Free-to-bound and light- and heavy-hole bound-exciton transitions in $Al_xGa_{1-x}As$-GaAs multiple quantum wells

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Observation of several optical transitions associated with the recombination of a free heavy hole with a neutral donor (D^0,HH) and with heavy- and light-hole excitons bound to shallow donors and acceptors in a GaAs-$Al_xGa_{1-x}As$ multiple-quantum-well (MQW) structure with a nominal well width of 350 Å is reported. These transitions are identified using high-resolution photoluminescence and photoluminescence excitation spectroscopies at 2 K. Temperature-dependent (2–20 K) data are also analyzed. To further aid in identifying these transitions, their behavior in the presence of a magnetic field applied parallel to the plane of the MQW structure is investigated. The measured diamagnetic shift agrees well with the calculated diamagnetic shift for the same size well.

INTRODUCTION

In this paper we report the observation of several optical transitions associated with the recombination of a free heavy hole with a neutral donor (D^0, HH) and of heavy- and light-hole excitons bound to shallow donors and acceptors in a GaAs-$Al_xGa_{1-x}As$ multi-quantum-well (MQW) structure with a nominal well width of 350 Å. These transitions are identified using high-resolution photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopies at 2 K, along with temperature-dependent PL. In addition, their behavior in the presence of a magnetic field applied parallel to the plane of the MQW structure is investigated. Shanabrook and Comas[1] were the first to report the observation of a (D^0,HH) transition in GaAs-$Al_xGa_{1-x}As$ MQW structures using PL spectroscopy. Recently, Liu *et al.*[2] performed a systematic PL study of confined donors in MQW structures and observed a transition at lower energy than that observed by Shanabrook and Comas.[1] They suggested that this transition is associated with (D^0,HH) and ascribed the transition observed by Shanabrook and Comas[1] to a heavy-hole exciton bound to an ionized donor (D^+,HHX). The behavior of these transitions in the presence of a magnetic field, however, was not studied to further aid in their identification.

We also report the observation of several other transitions observed in PL and PLE, all of which occur at energies above that of the heavy-hole free exciton (HHFE), except the transition involving a light-hole exciton bound to a neutral acceptor (A^0,LHX). These transitions are associated with (A^0,LHX), a light-hole exciton bound to a neutral donor (D^0,LHX), the 2*s* state of HHFE, and the first excited state of the (A^0,LHX) complex. Some of these identifications are made by comparison with theoretical calculations of transition energies and others from diamagnetic shift measurements for a magnetic field that is applied perpendicular to the growth direction.

EXPERIMENTAL DETAILS

The sample studied was a GaAs-$Al_xGa_{1-x}As$ MQW structure grown by molecular-beam epitaxy (MBE) on a n^+ GaAs substrate using a Varian Gen II MBE. The substrate was (nominally) misoriented 6° from (100) toward (111)Ga. A Perkin-Elmer cracker cell was used to produce dimeric arsenic as the arsenic growth species. The GaAs growth rate was 0.7 monolayer/sec for GaAs, and the x value was 0.3. The As/Ga beam pressure ratio was 14, which gave an As-stabilized (2×4) surface reconstruction during GaAs growth. The buffer-layer sequence consisted of 100 nm GaAs, followed by a 10-cycle (30-Å $Al_xGa_{1-x}As$–30-Å GaAs) superlattice, followed by 100 nm $Al_xGa_{1-x}As$, followed by 100 nm GaAs, followed by another 10-cycle (30-Å $Al_xGa_{1-x}As$–30-Å GaAs) superlattice. Grown on top of the buffer layer were 30 cycles of nominally 350-Å-wide GaAs quantum wells with 100-Å $Al_xGa_{1-x}As$ barriers. The center of each quantum well was δ doped with 3×10^{9} cm^{-2} Be acceptors per well. The substrate temperature during growth was 850 K for all layers except the 100-nm $Al_xGa_{1-x}As$ layer for which the substrate temperature was 920 K.

In all cases photoluminescence was excited with a tunable dye laser using styryl-9 dye, which was pumped by an Ar^{+}-ion laser. The dye-laser pump power was 50 mW/cm^2. A magnetic field directed along the (011) axis was used to observe diamagnetic shifts of the PL transitions. The PLE measurements were made with the same dye laser at the same pump power. The high-resolution PL and PLE measurements were made at 2 K with the sample immersed in liquid He. The spectra were analyzed with a high-resolution 4-m spectrometer equipped with an RCA C31034A photomultiplier tube for detection.

RESULTS AND DISCUSSION

The low-temperature (2 K) PL spectra of the 350-Å MQW sample obtained using an excitation energy of 1.5230 eV are displayed in Fig. 1. The solid curve shows the spectra in a zero magnetic field and the dashed curve in a magnetic field of 36 kG, which was applied perpendicular to the growth direction. At zero magnetic field the transition at 1.5160 eV is ascribed to the collapse of a heavy-hole exciton bound to a neutral acceptor (A^0,HHX). This transition has been observed previously.[3] The transition at 1.5172 eV is tentatively assigned to the recombination of a free heavy hole with a neutral donor located at the well center (D^0,HH); see below for the rationale for this assignment. The small peak at 1.5180 eV is due to the collapse of a heavy-hole exciton bound to a neutral donor at the well center.[4] It is suggested that the transition at 1.5190 eV is due to the radiative collapse of a light-hole exciton bound to a neutral acceptor (A^0,LHX). And finally, the transition at 1.5195 eV is due to the recombination of a heavy-hole free exciton in the ground state (HHFE) and has been observed by a number of groups.

The behavior of these transitions in the presence of a magnetic field is consistent with the foregoing assignments. For instance, the shift in energy with magnetic field (i.e., the diamagnetic shift) of the (A^0,HHX) transition at 36 kG is observed to be 0.7 meV, which is about the same as that of the HHFE. This is not unexpected, since the binding energy of the heavy-hole exciton to a neutral acceptor is rather small (3.5 meV). Similarly, the diamagnetic shift of the (A^0,LHX) transition at 36 kG is found to be 0.3 meV, which is about the same as that of the light-hole free exciton.[5] This and the fact that this peak is located at about 3.3 meV below the LHFE transition suggest that this transition is associated with a light-hole exciton bound to a neutral acceptor. It should be noted that this complex is a rather complicated system. The wave function of the neutral acceptor consists of a linear combination of light- and heavy-hole wave functions. Similarly, the wave function of the light-hole exciton consists of a somewhat different linear combination of light- and heavy-hole wave functions with emphasis on the light-hole character. When a light-hole exciton combines with a neutral acceptor to form a (A^0,LHX) complex, the two holes are indistinguishable and the complex is associated predominantly with the light-hole subband. A similar situation exists for the complex consisting of a heavy-hole exciton bound to a neutral acceptor (A^0,HHX). Calculations of the dissociation energies for such complexes represent a rather formidable task.

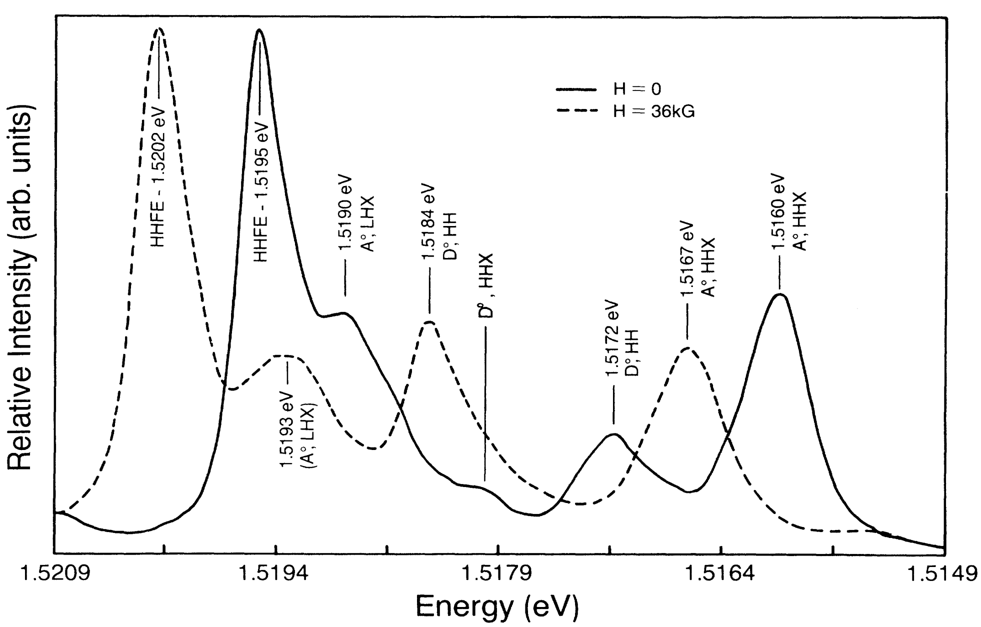

FIG. 1. PL spectra obtained at 2 K showing the optical transitions from the 350-Å MQW structure in a zero magnetic field (solid line) and in a magnetic field of 36 kG (dashed line).

As mentioned earlier, the transition at 1.5172 eV observed at zero magnetic field is tentatively assigned to the recombination of a free heavy hole with a neutral donor located at the well center (D^0,HH). This assignment is based on two criteria. First, the observed transition energy agrees very well with the calculated value obtained from the binding energy of a donor located at the well center[6] and the heavy-hole subband energy in a 350-Å well. Second, the observed diamagnetic shift of this transition at 36 kG is 1.2 meV, which is considerably larger than that observed for excitonic transitions. It is therefore highly unlikely that this transition is excitonic in nature.

The diamagnetic shift observed for the (D^0,HH) transition can be separated into two contributions: one associated with the heavy hole and one with the neutral donor. Greene and Bajaj[7] calculated the diamagnetic shift of a neutral donor in a quantum well as a function of well size and magnetic field applied perpendicular to the growth direction. For a 350-Å well at 36 kG, they find a diamagnetic shift of 0.70 meV. The difference between the observed value (1.2 meV) and this calculated value, namely, 0.5 meV, is due to the ground-state energy of a free heavy hole in the presence of a magnetic field. Recently, Platero and Altarelli[8] have calculated the valence-band sublevels in quantum wells in the presence of a magnetic field applied parallel to the plane of the quantum wells. They use an effective-mass approximation and extend the Luttinger oscillator formalism to noninteger quantum numbers. The holes perform cyclotron orbits in a plane intersecting both the well and the barrier; the quantum-well potential breaks the translational invariance and removes the degeneracy of the Landau levels producing a band. Thus the energies of the Landau levels depend on the center of the orbit. For well sizes considerably larger than the diameter of the cyclotron orbit, the holes near the center of the well do not "see" the barriers and behave almost as they do in bulk material. Platero and Altarelli[8] calculate the ground-state energy of a heavy hole near the center of a 350-Å GaAs quantum well in a magnetic field of 100 kG and find it to be 2.3 meV. Using a linear extrapolation, we derive this quantity to be 0.8 meV at 36 kG. This value is somewhat larger than the measured value of 0.5 meV but is still in good agreement. The values of the Luttinger parameters for GaAs, γ_1 and γ_2, used in their calculations[8] are 6.85 and 1.83, respectively. Further experimental evidence justifying the assignment of the transition at 1.5172 eV to (D^0,HH) comes from temperature-dependent PL data. The temperature dependence of the PL emission from the 350-Å MQW structure is displayed in Fig. 2 for temperatures varying from 2 to 20 K. The intensities within a given temperature run are relative, while the intensities between the different temperature runs are arbitrary. Although not indicated here, the overall emission intensity was observed to decrease as the temperature was increased. It is clear that the intensity of the (A^0,X) peak decreases with temperature more rapidly than the (D^0,HH) peak, as expected, since the binding energy of the exciton to the acceptor is less than the binding energy of the donor. These data support the magnetic-field data in ruling out a bound-exciton transition as the source of the emission peak at 1.5172 eV.

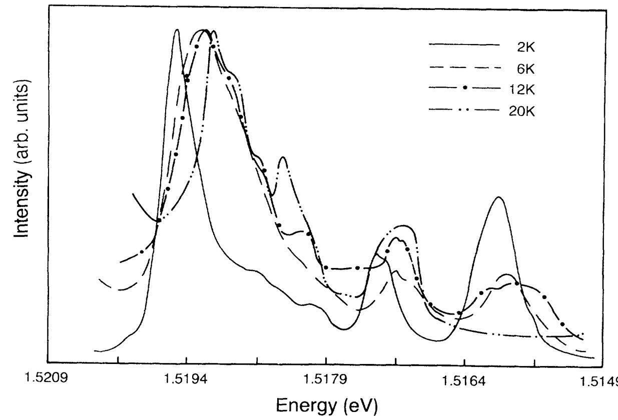

FIG. 2. Temperature-dependent PL of the 350-Å MQW structure. The inset identifies the temperature corresponding to each curve.

The PLE spectra of this sample are displayed in Fig. 3. The solid curve, the dashed curve, and the dot-dashed curve are obtained by positioning the detector at the HHFE, (D^0,HH), and (A^0,LHX) transition energies, respectively. When the detector is positioned on the HHFE transition, we observe the usual HHFE transition at 1.5195 eV. At 1.5209 eV, we observe a transition that we associate with the radiative recombination of a light-hole exciton bound to a neutral donor located at the center of the well (D^0,LHX). This tentative identification is based on two observations: (i) There are no predicted intrinsic transitions that occur between the HHFE and the LHFE in well sizes for which the $n=2$ state of the HHFE falls on the high-energy side of the LHFE (a 350-Å well fits this case), and (ii) the energy separation between this and the LHFE transition is 1.4 meV and nearly identical to the 1.5-meV separation between the (D^0,HHX) and HHFE transitions (shown in Fig. 1). The transition at 1.5223 eV is assigned to the LHFE based on our previous work.[5] The transitions observed at 1.5241, 1.5255, and 1.5264 eV are somewhat more difficult to identify. The transition at 1.5241 eV is 4.6 meV higher in energy than the HHFE transition at 1.5195 eV. This energy difference compares very well with the energy difference between the 1s and 2s states of a heavy-hole free exciton as calculated by Greene *et al.*[9] We therefore assign this transition at 1.5241 eV to the 2s state of HHFE. The exact identification of the transitions at 1.5255 and 1.5264 eV is not clear to us at this time, although the transitions fall in the region where the C1-H2 excitonic transition, associated with the first conduction subband and the second heavy-hole subband, is expected to occur.

When the detector is positioned at the (D^0,HH) transition energy, the spectrum does not show any pronounced resonances, as expected, since excitonic transitions are not well coupled to this decay channel. However, when the detector is held on the (A^0,LHX) transition, the spec-

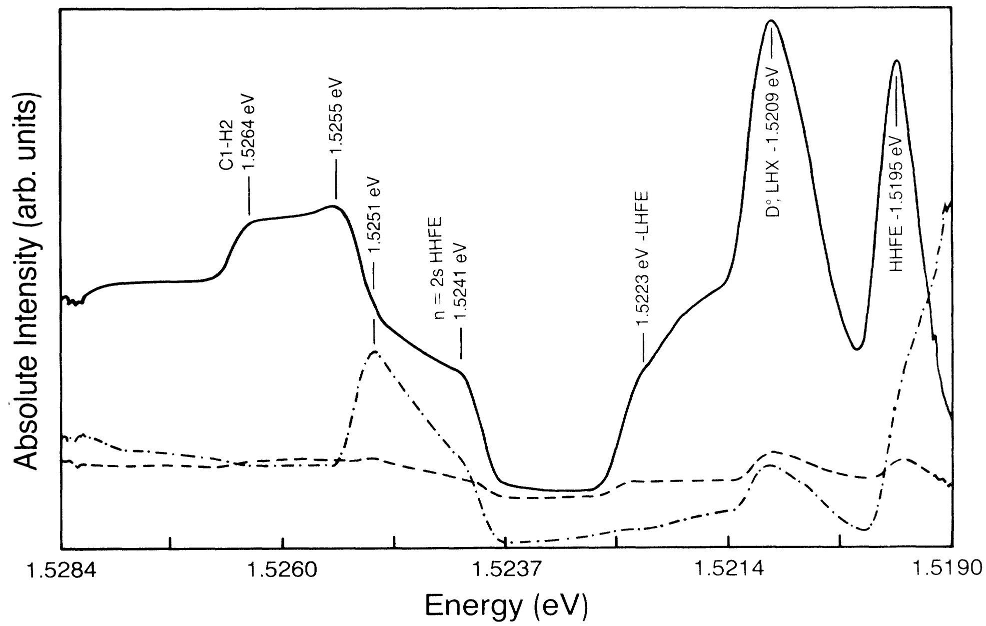

FIG. 3. PLE spectra of the 350-Å MQW structure. The solid curve, the dashed curve, and the double-dot-dashed curves are obtained by positioning the detector at the HHFE, (D^0,HH), and (A^0,LHX) transition energies, respectively.

trum shows two peaks, one at 1.5209 eV corresponding to (D^0,LHX) and a second at 1.5251 eV, which may be due to the first excited state of the (A^0,LHX) complex. The exact mechanism by which the formation of (D^0,LHX) leads to (A^0,LHX) collapse is unknown. One mechanism would be for the (D^0,LHX) complex to decay with the resulting photon directly creating the (A^0,LHX) complex. Another possible mechanism is for donors and acceptors that are spatially close together: the donor could trap the LHX exciton with the resulting wave function overlapping the acceptor; subsequently, the exciton could transfer to the acceptor site where the energy is lowest.

In Fig. 4, we display PL spectra of this sample as excited by different energies of excitation. When resonantly exciting HHFE at 1.5195 eV (solid line), we observe three transitions that we assign to (i) (D^0,HHX) at 1.5180 eV, (ii) (D^0,HH) (a doublet) at 1.5173 eV, and (iii) (A^0,HHX) at 1.5160 eV. The dashed curve shows the same transi-

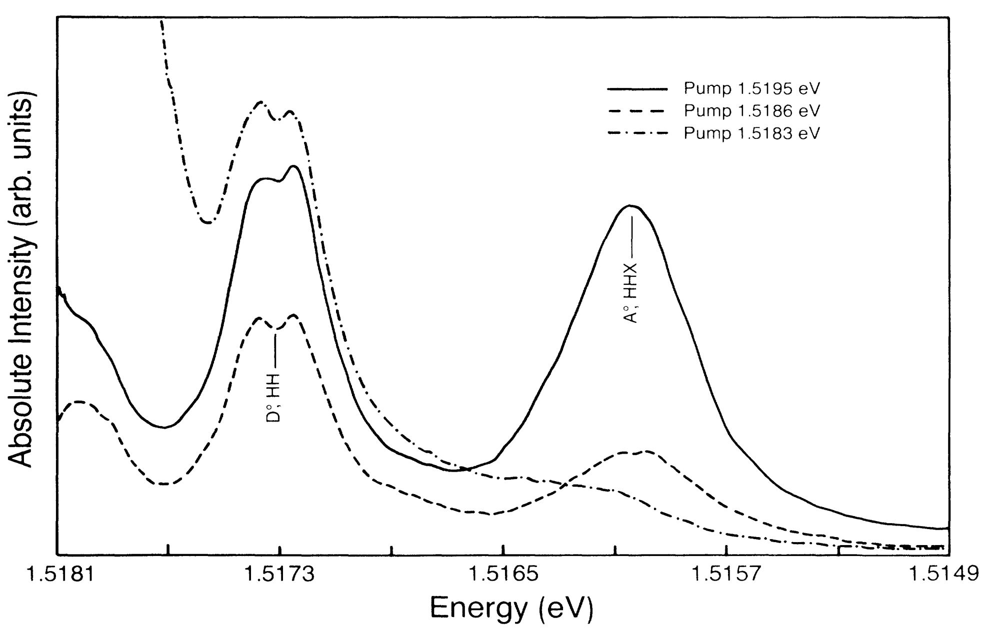

FIG. 4. PL spectra of the 350-Å MQW structure for various excitation energies ranging from the HHFE transition energy to lower energies.

tions when the excitation energy is 1.5186 eV, which is somewhat lower than the HHFE energy. With this excitation energy, the intensities of the (A^0,HHX) and (D^0,HHX) transitions are considerably reduced relative to that of the (D^0, HH) transition. The dot-dashed curve shows the relative intensities of these transitions when the excitation energy is further lowered to 1.5183 eV. In this case the (A^0,HHX) transition has almost disappeared, whereas the (D^0,HH) transition is still quite intense, as the excitation energy is very close to the (D^0,HH) transition energy of 1.5172 eV. Similarly, the (D^0,HHX) intensity is high because it is being resonantly excited. The doublet nature of the (D^0,HH) transition corresponds to a monolayer variation in well size, and inspection of Fig. 1 shows that the doublet is present in PL but is not fully resolved.

It is not unusual to observe monolayer fluctuations in well size for structures such as those being discussed that were grown as described. The nominal substrate misorientation of 6° from (100) toward (111)Ga allows the growth of sharp Al_xGaAs_{1-x}-GaAs interfaces at substrate temperatures, which are lower than those that are optimal for on-axis (100) growth.[10] Additionally, the relatively low As_2 flux used leads to high cation surface mobility[11] during growth and, together with the relatively low growth rate, favors the formation of long, flat terraces. It should be noted that the misorientation of 6° from (100) results in a built-in steplike surface structure along the (111)Ga direction with an average terrace size of 27 Å; the long, flat terraces, which are a result of the growth conditions used here, are superimposed on this steplike surface structure.

We also find that resonant excitation of the LHFE transition does not produce detectable emission due to the (A^0,LHX) transition. This may be due to the small Bohr radius of the acceptor and the limited exciton mobility, which results in a small probability of an exciton encountering and binding to an acceptor to form the (A^0,LHX) complex, as suggested by Miller *et al.*[3] Miller *et al.* observed the (A^0,HHX) complex; in the case of the LHFE, there is another recombination path competing with (A^0,LHX) and that is the creation of HHFE's. When LHFE is created it can decay via HHFE, (D^0, LHX), and (A^0,LHX), each of which may subsequently radiatively recombine. The least likely of these processes would be decay of LHFE via (A^0,LHX) since the Bohr radius of the acceptor is small. The low intensity of (A^0,LHX) emission upon direct excitation of LHFE is not inconsistent with the observation of Miller *et al.*[3] regarding (A^0,HHX). In contrast, significant emission from (A^0,LHX) is observed when resonantly exciting the excited state of the (A^0,LHX) complex at 1.5251 eV. This is shown in Fig. 5 along with several other transitions. The solid curve, the dashed curve, and the dot-dashed curve are obtained by exciting the sample with 1.5251-, 1.5257-, and 1.5215-eV energies, respectively. When the sample is excited with 1.5251 eV, we observe four distinct transitions, associated with HHFE, (A^0,LHX), (D^0,HH), and (A^0,HHX). When the pump energy is changed, the (A^0,LHX) transition becomes much weaker with considerably less effect on the other three transitions. This phenomenon strongly supports our suggestion that the transition at 1.5251 eV is closely associated with (A^0,LHX) and is very likely to be its first excited state.

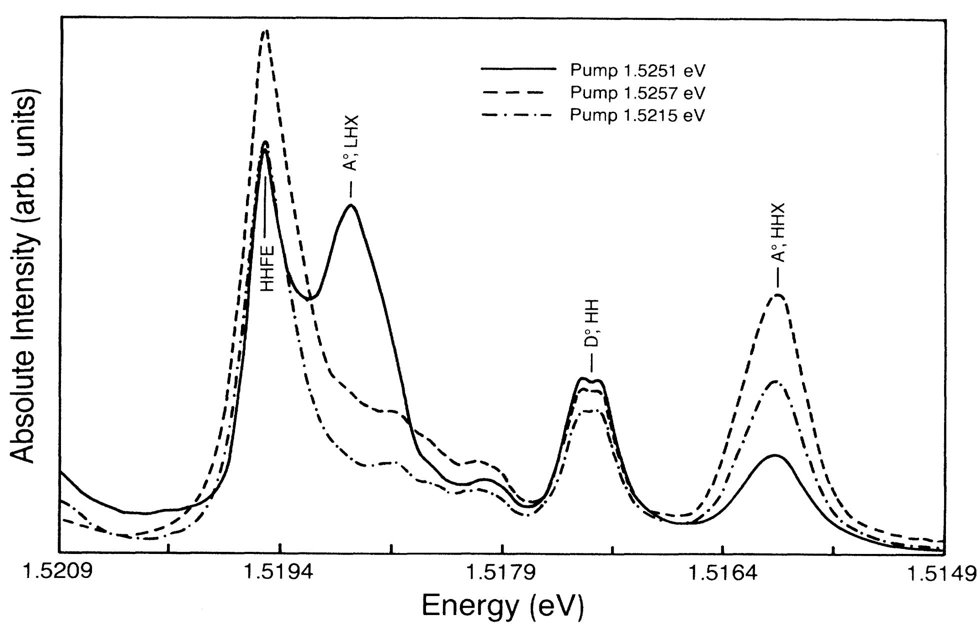

FIG. 5. The (A^0,LHX) transition is resonantly excited at an energy of 1.5251 eV; this is interpreted as an excited state of the (A^0,LHX) complex.

CONCLUSIONS

The recombination of a free heavy hole with a neutral donor located at the center of the well has been confirmed. Light-hole excitons bound to neutral donors and acceptors have been identified based on energy considerations and diamagnetic shifts. An excited state of the light-hole acceptor-bound excitation complex has been tentatively identified from selective excitation data. Selective excitation spectra also disclosed the 2*s* state of the HHFE determined from previously calculated energies. The exact identity of PLE transitions observed at 1.5255 and 1.5264 eV is not clear at this time.

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[1]B. V. Shanabrook and J. Comas, Surf. Sci. **142**, 504 (1984).

[2]X. Liu, A. Petrou, B. D. McCombe, J. Ralston, and G. Wicks, Phys. Rev. B **38**, 8522 (1988).

[3]R. C. Miller, A. C. Gossard, W. T. Tsang, and O. Munteanu, Solid State Commun. **43**, 519 (1982).

[4]D. C. Reynolds, C. E. Leak, K. K. Bajaj, C. E. Stutz, R. L. Jones, K. R. Evans, P. W. Yu, and W. M. Theis (unpublished).

[5]K. K. Bajaj, D. C. Reynolds, C. W. Litton, R. L. Greene, P. W. Yu, C. K. Peng, and H. Morkoc, in *Gallium Arsenide and Related Compounds,* Proceedings of the Gallium Arsenide and Related Compounds Conderence, edited by W. T. Londley, IOP Conf. Proc. No. 83 (Institute of Physics, Bristol, 1987), p. 325.

[6]R. L. Greene and K. K. Bajaj, Solid State Commun. **45**, 825 (1983).

[7]R. L. Greene and K. K. Bajaj, Phys. Rev. B **37**, 4604 (1988).

[8]G. Platero and M. Altarelli, Phys. Rev. B **39**, 3758 (1989).

[9]R. L. Greene, K. K. Bajaj, and D. E. Phelps, Phys. Rev. B **29**, 1807 (1984).

[10]R. K. Tsui, G. D. Kramer, J. A. Curless, and M. S. Peffley, Appl. Phys. Lett. **48**, 940 (1986).

[11]A. Madhukar and S. V. Ghaisas, Appl. Phys. Lett. **47**, 247 (1985).