Mixing between heavy-hole and light-hole excitons in GaAs/Al_xGa_{1-x}As quantum wells in an electric field

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Photocurrent and photoluminescence excitation spectra of GaAs/Al_xGa_{1-x}As quantum wells in an electric field exhibit two exciton peaks in the energy range where only a single exciton is expected to occur. Uniaxial stress and polarization-dependent measurements indicate that the two peaks have strongly mixed heavy- and light-hole characters. The observation of an additional peak is attributed to mixing between the $n=2$ heavy-hole and $n=1$ light-hole valence subbands. Our measurements provide direct evidence for the large effect that valence-band mixing has on excitons in quantum wells.

Valence-band mixing in *III-V* semiconductor quantum wells and superlattices has been the subject of intense theoretical investigation (see for example Refs. 1–7). Much of this work has concentrated on GaAs/Al_xGa_{1-x}As quantum wells. In bulk GaAs and Al_xGa_{1-x}As the heavy- and light-hole valence bands are degenerate at the center of the Brillouin zone ($k=0$). When a quantum well is grown, the confining potential lifts the degeneracy, and a sequence of two-dimensional subbands are formed. In the simplest approximation, the valence subbands are associated with either the heavy- or light-hole valence bands of the bulk materials. In reality, anticrossings between the subbands give rise to considerable mixing between heavy- and light-hole states at points away from $k=0$.[1–7] Mixing may even occur at $k=0$.[2,3] This is true for symmetric quantum wells such as the square wells commonly used in optical studies and for asymmetric wells[7] such as the well which contains the two-dimensional electron gas in a modulation-doped GaAs/Al_xGa_{1-x}As heterojunction.[8] The mixing is predicted to have a large effect on the electronic structure of the valence subbands and, in particular, on the properties of the excitonic states associated with transitions between the conduction and valence subbands.[5–7] Nevertheless, unambiguous observations of the effects of mixing on the excitons have been difficult to make. The primary evidence for mixing has been the observation of forbidden excitonic transitions in optical measurements on square quantum wells.[9] Valence-band mixing has also been used to explain optical and electrical measurements on quantum wells containing two-dimensional electron or hole gases.[10,11] Interpretations of the latter measurements are complicated by many-body effects.[8,11]

We have made a study of the excitonic transitions in square GaAs/Al_xGa_{1-x}As quantum wells in an electric field. When a field is applied to wells with widths greater than approximately 120 Å, we observe two prominent excitonic peaks in the energy range where only the 1*s* ground state of the exciton associated with the $n=2$ heavy hole and $n=1$ conduction subbands ($h_{12}^{(1s)}$) is expected to occur. Uniaxial stress[12] and polarization-dependent measurements indicate that the two peaks have a strongly mixed heavy- and light-hole character, thereby confirming that valence-band mixing has a large effect on the electronic properties of excitons in quantum wells.

Figure 1 presents a sequence of low-temperature photoluminescence excitation (solid line) and photocurrent[13,14] (dashed line) spectra for a sample composed of five 160-Å quantum wells imbedded in the depletion region of a *p-i-n* GaAs/Al_xGa_{1-x}As diode. Each spectrum corresponds to a different external electric field (given in kV/cm at the side of each spectrum).[15] When no electric field is present a peak due to the 1*s* ground state of the exciton from the $n=1$ light-hole subband to the $n=1$ conduction subband ($l_1^{(1s)}$) is visible in the spectrum. The high-energy side of $h_1^{(1s)}$ (ground state of the $n=1$ heavy hole to $n=1$ conduction subband) is also present.[16] Since both of these transitions are allowed ($\Delta n=0$) at zero electric field, it is expected that they will dominate the spectrum for the wavelengths of Fig. 1. Three additional peaks with considerably smaller integrated intensities are seen in the blowup of the 0-kV/cm spectrum given in the inset to Fig. 1. Two of these ($h_1^{(2s)}$ and $l_1^{(2s)}$) are identified as the 2*s* excited states of the lowest-energy heavy- and light-hole excitons, respectively. This identification is based on the fact that the separations of $h_1^{(2s)}$ and $l_1^{(2s)}$ from $h_1^{(1s)}$ and $l_1^{(1s)}$, respectively, correspond to published[17,18] values for the 1*s* ground state to 2*s* excited-state separations. As the field is increased, the third peak (h_{12a}) grows in intensity. A new peak (h_{12b}) also becomes visible at an energy slightly greater (approximately 1.0 meV) than the $l_1^{(2s)}$ peak. At a field of 50 kV/cm, h_{12a} and h_{12b} are nearly equal in intensity to $h_1^{(1s)}$ and $l_1^{(1s)}$. At higher fields the intensity of h_{12a} decreases relative to the rest of the exciton peaks until it is only visible as a step on the high-energy side of $l_1^{(1s)}$.

When an electric field perpendicular to the plane of a square quantum well is present in the well, the well be-

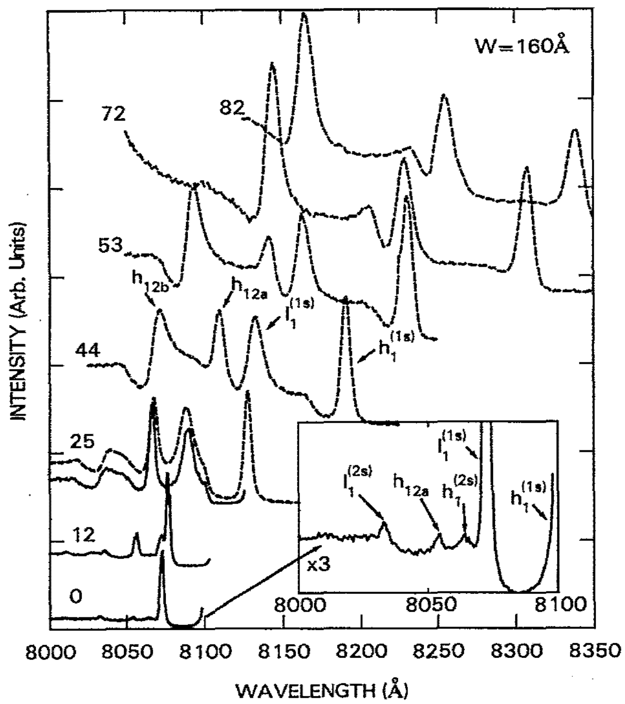

FIG. 1. Photocurrent (dashed) and photoluminescence excitation (solid) spectra for 160-Å quantum wells in an electric field. Fields are given beside the spectra in kV/cm. Photocurrent measurements were made at 10 K. Excitation spectra were recorded at 5 K. The baselines for the spectra have been offset for clarity.

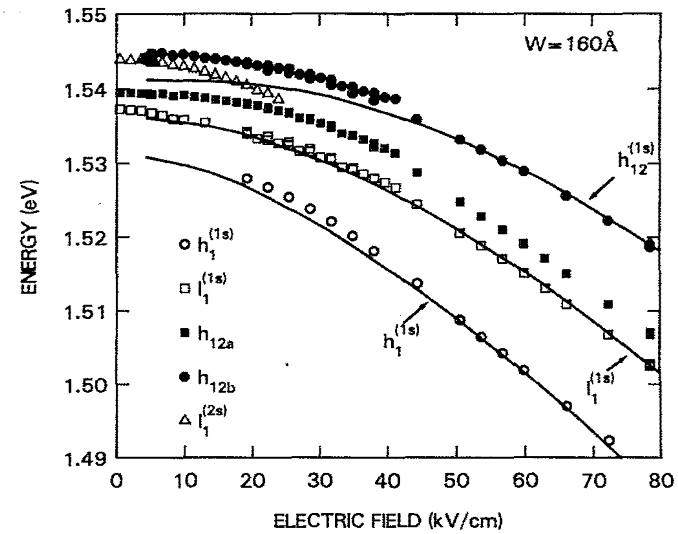

FIG. 2. Energies of some of the exciton peaks in Fig. 1 as a function of electric field. Solid lines are numerically calculated energies of $h_1^{(1s)}$, $l_1^{(1s)}$, and $h_{12}^{(1s)}$ in the envelope-function approximation.

comes asymmetric and forbidden excitonic transitions ($\Delta n \neq 0$) become visible in optical measurements.[14] In particular, $h_{12}^{(1s)}$ should become visible within the wavelength range where h_{12a} and h_{12b} are observed. Figure 2 is a plot of the energies of some of the exciton peaks in Fig. 1 as a function of electric field. Also included in Fig. 2 are envelope-function calculations,[19,20] of the energies of $h_1^{(1s)}$, $l_1^{(1s)}$, and $h_{12}^{(1s)}$ using standard masses and offsets,[21] and assuming binding energies of 6.5, 9.0, and 6.0 meV,[6,17] respectively. Although the calculations reproduce the Stark shifts of $h_1^{(1s)}$ and $l_1^{(1s)}$ reasonably well, they predict that only a single exciton peak should be visible ($h_{12}^{(1s)}$) in the wavelength range where h_{12a} and h_{12b} are observed. A variation of the parameters in this model will affect the agreement between calculation and experimental data in Fig. 2 but will not alter the fact that only a single exciton peak should be seen in the energy range of h_{12a} and h_{12b}. The next exciton peak which should be visible at a higher energy than $h_{12}^{(1s)}$ is the exciton from the $n=3$ heavy hole to $n=1$ conduction subband ($h_{13}^{(1s)}$). The energy of this peak is predicted to be at least 16 meV greater than that of $h_{12}^{(1s)}$. $h_{13}^{(1s)}$ is actually observed in the measurements at the predicted energy. At electric fields less than 30 kV/cm, the calculated energy of $h_{12}^{(1s)}$ may be associated with either h_{12a} or h_{12b}. At larger fields the calculated value agrees closely with h_{12b}. The energy of $l_1^{(2s)}$ has also been plotted in Fig. 2 for the fields in which it was visible. This peak serves as a marker for the beginning of the continuum edge of the l_1 exciton. At zero fields, $l_1^{(2s)}$ approximately coincides with h_{12b}. When the field increases, $l_1^{(2s)}$ moves closer to h_{12a} until, at 30 kV/cm, they have nearly the same energy. The presence of an extra exciton peak in the energy range of $h_{12}^{(1s)}$ was observed in all of the samples studied which had well widths greater than approximately 120 Å. The widest wells used in the measurements were 250-Å wide. Previous measurements on quantum wells with widths of 80 Å did not reveal two peaks,[14] while published spectra of 110-Å quantum wells exhibited a small additional exciton peak in this energy range, although the authors did not discuss the peak.[22] To determine the origin of the additional peak, polarization and uniaxial stress-dependent measurements were made.

The symmetries of the zone-center valence subbands are such that for light polarized perpendicular to the [100] growth axis (*XY* polarized), transitions from the heavy- and light-hole subbands to the conduction subbands are both dipole allowed. (*XY*-polarized light was used for all of the measurements in Fig. 1.) For light polarized parallel to the growth axis (*Z* polarized), only the light-hole transitions should be seen.[23] Figure 3(a) gives polarization-dependent photocurrent measurements for a sample in which two 130-Å quantum wells were imbedded in an $Al_xGa_{1-x}As$ wave guide.[23] The sample was illuminated from a cleaved edge. Although the exciton peaks are broader than in Fig. 1 because the measurements were made at a higher temperature, $h_1^{(1s)}$, $l_1^{(1s)}$, h_{12a}, and h_{12b} are all visible in the *XY*-polarized spectra. In the *Z* polarization a small $h_1^{(1s)}$ peak is seen. This is probably due to *XY* polarized light scattered in from the face of the sample. A large $l_1^{(1s)}$ peak is visible in the *Z* polarization as expected. Some structure which could be attributed to h_{12a} and h_{12b} is also visible in the *Z*-polarized spectra, but it is much smaller in amplitude relative to $l_1^{(1s)}$ than for *XY* polarization. This allows us to conclude that h_{12a} and h_{12b} have oscillator strengths which arise primarily from the heavy-hole valence band. The small

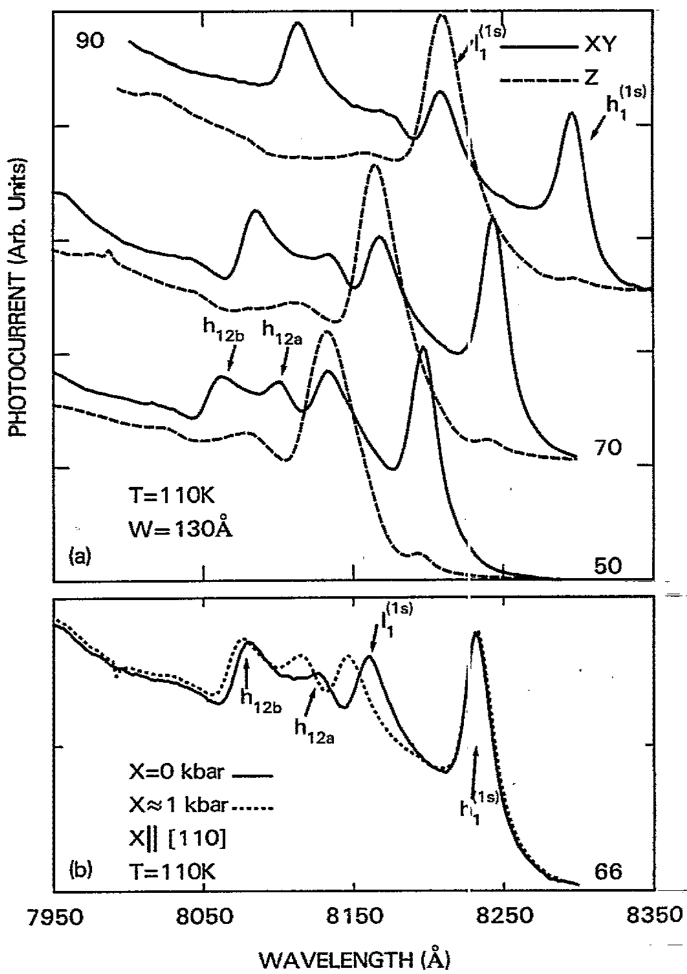

FIG. 3. (a) Polarization-dependent photocurrent measurements for two 130-Å quantum wells imbedded in an $Al_xGa_{1-x}As$ wave guide. (b) Uniaxial stress-dependent photocurrent spectra for the same sample. The $h_1^{(1s)}$ peaks have been aligned.

structure which is present in the Z polarization does not coincide in energy with h_{12a} and h_{12b}. It is probably not directly due to these two excitons but rather to the continuum edge of the $l_1^{(1s)}$ exciton and to the response of the continuum to the presence of h_{12a} and h_{12b} (Fano resonances).

In bulk GaAs uniaxial stress splits the degeneracy between the heavy- and light-hole valence bands at $k=0$.[24] Similarly, heavy- and light-hole valence subbands in a quantum well should exhibit different shifts under a uniaxial stress. For compressive uniaxial stress along a [110] crystal axis, calculations using a $\mathbf{k}\cdot\mathbf{p}$ theory[4] predict that the energies of both the light- and the heavy-hole excitons will increase with the largest shift occurring in the light-hole excitons.[25] Figure 3(b) presents spectra for the 130-Å sample of Fig. 3(a) with and without an applied uniaxial stress. The shift in $h_1^{(1s)}$ was less than 0.5 meV so this peak was aligned in the spectra. We then expect all of the excitons derived from the heavy-hole valence band to show small shifts, while the light-hole excitons show a larger shift. In the stressed spectrum $l_1^{(1s)}$ and h_{12a} shifted more than 2.25 meV, while the shift in h_{12b} was approximately 0.6 meV. At smaller electric fields (<25 kV) the shifts of h_{12a} and h_{12b} were nearly equal, while at large fields (>100 kV/cm) the shift in h_{12b} was even smaller for a given stress. It was difficult to determine the magnitude of the stresses due to the small sample size, but the stress in the dotted spectrum of Fig. 3(b) was roughly 1 kbar.

The above polarization-dependent measurements indicate that h_{12a} arises from the heavy-hole valence band, while the uniaxial stress measurements indicate that, for the electric field of Fig. 3(b), the wave function of h_{12a} is predominantly light hole in character. This apparent contradiction is resolved by realizing that the polarization-dependent measurements only provide information about the part of the exciton wave function which contributes to absorption, while uniaxial stress gives the symmetry of the whole wave function. If a forbidden light-hole transition mixes with an allowed heavy-hole transition, both will be visible and have heavy-hole oscillator strengths as measured by absorption. Depending on the amount of mixing, uniaxial stress will indicate a mixed heavy- and light-hole character for the transitions. From this we conclude that h_{12a} has a mixed heavy- and light-hole character. In addition, only the heavy-hole component is contributing to absorption. At the electric field of Fig. 3(b) h_{12a} is mostly light hole in character but has a small heavy-hole component which gives rise to the h_{12a} peak in the XY polarized spectrum. At lower electric fields both h_{12a} and h_{12b} are strongly mixed since they show similar shifts under uniaxial stress. At these fields both excitons derive their oscillator strengths primarily from the heavy-hole components of their wave functions. The presence of two excitons with mixed symmetry in the energy range where only $h_{12}^{(1s)}$ is expected to occur is probably due to mixing between the $n=1$ light-hole and $n=2$ heavy-hole valence subbands. For the well widths used in this study, the $n=1$ light- and $n=2$ heavy-hole subbands have nearly the same energy and are predicted to be strongly mixed.[2] Since both h_{12a} and h_{12b} increase in intensity with increasing electric field, and since they are in the energy range where the $h_{12}^{(1s)}$ exciton should be observed, they must be associated with $h_{12}^{(1s)}$, and, therefore, with the $n=2$ heavy-hole subband. The fact that the continuum of l_1 coincides with h_{12b} at zero field and with h_{12a} at high fields suggests that h_{12a} and h_{12b} are also associated with the $n=1$ light-hole valence subband. If h_{12a} and h_{12b} arise from mixing between the $n=1$ light- and $n=2$ heavy-hole valence subbands, the absence of extra peaks in 80-Å wells can be explained, since, as the well width is decreased, the subbands separate and mixing is reduced. The two subbands will also separate and mixing will be reduced when the electric field is increased, because the Stark shift of the $n=1$ light-hole subband will be larger than the shift in the $n=2$ heavy-hole subband.[13] This explains why the extra peak weakens considerably at high electric fields and also serves to identify h_{12b} as the true $h_{12}^{(1s)}$ exciton in the limit of large electric fields.

Mixing between the $n=2$ heavy- and $n=1$ light-hole valence subbands can affect the excitons arising from these subbands in two ways.[5] First, the Bloch states from which the excitons are derived will have mixed heavy-and light-hole characters. Second, because the Bloch states are mixed, the Coulomb interaction couples the excitons arising from each of the subbands. The degree of this coupling is related to the degree of mixing in the Bloch states. We speculate that mixing between $h_{12}^{(1s)}$ and an excited state of l_1 gives rise to h_{12a} and h_{12b}. In the absence of mixing an excited state would not be expected to contribute significantly to absorption, since excited states of excitons have small oscillator strengths compared to ground states. When mixing does occur, the excited state may become visible because it shares the $h_{12}^{(1s)}$ oscillator strength. This would give rise to an additional peak in the spectrum. Both peaks would have heavy-hole oscillator strengths. The fact that h_{12b} first becomes visible at the continuum edge of l_1 and that h_{12a} disappears at the approximate location of the l_1 continuum in high electric fields supports this explanation. However, it is clear that the 2s excited state of l_1 is not involved in the mixing since $l_1^{(2s)}$ could be observed as a separate peak at fields between 0 and 30 kV/cm (Fig. 2). Recently, Chan[6] has suggested that mixing between the p-like excited states of l_1 and the s-like states of h_{12} should occur. Such a mixing would explain our observations.

To summarize, for quantum wells with widths greater than 120 Å we observe two exciton peaks in the energy range where only the $h_{12}^{(1s)}$ exciton is predicted to occur. Polarization and uniaxial stress measurements show that the peaks have a mixed heavy-hole and light-hole character. We conclude that they arise from a mixing between the $n=2$ heavy-hole and $n=1$ light-hole valence subbands. A possible model for the mixing is that it occurs between $h_{12}^{(1s)}$ and an excited state of l_1. The observation of the additional exciton peak is significant since it confirms that valence-band mixing can have a large effect on the electronic properties of quantum wells and superlattices.

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