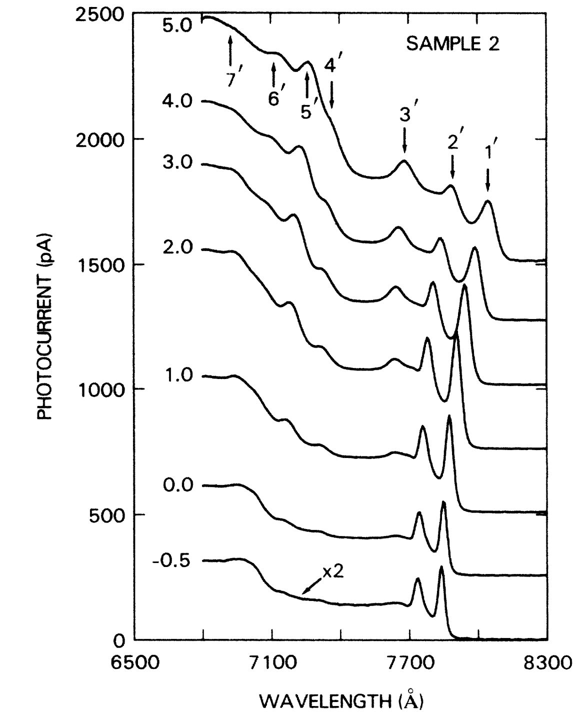

FIG. 2. Photocurrent spectra for sample 2 at different bias voltages. The bias voltage is given to the left of each spectrum. Reverse bias is positive. The base lines for the spectra have been offset by 250 pA relative to the spectrum at the next lowest voltage. There is no offset in the −0.5 V spectrum. The exciton peaks have been labeled (1′–7′) in the figure. Measurements were made at 10 K.

were too small at certain bias voltages to allow an accurate determination of their positions to be made, so data points for these peaks at these voltages could not be included. The total width of the intrinsic quantum well regions in both samples should have been approximately 2100 Å. Assuming this width and a built-in voltage for the diodes of 1.52 V, the average field can be determined. The range of electric fields used in these measurements extends from 2.5×10^4 to 3×10^5 V/cm with a field of 1×10^5 V/cm at approximately 0.5 V reverse bias.

The observation of a photoinduced current requires that the incident light creates free carriers and that transport of the carriers occur in the electric field. To the extent that the second of these processes is independent of wavelength, the spectra should resemble absorption spectra for multiple quantum wells. The resemblance of the spectra presented here to absorption data in, for example, Ref. 11, is close. The exact mechanisms by which the excitons are ionized and current passes through the quantum wells are not completely understood. As temperature was reduced from 300 to 100 K, the short-circuit photocurrent for a given excitation wavelength decreased, suggesting that in this temperature range thermionic emission accounted for the transport of carriers across the barriers. From 100 to 10 K, the photocurrent actually increased. Since tunneling is the most likely transport mechanism for these temperatures and barrier widths, this was probably due to a reduction in phonon scattering of the carriers as they tunneled through the barriers. The four lowest-energy peaks in each sample can be identified by comparing their energies to transition energies predicted in envelope function calculations.[9] In Fig. 1, peak 1 corresponds to h_1, 2 to l_1, 3 to h_{12}, and 4 to h_{13} (where h_{ij} is the exciton associated with the $n=i$ conduction-band subband and the $n=j$ heavy-hole valence-band subband). Similarly, in Fig. 2 peaks 1′, 2′, 3′, and 4′ can be identified as the h_1, l_1, h_{12}, and h_{13} excitations in sample 2, respectively. The energies of the rest of the peaks agree with the calculated energies of more than one possible exciton resonance. Because of this and the possibility that the heavy- and light-hole subbands are strongly mixed,[12] no attempt has been made to label the rest of the transitions. In both Figs. 1 and 2 we observe that as the reverse bias voltage on the samples is increased, the overall photocurrent collected increases. Presumably, this is due to an increase in the internal quantum efficiency of the devices with reverse bias.

The h_1 and l_1 peaks exhibit the largest Stark shifts (Figs. 3 and 4). At low reverse bias voltages some of the higher-energy excitons show extremely small shifts. In particular, this is true of the h_{12} (3 and 3′) and h_{13} (4 and 4′) exciton peaks. The h_{12} peaks show a decrease in energy of less than 1 meV at low bias voltages ($<$ 0.0 V in Fig. 3 and $<$ 2.5 V in Fig. 4) while the shifts in h_1 and l_1 are approximately 10 and 20 meV in samples 1 and 2, respectively. Calculations using the resonant tunneling technique of Ref. 6 have been made and predict that the shifts in the energies of h_{12} (3 and 3′) and h_{13} (4 and 4′) in an electric field should be less than the shifts for h_1 and l_1. This is due to a smaller shift in the energy of the $n=2$ and $n=3$ heavy-hole subbands

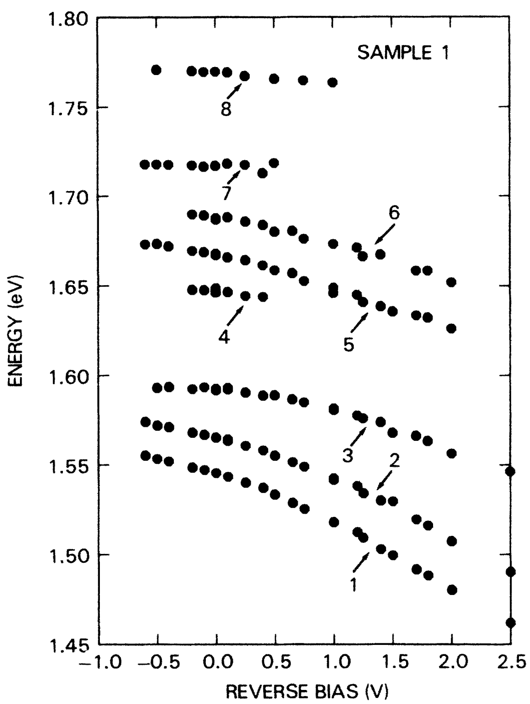

FIG. 3. Energies of the exciton peaks as a function of bias voltage for sample 1. Reverse bias is positive. Each curve is identified by the corresponding peak number from Fig. 1.

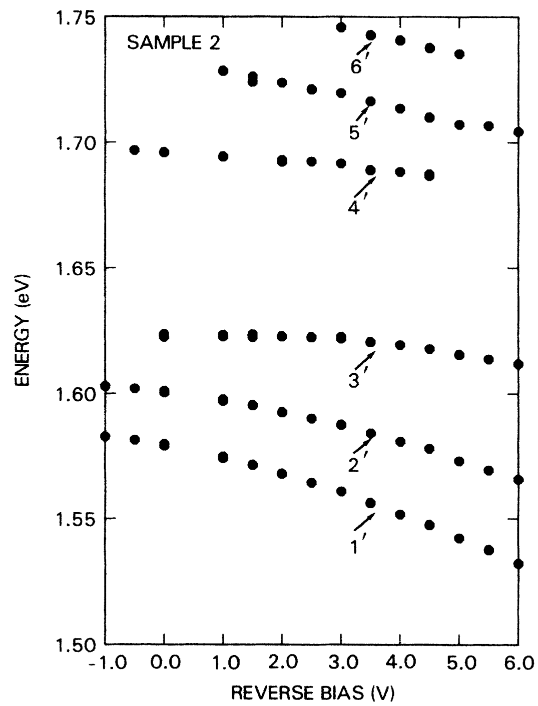

FIG. 4. Energies of the exciton peaks in sample 2 as a function of bias voltage. Reverse bias is positive. Each curve is identified by the corresponding peak number from Fig. 2.

toward the GaAs valence-band edge in comparison to the $n=1$ heavy- and light-hole subbands. The calculated $n=2$ heavy-hole subband energies actually exhibit a slight shift in energy away from the top of the GaAs valence band at low electric fields. Qualitatively, the differences in the Stark shifts of the subbands follow from a second-order perturbation theory analysis of the Stark shifts of the states in a quantum well.

$$\Delta E_n = e^2F^2 \sum_{i\neq n} |\langle i|x|n\rangle|^2/(E_n - E_i) \ ,$$

where E_n is the energy of eigenstate $|n\rangle$ and F is the electric field. The terms in the series for the $n=1$ state are negative due to the energy denominator. Its energy moves toward the bottom of the well with increasing field. For $n>1$, the terms due to lower-energy states are positive, while the terms due to higher-energy states are negative. The net effect is a smaller decrease in energy with field than for the $n=1$ state. To obtain quantitative agreement between the calculations and measurements requires using a smaller intrinsic region width for sample 1 and a larger width for sample 2 than predicted from growth parameters. Since the measured Stark shifts in sample 1 are larger at a given electric field than those reported in Ref. 6 on similar samples, it is possible that the intrinsic region widths are somewhat different from the widths given here. We also observe that the shift in peak 4 (Fig. 3) is less than the shifts in peaks 5 and 6, even though peak 4 is at a lower energy. Peaks 4', 5', and 6' (Fig. 4) show a similar behavior with field. The arguments given above can probably be extended to explain the differences in the Stark shifts of these resonances.

Peaks 3 and 6 in Fig. 1, and 3', 4', 5', and 6' in Fig. 2 are barely visible in the forward bias spectra, but as the reverse bias voltage is increased their amplitudes increase relative to the background current. These peaks are probably associated with forbidden excitonic transitions. In the case of the h_{12} peaks (3 and 3') this is definitely true. The perturbing field distorts the wave functions of the electrons and holes in the wells. For h_1 and l_1 this leads to a separation of charge, a reduction in the overlap of the wave functions for electrons and holes, and a reduced absorption coefficient.[1] For forbidden transitions the distortion of the wave functions can lead to an increase in the optical matrix element and absorption coefficient. Similar observations and explanations have been presented in Ref. 4. It is also evident in Figs. 3 and 4 that for a given electric field, the Stark shifts in the h_1, l_1, and h_{12} excitons for sample 1 are larger than for sample 2. The AlAs barriers of sample 2 may provide greater confinement and allow less penetration of the subband wave functions into the barriers. This would result in a smaller polarization of the wave functions at a given field leading to a smaller Stark shift. Assuming that the barrier between GaAs and AlAs is defined by the Γ-point offset,[10] the above-mentioned calculations do predict a smaller Stark shift for sample 2, although the measured reduction in shift at a given field is larger than the calculated value, possibly because of uncertainty in the intrinsic region widths as mentioned above.

As a final comment, we find that photocurrent spectroscopy can provide information about the electronic structure of quantum wells which is comparable to that obtained using the optical techniques commonly employed in quantum well studies. Most of these measurements require high light intensities. The light intensities involved in this study are extremely small (10 $\mu W/cm^2$ or less), making PCS a very sensitive alternative to these optical techniques.

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[1]E. E. Mendez, G. Bastard, L. L. Chang, L. Esaki, H. Morkoç, and R. Fischer, Phys. Rev. B **26**, 7101 (1982).

[2]T. H. Wood, C. A. Burrus, D. A. B. Miller, D. S. Chemla, T. C. Damen, A. C. Gossard, and W. Wiegmann, Appl. Phys. Lett. **44**, 16 (1984).

[3]J. A. Kash, E. E. Mendez, and H. Morkoç, Appl. Phys. Lett. **46**, 173 (1985).

[4]H. Iwamura, T. Saku, and H. Okamoto, Jpn. J. Appl. Phys. **24**, 104 (1985).

[5]C. Ailbert, S. Gaillard, J. A. Brum, G. Bastard, P. Frijlink, and M. Erman, Solid State Commun. **53**, 457 (1985).

[6]D. A. B. Miller, D. S. Chemla, T. C. Damen, A. C. Gossard, W. Weigmann, T. H. Wood, and C. A. Burrus, Phys. Rev. B **32**, 1043 (1985).

[7]R. Tsu, L. L. Chang, G. A. Sai-Halasz, and L. Esaki, Phys. Rev. Lett. **34**, 1509 (1975).

[8]H.-J. Polland, Y. Horikoshi, E. O. Göbel, J. Kuhl, and K. Ploog, in *Proceedings of the Second International Conference on Modulated Semiconductor Structures, Kyoto, Japan, 1985* [Surf. Sci. (to be published)].

[9]G. Bastard, Phys. Rev. B **24**, 5693 (1981).

[10]C. Mailhiot and T. C. McGill, J. Vac. Sci. Technol. B **1**, 439 (1983).

[11]S. W. Kirchoefer, N. Holonyak, Jr., K. Hess, D. A. Guilno, H. G. Drickamer, J. J. Coleman, and P. D. Dapkus, Appl. Phys. Lett. **40**, 821 (1982).

[12]Y. C. Chang and J. N. Schulman, Appl. Phys. Lett. **43**, 536 (1983).