Determination of the binding energy of excitons to neutral donors located at the center or edge of the well or at the center of the barrier in $Al_xGa_{1-x}As/GaAs$ multiple-quantum-well structures

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The binding energy of excitons to neutral donors (D^0,X) in GaAs-$Al_xGa_{1-x}As$ quantum wells is determined by high-resolution resonant-excitation photoluminescence and temperature-dependent photoluminescence measurements. Changes in the binding energy of excitons are observed when donors are located in the center of the well, at the edge of the well in the interface region, or in the center of the barrier. The variations in these binding energies are investigated as a function of well size from 75 to 350 Å. The binding energies are found to increase as well size was reduced until about 100 Å, after which they decreased. An additional transition is observed which is tentatively assigned to excitons bound to ionized donors located at the center or edges of the well.

INTRODUCTION

There are few measurements available of the binding energy of excitons to neutral donors (D^0,X) or ionized donors (D^+,X) in quantum wells (QW's). The original report of donor-related complexes in quantum wells was by Shanabrook and Comas.[1] Reynolds *et al.*[2] reported sharp lines observed in photoluminescence (PL) associated with D^0,X transitions in nonintentionally doped GaAs-$Al_xGa_{1-x}As$ multiple quantum wells (MQW's). D^0,X transitions are also reported by Nomura *et al.*[3] in Si-doped GaAs-$Al_xGa_{1-x}As$ single QW's (SQW's). Recently, Liu *et al.*[4] have also observed transitions in PL associated with excitons bound to neutral and ionized donors located at the center of the quantum wells. Both Nomura *et al.*[3] and Liu *et al.*[4] plot the variation of the binding energy of excitons to neutral donors as a function of well size and find that the value of the binding energy decreases as the well size is increased, in agreement with the variational calculations of Kleinman.[5] An impurity-bound exciton (probably D^0,X) transition was reported by Charbonneau *et al.*[6] in a 180-Å SQW where interrupted growth was used. Also observed was a transition identified as due to the biexciton in a 142-Å SQW grown without interruption.

In this paper, we report a systematic study of the binding energy of D^0,X in several QW's of varying sizes and as altered by the physical location of the neutral donors. The GaAs-$Al_xGa_{1-x}As$ QW samples investigated were either nominally undoped, Si doped in the center of the well (CW), the edges of the well (EW), or doped in the center of the $Al_xGa_{1-x}As$ barrier (CB). We also speculate on the binding energy of D^+,X by tentatively identifying some transitions with this feature. Although several of the samples showed acceptor bound exciton (A^0,X) transitions, they will not be discussed here. The experimental techniques used in this study include high-resolution PL, resonant excitation (RE), as well as temperature-dependent PL. Temperature-dependent PL measurements were used to distinguish between free- and bound-exciton transitions.

An estimate of the energetic ordering of excitonic transitions in semiconductors has been made. An empirical relationship between the binding energy of the exciton (E_1) to the neutral donor and the donor binding energy (E_D) was first postulated by Haynes[7] from experiments performed on Si. This relation can be expressed as follows:

$$E_1 = BE_D \ , \tag{1}$$

where B is a constant of proportionality having a value of 0.1 for Si. It was shown by Hopfield[8] that the binding energy of D^0,X could be obtained by subtracting the free-exciton energy (E_{ex}) from the energy required for removing an electron and a hole from a neutral donor (E_t). Furthermore, the binding energy of an exciton to an ionized donor can be approximately obtained[8] by subtracting E_{ex} from E_D, since the binding energy of the hole to a neutral donor is small. The relationship between E_{ex} and E_D can then be expressed as follows:

$$E_{ex} = E_D/(1+\sigma) \ , \tag{2}$$

where σ is the ratio of the electron mass to the hole mass. It was also shown[8] that E_t varied from $1.33E_D$ for $\sigma=0$ to $0.055E_D$ for $\sigma=\infty$ which crosses E_D for a value of σ somewhere between 0.2 and 0.25. Thus for σ values less than the crossover value, the D^+,X transition will fall on the high-energy side of D^0,X and for values greater than the crossover value, on the lower-energy side of D^0,X transition.

In addition to the usual heavy-hole free-exciton (HHFE) transition, very clear D^0,X transitions were observed in all samples regardless of the position of the dopant in the QW. Interpretation of the other transitions observed in the GaAs-$Al_xGa_{1-x}As$ quantum wells is assisted by an extension of the above arguments. The calculated value of σ, obtained from Eq. (2) using calculated values of E_{ex} (Ref. 9) and E_D of CW donors[10] for all of the well dimensions investigated, is approximately 0.5, which is higher than the crossover value of 0.25, thereby predicting that the D^+,X transition will occur at lower energy than the D^0,X transition. However, no transitions were observed in CW-doped samples on the low-energy side of D^0,X that could be attributed to D^+,X. These transitions, if present, are apparently weak and thus not observable in our experiments. In donor-doped samples, doped at sufficient levels to produce n-type material, the dominant transition is the D^0,X transition.

For EW or CB donors, one cannot use the above-mentioned arguments, which are applicable only to bulk-like donors. As a result, the energy ordering of D^0,X and D^+,X for these donor positions cannot be predicted by these arguments. No transitions were observed with energies lower than that of D^0,X. However, prominent transitions on the high-energy side were observed in both EW- and CB-doped samples which may be D^+,X transitions since the ordering is unknown. These transitions were also observed in the nominally undoped samples as well. A transition involving D^0,X associated with CW donors was also observed in spite of no intentional doping at this location. This is attributed to the enhanced density of states for residual donors located in the well center. It is the detailed comparison of the relative transition energies of D^0,X associated with donors located at CW, EW, or CB versus well size that is the primary object of this study.

EXPERIMENTAL METHOD

The samples used were MQW's grown by molecular-beam epitaxy (MBE) in a Varian Gen II system. A 1000-Å buffer layer was grown on the n^+ substrates oriented 6° off (100) followed by a ten-cycle superlattice consisting of 30 Å $Al_xGa_{1-x}As$ and 30 Å GaAs. The wells varied in size from 75 to 350 Å and the barriers of $Al_{0.25}Ga_{0.75}As$ were 100 Å wide. The single donor dopant used was Si. The CW-doped samples were doped over the central 50 Å (25 Å each side of the center of the well) at a concentration of $1\times10^{16}/cm^3$.

However, samples for the narrowest well widths studied (≤ 100 Å) were doped only in the central 25 Å (12.5 Å each side of the center of the well) at $2\times10^{16}/cm^3$, so that the net dopant level was the same as for other samples. The EW-doped samples were doped 25 Å at each interface within the well, also at a concentration of $1\times10^{16}/cm^3$. The EW-doped samples of ≤ 100 Å well width were doped 12.5 Å at each interface at $2\times10^{16}/cm^3$. The CB-doped samples were doped at the central 25 Å of the barrier (12.5 Å each side of the center of the barrier) at a concentration of $2\times10^{16}/cm^3$. All the

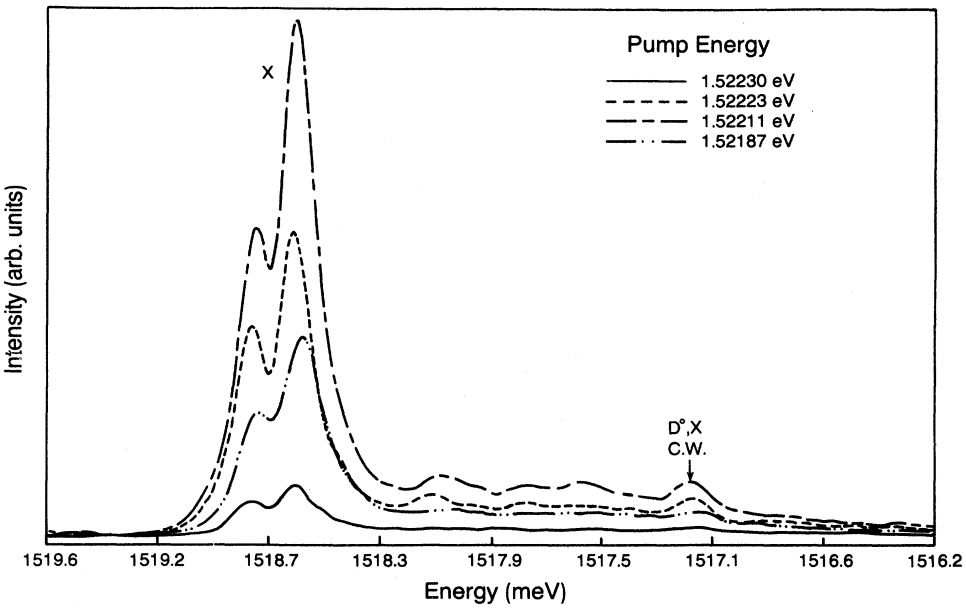

FIG. 1. Variation of emission intensity of the HHFE ($\times$) and CW (D^0,X) for an undoped nominal 300-Å MQW for very small changes in the pump energy.

samples were grown at a nominal temperature of 580 °C using dimeric arsenic.

The PL was excited either with the Ar^+-ion laser or with a tunable dye laser using Styryl 9 dye, which was pumped by an Ar^+-ion laser. The RE differs from conventional PL in that it was excited by the aforementioned dye laser tuned to a particular excited state of the transition of interest causing enhanced emission of this transition. We have observed that RE from tuning the laser either to the light-hole free exciton (LHFE), the $n=2$ state of the heavy-hole free exciton (HHFE), or the exciton transition associated with the first conduction subband and the second heavy-hole subband ($C1$-$H2$), all gave very similar emission results. For the spectra reported, the samples having well widths ≥ 100 Å were resonantly excited either from the LHFE or the $n=2$ state of the HHFE. However, for narrower well widths, RE could not be excited due to tuning limitations of the Styryl 9 dye. In the case of RE the transition intensities are extremely sensitive to very small changes in the exciting wavelength. This is demonstrated in Fig. 1. The highest-intensity transition is excited at an energy of 1.522 11 eV. At a pump wavelength approximately 1 Å to either side of the pump wavelength giving maximum emission intensity, the intensity of the free-exciton transitions is markedly reduced and the D^0,X transition has disappeared. This demonstrates the power of RE in highlighting emission features. The pump power used in all RE experiments in this study was approximately 50 mW/cm^2; this was the maximum intensity of our dye laser. The above power was measured at the exit of the laser; the intensity at the sample was reduced by at least a factor of 2.

In straight PL measurements using the Ar^+-ion laser, the pump power was varied from <50 to 1500 mW/cm^2. The donors could be saturated and the relative intensities of free-exciton to bound-exciton peaks could be varied. In the PL experiments a pump power of 200 mW/cm^2 was found to produce satisfactory results and was used throughout this study except for Fig. 8, where a pump power of 600 mW/cm^2 was used. As in the case of RE, this was the pump power measured directly from the laser. The high-resolution PL and RE measurements were made at 2 K with the sample immersed in liquid He. In the intrinsic region of GaAs a dispersion of 0.54 Å/mm was achieved using a 4-m spectrometer equipped with an RCA C31034A photomultiplier tube for detection.

EXPERIMENTAL RESULTS

Prior to beginning the comparison of the various doping schemes, some observations common to all will be noted. It is not possible to control the exact well size sufficiently so that the excitonic features align exactly. To remove this effect, we artificially align the D^0,X transitions due to CW donors in spectra of nominally the same well size. The indicated energy scale corresponds to the solid curve in each figure. The displacement of dashed or dot-dashed curves with respect to this scale is indicated in the figure caption. Thus the absolute transition energies observed may be recovered by subtracting the indicated shift from the displayed spectrum. The binding energy of D^0,X is a function of well size. Consequently, if the correction is small (the well sizes being nearly equal), alignment of D^0,X also has the effect of aligning the HHFE included in the figures. It should be pointed out that the intensities for different transitions within a given spectrum for a MQW are relative, but the intensities between spectra from different MQW's are arbitrary.

The emission spectra from a CW-doped (solid curve) and undoped (dashed curve) nominal 350-Å MQW's are shown in Fig. 2. The transition intensity for the D^0,X transition in the undoped sample is weak as would be expected since both the well and the barrier are probably p type; therefore, in the dark the residual donors will be ionized. In the light, as photoexcited electrons are added to the system, the donors at the center of the well will be preferentially neutralized since they have the greatest binding energy. These donors can then form D^0,X complexes in the presence of light and recombine producing this D^0,X transition. We shall now speculate on the identity of the peak at 1.516 90 eV. Since the D^+,X for CW donors is expected to occur at lower energy than CW D^0,X, the remaining possibilities are either D^0,X or D^+,X complexes involving either EW or CB donors. In the controlled doping location studies which follow, the D^0,X transition associated with either EW or CB donors is observed to have a smaller shift to higher energy above CW D^0,X than the feature at 1.516 90 eV. This leaves the possibility of it being D^+,X for either EW or CB donors. This is plausible since these EW and CB donors will be the last to be photoneutralized and are thus available for D^+,X formation. However, it is also possible that this feature arises from some other unknown origin. The peaks at 1.517 91 and 1.517 78 eV in the undoped

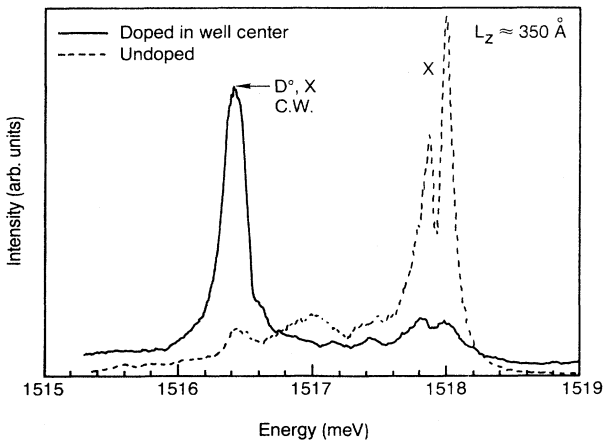

FIG. 2. RE emission spectra from an undoped (dashed curve) and a center of the well-doped (solid curve) nominal 350-Å MQW's resonantly excited from the $n=2$ state of the HHFE. To account for well-width variation, the undoped sample (dashed) has been displaced by 0.1 meV, which aligns the CW D^0,X.

sample are the HHFE transitions corresponding to a one-monolayer variation in well width. The correspondingly weaker transitions in the doped sample are also the HHFE transitions. Similar observations may be made about the spectra in narrower wells such as in the nominal 250-Å MQW's as shown in Fig. 3. The spectra are very similar to what are displayed in Fig. 2, however, shifted to higher energies commensurate with the narrower well size. The transition energy for D^0,X in the doped well is 1.519 63 eV. In agreement with the previous data, the corresponding transition in the undoped sample is again weak. The transition at 1.5203 eV in the undoped sample we again suggest may be due to the D^+,X transition associated with EW or CB donors. The transitions at 1.521 23 and 1.521 06 eV in the undoped sample are HHFE transitions separated by one-monolayer variation in well size with corresponding weaker HHFE transitions in the doped well.

The PL emission spectra resulting from 350-Å MQW's doped at the CW, EW, and CB are shown in Fig. 4. The CW D^0,X transition for the sample doped at the center of the well is dominant over all transitions including HHFE. The EW and CB D^0,X transitions are observed in EW- and CB-doped samples, respectively, and are accompanied by the CW D^0,X transition. They are absent in the CW-doped sample. This is expected since electrons will tend to preferentially relax to the lowest-energy state available, which would be the CW donor, which also has the highest density of states. Theoretical calculations of Greene and Bajaj[11] show that for samples spike-doped at the edge of the well, there is still a transition associated with CW donors. Similarly, there are two well-defined peaks expected for the CB-doped sample. The theory of Lane and Greene[12] predicts that for a uniform distribution of donors in samples where the barrier width equals

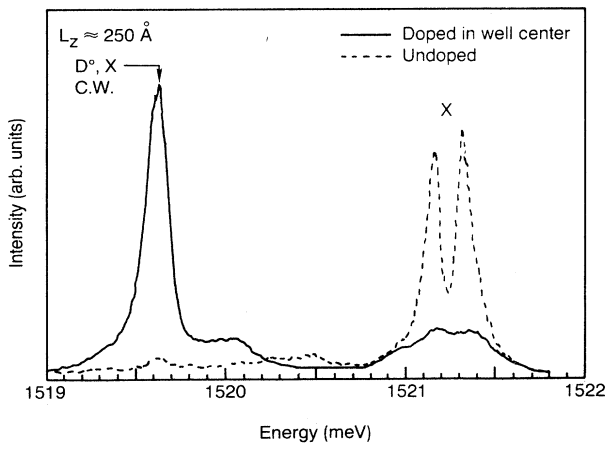

FIG. 3. RE emission spectra from an undoped (dashed curve) and a center of the well-doped (solid curve) nominal 250-Å MQW's resonantly excited from the $n=2$ state of the HHFE. To account for well-width variation, the undoped sample (dashed) has been displaced by 0.09 meV, which aligns the CW D^0,X.

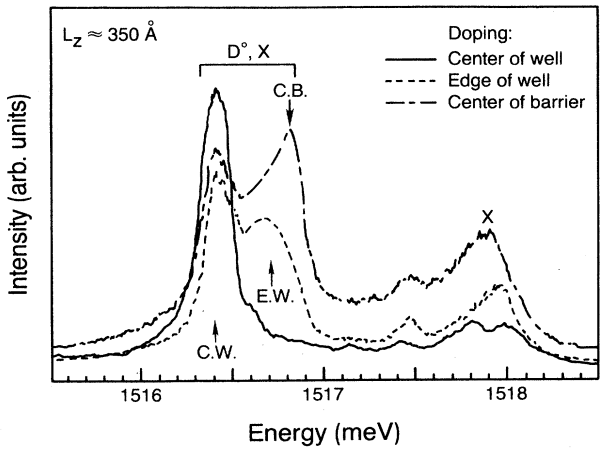

FIG. 4. RE emission spectra from CW doped (solid curve), EW doped (dashed curve), and CB doped (dot-dashed curve) for nominal 350-Å MQW's. The CW D^0,X transitions have been aligned to account for well-width variation. The energy scale on the abscissa relates to the solid curve. The EW-doped (CB-doped) spectra represented by the dashed (dot-dashed) curves have been displaced by 0.35 meV (0.30 meV) which must be subtracted to recover actual energies.

the well width that two peaks should be observed in PL, one associated with the CW donors and the other with CB donors. It is clear from Ref. 12 that the CW donor binding energy is appreciably greater than that of the EW or CB donor. Earlier calculations by Greene and Bajaj[10] showed the same trend. Therefore, since the CW donor binding energy is greater than that of the EW or CB donor, it would be expected that the exciton would also have a greater binding energy to CW donors than to either EW or CB donors. This is clearly the case as shown in Fig. 4. Furthermore, Ref. 12 indicates that EW donors have a greater binding energy than CB donors which is also consistent with the results in Fig. 4. The highest-energy peaks in this figure are the HHFE transitions. The peak in the region of 1.5171 eV will be treated separately in another publication.

A complementary set of data to that shown in Fig. 4 is shown in Figs. 5, 6, and 7 for nominal 250-, 200-, and 150-Å-well-size MQW's, respectively, for CW, EW, and CB doping. The D^0,X transitions in these figures are very similar to the analogous transitions in Fig. 4 with the energy shift taken into account due to the change in well size. The highest-energy peaks again are the HHFE transitions. There are some features that should be noted, however, in the samples with narrower well widths. For the 200-Å-well-width sample shown in Fig. 6, the CW D^0,X transition appears to contain some contribution from donors nearer the edge of the well. As the wells get narrower, the effects of diffusion of donors away from the positions at which they were intended may be magnified. The segregation of donors away from the intended doping location in the direction of growth by as much as 70 Å has been reported.[13,14] This effect is enhanced in the 150-Å wells in Fig. 7 where the CW-

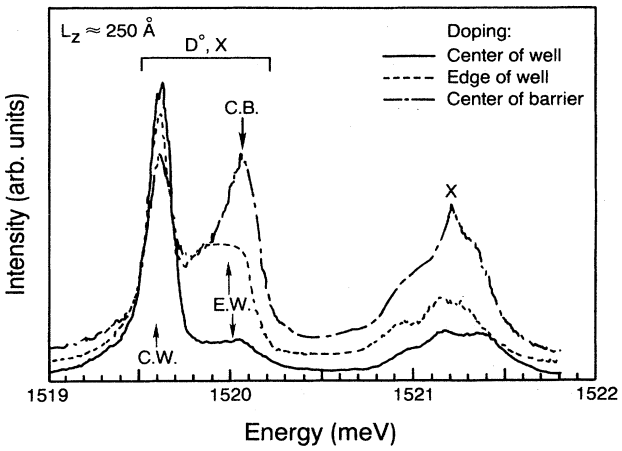

FIG. 5. RE emission spectra from CW doped (solid curve), EW doped (dashed curve), and CB doped (dot-dashed curve) for nominal 250-Å MQW's. The CW D^0,X transitions have been aligned to account for well-width variation. The energy scale on the abscissa relates to the solid curve. The EW-doped (CB-doped) spectra represented by the dashed (dot-dashed) curves have been displaced by 0.62 meV (0.51 meV) which must be subtracted to recover actual energies.

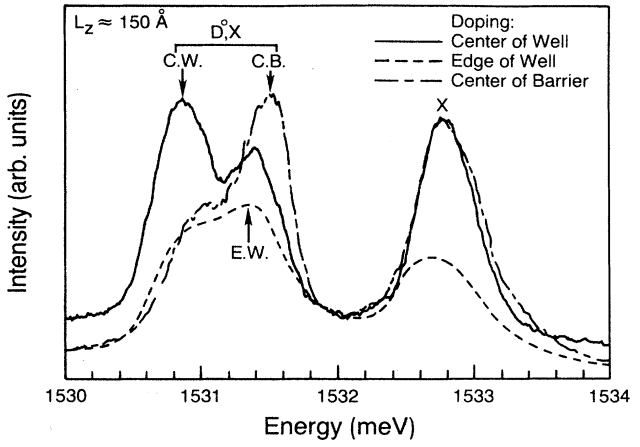

FIG. 7. RE emission spectra from center-of-the-well doped (solid curve), edge-of-the-well doped (dashed curve), and center-of-the-barrier doped (dot-dashed curve) nominal 150-Å MQW's. The CW D^0,X transitions have been aligned to account for well-width variation. The energy scale on the abscissa relates to the solid curve. The EW-doped spectrum represented by the dashed curve has been displaced by 2.53 meV which must be subtracted to recover actual energies. The CB-doped spectrum represented by the dot-dashed curve has been displaced by 0.17 meV which must be added to recover actual energies.

doped sample shows a well-defined CW D^0,X transition and, in addition, shows a well-defined but less intense EW D^0,X transition. The CB-doped sample shows a well-defined CB D^0,X transition and also shows contributions from CW D^0,X transitions. The CW D^0,X transitions most likely result from the CW donors becoming neutralized since they have the greatest binding energy. The neutral donors can then trap excitons with the resulting CW D^0,X transition being observed. It is clear from Figs. 4–7 that the donor doping positions can be clearly tracked as the well size changes from 350 to 150 Å. As one proceeds in doping to still narrower wells, the transition lines broaden and resolution of the D^0,X transitions from the three doping positions in the sample decreases. Only one emission peak is resolved for each doping position (not shown). The accuracy in determining the energy of the transitions, therefore, is not as precise as it is for the wider wells.

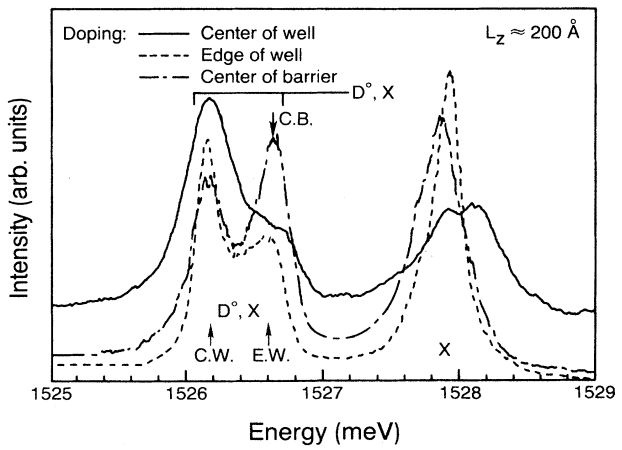

FIG. 6. RE emission spectra from CW doped (solid curve), EW doped (dashed curve), and CB doped (dot-dashed curve) nominal 200-Å MQW's. The CW D^0,X transitions have been aligned to account for well-width variation. The energy scale on the abscissa relates to the solid curve. The EW-doped (CB-doped) spectra represented by the dashed (dot-dashed) curves have been displaced by 3.86 meV (3.57 meV), which must be subtracted to recover actual energies.

It is furthermore noted that both the CW and CB D^0,X transitions are generally narrower than the EW D^0,X transitions. CW D^0,X complexes have emission lines as narrow as 0.15 meV full width at half maximum, which is more than an order of magnitude narrower than the lines observed by Nomura *et al.*[3] The EW and CB D^0,X transitions have somewhat larger half-widths. This would be expected from the shape of the curve shown in Fig. 1 of Ref. 12 which describes the binding energy of the donor as a function of the donor position in the sample. It is seen that the slope of the curve flattens for both doping positions (CW and CB) producing a degenerate contribution for a range of these positions. This would predict narrower emission lines. On the contrary, EW donors would produce an energy spread given the same range of positions with respect to the interface, thereby producing a broader emission line.

The temperature dependence of PL emission from EW-doped MQW sample of nominal 350, 250, and 200-Å well widths is shown in Fig. 8. This is a single sample containing the three different well widths. The CW D^0,X

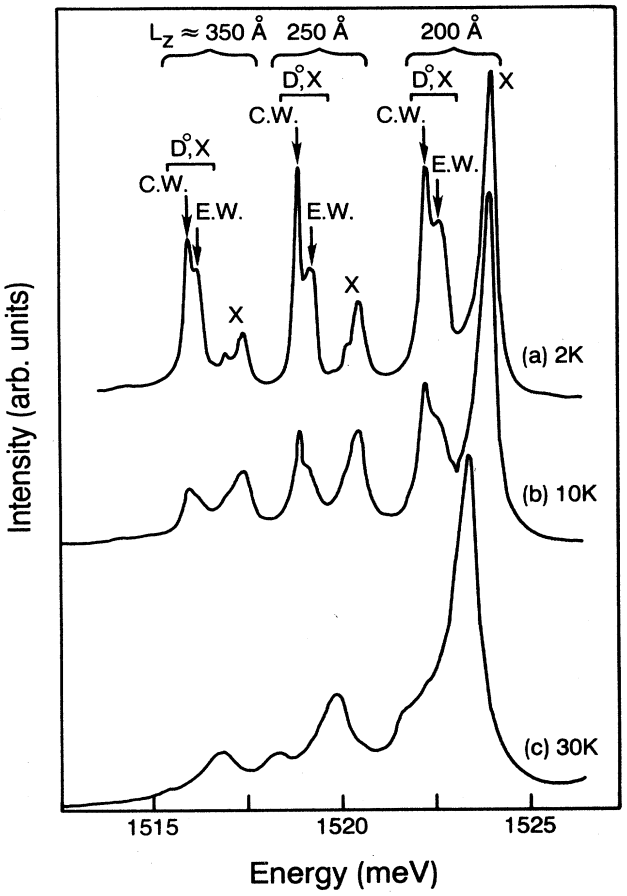

FIG. 8. Temperature-dependent PL excited with an Ar^+-ion laser from three edge-doped MQW samples of nominal 350-, 250-, and 200-Å well widths. Curves *a*, *b*, and *c* are for temperatures of 2, 10, and 30 K, respectively.

transitions have greater intensity than the EW D^0,X transitions, as was observed in Figs. 4–6. In Fig. 8(a) the relative intensities of the labeled transitions at 2 K are shown. At 10 K shown in Fig. 8(b) and 30 K in Fig. 8(c), it is noted that intensities of the various D^0,X transitions fall off much faster with temperature than the intensities of the HHFE transitions. The intensities of the transitions for a given temperature are relative, whereas the intensities for the same transitions at different temperatures are arbitrary. The intensities of the D^0,X transitions would also be expected to fall off much faster with increasing temperature than free-hole to bound-electron transitions, especially for CW donors. In Fig. 8(c), the D^0,X transition intensities have almost vanished while the HHFE transitions are still plainly visible, demonstrating that the D^0,X transitions are properly identified.

DISCUSSION AND CONCLUSIONS

In Fig. 9, we display the variations of the binding energies of excitons to neutral donors located at the center and edges of the wells and at the center of the barriers as a function of the HHFE exciton emission energy and the well size. The well sizes are calculated from the measured HHFE emission energies using the theoretical results of Greene *et al.*[9] Included in Fig. 9 (indicated by ⊗) is also the CW D^0,X transition energy for a single QW of 300 Å as reported by Nomura *et al.*[3] The solid lines drawn through the experimental points are merely aids to the eye and are not the result of any calculation. It is clear from Fig. 9 that the binding energies of D^0,X complexes increase as the well size is reduced for all three doping situations. However, for well width of about 100 Å, they tend to reach their respective maximum values and then decrease as the well widths are further reduced. The binding energies of HHFE (Ref. 9) and of isolated donors[10] are known to increase as the well size is reduced and reach their respective maximum values in basic quantum-well systems at values less than about 50 Å. It is not clear why the binding energy of excitons to neutral donors reaches a maximum at well sizes of about 100 Å. We observe that our measured values of the binding energies of excitons to neutral donors located at the center of the wells as a function of well size are consistently larger than those calculated by Kleinman.[5] For a 150-Å quantum well, for instance, we measure for the binding energy a value of about 1.95 meV compared to the theoretical value of 1.43 meV. A similar situation exists for other values of the well size. This disagreement between theory and experiment is not surprising because of the approximations made in the calculation[5] of the total ground-state energy of the (D^0,X) complex using a variational approach which thus obtains an upper bound for its value. This quantity is subtracted from the sum of the ground-state energies of a free heavy-hole exciton and an isolated CW donor to obtain the binding energy of the exciton bound to a neutral donor. Since the degree of accuracy with which the binding energies of free excitons and donors is determined is not the same as that for the (D^0,X) complex, disagreement between theory and experiment of 0.5 meV is not unreasonable. For well sizes larger than about 230 Å, calculated[5] values of the binding energies are smaller than the experimentally determined value (1.2 meV) for bulk GaAs, a result contrary to physical expectations. However, for the range of the well sizes studied, our values of the binding energies are always larger than 1.2 meV, the bulk value. The calculations include an assumption of potential barriers which predicts a monotonic increase in the binding energy of excitons to neutral donors as the well size is reduced. This disagrees with the observations summarized in Fig. 9 which do not monotonically increase as the well size decreases. The binding energy of excitons in quantum wells does not monotonically increase as the well size decreases, nor does the binding energy of donors increase monotonically as the well size decreases. It is not surprising, therefore, that the binding energy of excitons to donors in quantum wells does not monotonically increase as the well size decreases.

We now compare our results to other experimental observations involving excitons bound to donors in MQW's. Nomura *et al.*[3] have made photoluminescence measurements on MBE-grown Si-doped $GaAs/Al_{0.22}Ga_{0.78}As$ single quantum wells at 1.8, 4.2, and 77 K. In addition to

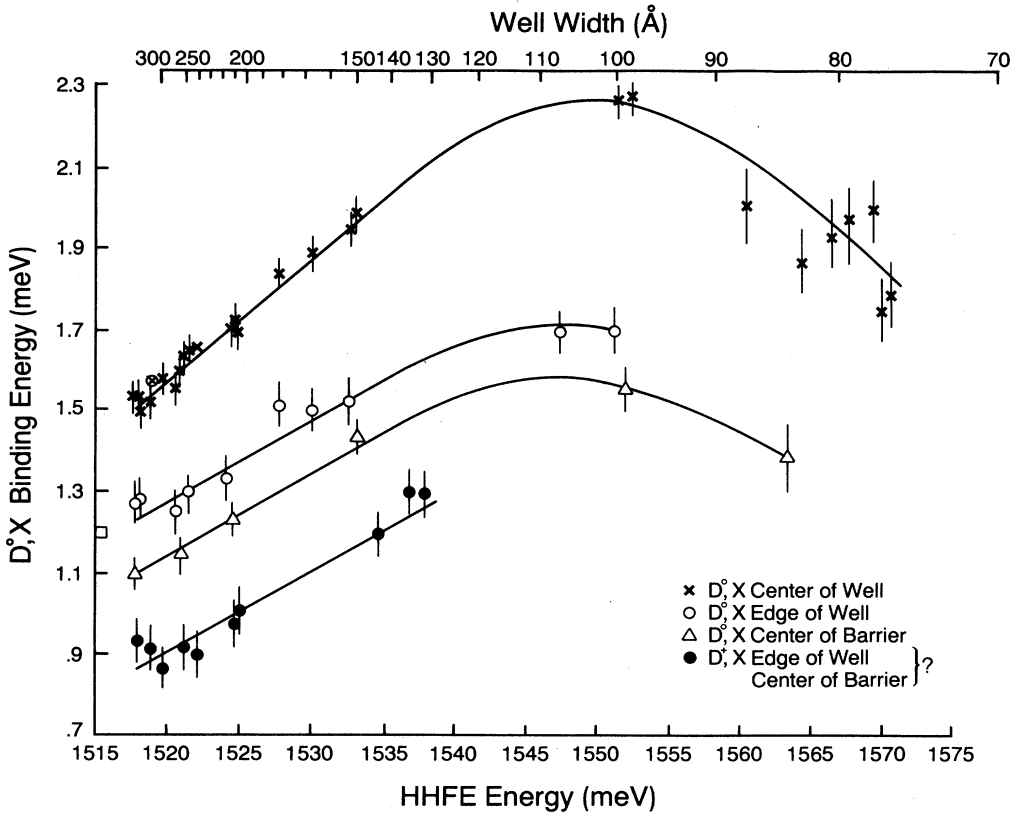

FIG. 9. Binding energies of excitons to neutral donors located at CW (indicated by ×), EW (○), and CB (△) as a function of HHFE energy. A scaling containing the calculated well sizes corresponding to HHFE energies is included at the top of the figure. Included are data (indicated by ●) speculated to be the D^+,X binding energy of excitons to EW and/or CB ionized donors as a function of HHFE energy. The binding energy of D^0,X in bulk GaAs is indicated by □ and the 300-Å-well data of Nomura *et al.* (Ref. 3) by ⊗.

the HHFE transition, they observed a transition on the lower-energy side which they associate with an exciton bound to a neutral donor located at the center of the well. They studied the behavior of this transition as a function of excitation intensity and temperature and find that it is consistent with their identification. They also investigated the variation of the exciton binding energy to the donor as a function of well size in samples doped with Si at $2\times10^{16}/\text{cm}^3$ at the well centers for well sizes from 74 to 300 Å. Their values of the binding energies are consistently smaller than those we observe except for the 300-Å well which is similar. The typical linewidth of the D^0,X peak they observe is about 2.4 meV, which is almost an order of magnitude larger than ours. It is not clear why their values of the binding energies are so much lower than ours, though it is more difficult to determine the exact energy of a transition when it is relatively broad. Their results, however, are in agreement with those calculated by Kleinman.[5]

Recently, Charbonneau *et al.*[6] have reported the observance of a peak on the lower-energy side of the HHFE transition in a 180-Å GaAs-$Al_xGa_{1-x}As$ MQW structure using PL spectroscopy. This structure was grown by MBE using growth interruption at the interfaces. They performed excitation density dependence of the luminescent intensity and time-resolved PL measurements and associated this peak with an exciton bound to a neutral donor. The binding energy of the exciton to the neutral donor they determined is about 1.25 meV, which is lower than our value, but compares well with the calculated value of Kleinman.[5] They, however, do not study the variation of the binding energy with different well sizes.

Recently, Liu *et al.*[4] have reported the observation of several peaks on the lower-energy side of the HHFE transition in inhomogeneously Si-doped MQW structures varying in well size from 80 to 375 Å using PL spectroscopy. Two sets of samples were grown using MBE: one set was doped at the centers of the wells and the other at the edges with a Si concentration of about $1\times10^{16}/\text{cm}^3$. In the center-doped samples four peaks were observed. The highest-energy peak was identified as due to a HHFE transition and the other three peaks, referred to as (ii), (iii), and (iv), were associated with excitons bound to neutral donors (CW), excitons bound to ionized donors (CW), and free heavy-hole to neutral-donor (CW) transitions, respectively. The binding energy of an exciton to a neutral donor versus well size was found to agree well with that calculated by Kleinman,[5] but these values are again considerably lower than those determined by us. The temperature dependence of the donor-related peaks is some-

what surprising since only peak (iii) is still observed at 30 K. As the temperature of the sample is raised the exciton-ionized donor complex is the first to dissociate into a neutral donor and a free hole since the binding energy of the hole to the neutral donor is very small (fraction of a meV). If one alternatively identities peak (iii) as an exciton bound to a neutral donor, then the values of the exciton binding energies to neutral donors are in better agreement with our values. It is also not clear why peak (iv) disappeared at 30 K as this temperature is too low to ionize significant number of neutral donors. Also, Liu *et al.*[4] did not observe transitions associated with excitons bound to edge donors in their edge-doped quantum wells, in contrast to our observations.

The transitions marked by ●'s in Fig. 9 do not have a clear identification. These transitions occur in undoped samples (mildly p type) where the donors are expected to be ionized. CW D^+,X may be eliminated as a candidate since it is expected to fall on the low-energy side of CW D^0,X. Likewise, EW and CB D^0,X have been shown to have greater binding energies. We may thus speculate on the remaining possibilities. A weak CW D^0,X transition is observed in undoped samples as shown in Figs. 2 and 3, indicating that some CW donors are photoneutralized at this pump power. The EW and CB donors are less likely to be neutralized than the CW donors due to their respective reduced binding energies. Therefore, this transition is consistent with the ionized-donor bound-exciton transitions D^+,X associated with donors at the center of the barrier and/or edge of the well. Temperature-dependence measurements of these transitions confirm that they result from bound excitons. There, of course, remain other complexes which are possible alternatives.

In conclusion, we have determined the binding energy of excitons to neutral donors in quantum wells and have observed changes when the dopant was located in the center of the well, at the edge of the well, or in the center of the barrier. This was investigated as a function of well size from 75 to 350 Å, which yielded an increase in binding energy as the well size was reduced to about 100 Å, after which the binding energy decreased. This behavior was compared to existing theoretical descriptions. The increase in binding energy as well size is reduced is due to the increase in donor as well as exciton binding energy and consequently that of D^0,X. Below 100 Å the binding energy decreases. An additional transition is tentatively identified as due to excitons bound to EW and/or CB ionized donors (D^+,X).

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