Photoluminescence and reflectance studies of negatively charged excitons in GaAs/$Al_{0.3}Ga_{0.7}As$ quantum-well structures

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We report the results of a systematic photoluminescence and reflectance study of negatively charged excitons (X^-) in several GaAs/$Al_xGa_{1-x}As$ quantum well structures. Samples are either doped *n*-type in the wells or not intentionally doped, and thus the appearance of X^- (present in modulation doped samples) is not expected. The combination of the two spectroscopies allowed us to explore the possible mechanisms responsible for the formation of the X^- complex. In all cases the X^- signature is related to excess electrons in the wells. These results provide positive evidence that the original identification of the X^- photoluminescence feature is correct.

I. INTRODUCTION

The electron-hole hydrogenlike system, the exciton, associated with conduction and valence confinement subbands in GaAs/$Al_xGa_{1-x}As$ quantum wells has been extensively investigated during the last twenty five years. As a matter of fact it was the observation of optical absorption connected with the excitons that provided the first conclusive evidence on the formation of quantum wells.[1] The exciton is the solid-state analog of the hydrogen atom and for this reason the same atomic spectroscopic labels for the various hydrogenic states are also used to describe their solid-state counterparts. Another atomic analog has been predicted in semiconductor systems, namely that of the negatively charged hydrogen ion H^-. This is formed when a second electron is added to the electron-hole pair, which forms the exciton.[2,3] The negatively charged entity is known as the X^- or the trion. The first observation of the X^- was made in *n*-type modulation-doped CdTe/$Zn_xCd_{1-x}Te$ quantum wells using absorption spectroscopy.[4,5] An absorption feature 3.1 meV below the e_1h_1 neutral exciton (X^0) was identified as associated with the X^- singlet state on the basis of its circular polarization characteristics in the presence of a magnetic field. The X^- was also observed and studied in detail in GaAs/$Al_xGa_{1-x}As$ quantum wells using photoluminescence (PL) and electroreflectance spectroscopies.[6–10] In the presence of a magnetic field applied perpendicular to the structure's layers, the PL feature associated with the singlet ground state of X^- splits into two components, which correspond to the $\pm 3/2$ heavy-hole states. The externally applied magnetic field increases the binding energy of the second electron so that a PL feature associated with the X^- triplet excited state can be observed for $B > 2$ tesla.[7] The behavior of the X^- in a magnetic field has been theoretically studied by Stébé and coworkers.[11,12]

In recent PL studies Volkov *et al.*[13,14] have suggested that the PL feature previously identified as associated with X^- recombination is rather a barrier-neutral donor-bound exciton. In the present paper, we provide detailed evidence in favor of the prevailing interpretation. This evidence is presented in the results and discussion section. Thus, throughout this paper we continue to refer to the spectroscopic features below the neutral exciton (and not otherwise associated with impurities) as X^- related.

In this work, we have systematically investigated the appearance in the PL and reflectance spectra of features associated with the X^- from a number of GaAs/$Al_xGa_{1-x}As$ quantum-well structures in which the negatively charged exciton was not expected. These structures were doped *n* type in the GaAs wells or were not intentionally doped. A comparison of the spectra with those from a GaAs/$Al_xGa_{1-x}As$ quantum well structure-doped *n* type in the barriers (and in which the X^- is expected) has allowed us to identify two mechanisms that could be responsible for the formation of X^- in these structures. In the case of GaAs wells doped *n* type at the well edge it was found that donors diffuse into the $Al_xGa_{1-x}As$ barriers; these barrier donors ionize and their electrons are confined in the GaAs wells, where they can bind with a photoexcited neutral exciton to form the negatively charged X^- complex. These electrons can also bind weakly to their parent positive donor ions leading to neutral barrier donors.[15] This is the basis of the alternative interpretation by Volkov *et al.*[13,14] In the case of the wells doped at the center and the unintentionally doped structures the proposed mechanism is different. The excess electrons required for the formation of the X^- are generated from an unequal distribution of electrons and holes among the GaAs wells. These carriers are photogenerated in the barriers when the exciting photon energy is higher than the $Al_xGa_{1-x}As$ band gap. The basis of the present work is a comparison between PL and reflectance spectra on the same samples and the fact that reflectance is not sensitive to impurity bound excitons.[16,17]

TABLE I. Sample parameters.

Sample	Well width Å	Barrier width (Å)	Periods	Doping
1	200	400	40	Si δ-doped, 2×10^{10} cm^{-2}, barrier center
2	210	125	20	Si, $10^{16}\,cm^{-3}$, bottom $\frac{1}{3}$ of the well
3	210	125	20	Si, $10^{16}\,cm^{-3}$, top $\frac{1}{3}$ of the well
4	210	125	6	Si, $10^{16}\,cm^{-3}$, central $\frac{1}{3}$ of the well
5	200	600	20	Not intentionally doped
6	150	40	30	Si, $10^{16}\,cm^{-3}$, central $\frac{1}{3}$ of the well

II. EXPERIMENT

We have used six $GaAs/Al_{0.3}Ga_{0.7}As$ quantum well structures grown by molecular-beam epitaxy in this study. Some of their characteristics are summarized in Table I. Sample 1 is delta doped *n* type in the $Al_xGa_{1-x}As$ barriers and is used as a reference sample in the sense that the X^- is expected to form due to the presence of the confined electrons that result from the ionization of the barrier donors. Samples 2, 3, and 4 are doped with Si donors inside the GaAs wells. Sample 2(3) was doped in the ''bottom'' (''top'') one third of the well. ''Bottom'' and ''top'' are defined as regions of the GaAs wells grown immediately after and immediately before the $Al_xGa_{1-x}As$ barrier, respectively. Samples 4 and 6 were doped *n* type in the central one third of the GaAs well layers. Sample 5 was not intentionally doped. The samples were placed in a liquid helium cryostat with windows that allow optical work in the 5-300 K temperature range. The PL spectra were excited with either the 632.8 nm line from a helium-neon laser (photon energy=1.96 eV, i.e., higher than the band gap of the $Al_xGa_{1-x}As$ barriers) or a diode laser operating at 670 nm (photon energy=1.85 eV, i.e., below the band gap of the $Al_xGa_{1-x}As$ barriers). The 632.8 nm line excites electron-hole pairs in the wells and in the barrier layers. The electrons and holes excited in the barriers then drift and are captured by the wells. The presence of a weak electric field along the growth direction will result in carrier drift in opposite directions (holes in the direction of the electric field, and electrons in the direction opposite to the electric field). Thus, the possibility exists that in some wells there is an excess of electrons. Excitation with the 670 nm laser on the other hand results in the creation of electron-hole pairs inside the wells only, and thus insures that equal number of electrons and holes are confined in each GaAs well. The PL spectra were analyzed by a double monochromator equipped with a cooled photomultiplier tube and standard photon counting electronics. For reflectance work a monochromatic beam created by the combination of a broad band tungsten-halogen source and a grating spectrometer was used. The intensity of the reflected beam was synchronously detected by a photomultiplier tube operating in current mode.

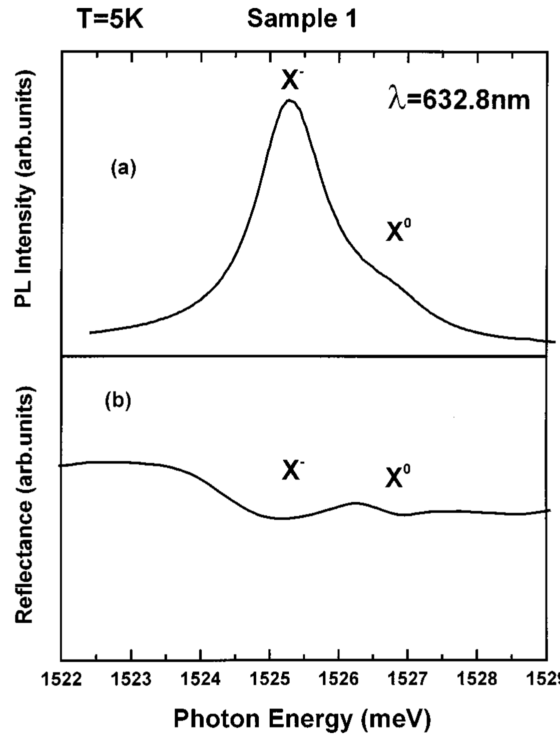

FIG. 1. (a) PL and (b) reflectance spectrum from sample 1; $T=5$ K, PL excitation wavelength=632.8 nm.

III. RESULTS AND DISCUSSION

As stated in the introduction spectral features associated with the negatively charged exciton X^- have been observed in the present work in $GaAs/Al_xGa_{1-x}As$ structures doped in the wells or unintentionally doped. In either case, the presence of X^- was not anticipated and for this reason the mechanisms involved were investigated in detail. Sample 1, on the other hand, is doped in the barriers and will be used as our reference. The rest of the presentation is organized as follows: We discuss the results from samples 2 and 3 and a mechanism responsible for the presence of the X^-. Then the results from samples 4, 5, and 6 are presented, and a possible mechanism for the creation of the X^- complex in samples 4 and 5 is proposed.

A. Reference sample

In this section we discuss the band-edge PL and reflectance spectra from reference sample 1, shown in Figs. 1(a) and 1(b), respectively. Both spectra exhibit features at 1526.6 and 1525.3 meV, which are identified as the e_1h_1 neutral exciton X^0 and the singlet state of the negatively charged exciton X_S^-, respectively. The identification is made by comparing the spectra with those reported in previous published work. The interpretation of Volkov *et al.* is discussed at the end of this section. In particular, the energy difference between the X^0 and the X^- features agrees with the value reported by Shields *et al.*[7] and in magneto-PL studies the X_s^- exhibits the characteristic initial small decrease in energy with increasing magnetic fields as discussed below.

The photoluminescence spectra from sample 1 and sample 5 have been studied as function of magnetic field *B* applied perpendicular to the structure's layers. The depen-

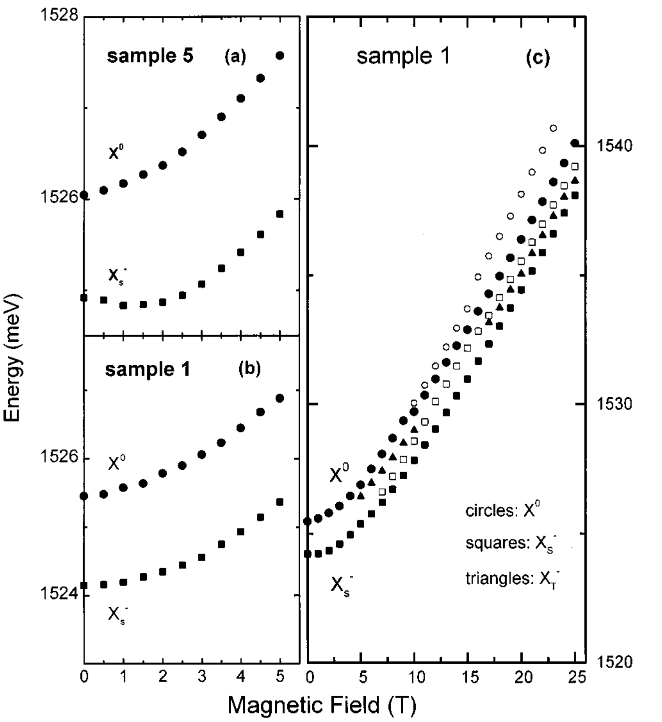

FIG. 2. Energies of the X^0, X_S^-, and X_T^- components plotted as function of magnetic field. (a) Low-field data from sample 5. (b) low-field data from sample 1. (c) High-field data from sample 1. Circles: X^0; squares: X_S^-; triangles: X_T^-.

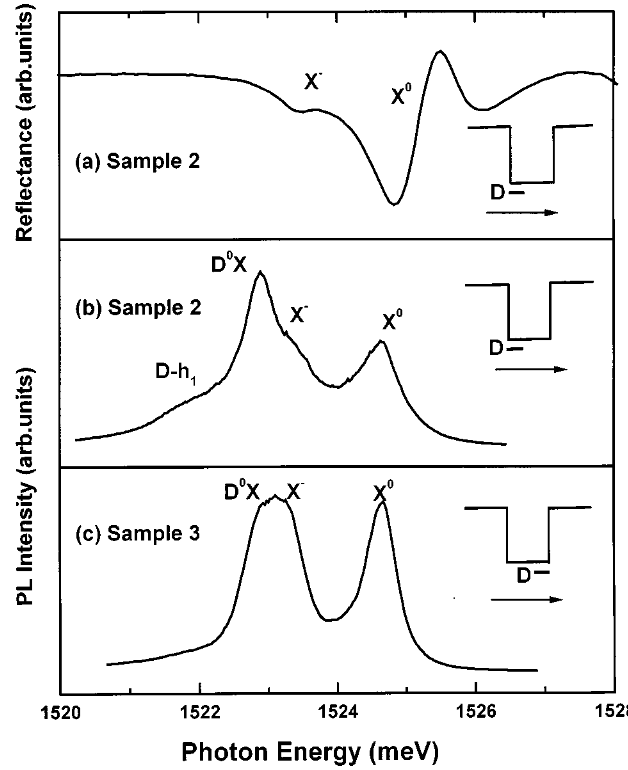

FIG. 3. (a) Reflectance spectrum from sample 2. (b) PL spectrum from sample 2. (c) PL spectrum from sample 3. $T=5$ K; PL excitation wavelength $=632.8$ nm. The insets are schematics of the conduction band. The arrows indicate the growth direction.

dence of the energies of the X^0 and X^- components as a function of B is very similar to that observed by Shields *et al.*[7] In Fig. 2, we plot the energies of the excitonic (X^0 and X^-) features as function of magnetic field. In Fig. 2(a) [2(b)] we present the low-field data from sample 5 (sample 1). The magneto-PL from sample 5 shows the characteristic initial small decrease in energy with magnetic field. The minimum in energy occurs at 1.5 T and the overall energy redshift is 0.1 meV. This behavior is the hallmark of X_S^- and allows us to distinguish the negatively charged exciton feature from features associated with bound excitons. The low-field magneto-PL data from sample 1 do not show the initial small energy decrease. This is attributed to the large electron density ($2\times10^{10}\,\mathrm{cm}^{-2}$) in this structure, which results in an increase of the line width of all excitonic PL features. The full width of half maximum is approximately 1 meV, which is 10 times the initial energy decrease of 0.1 meV observed in the undoped sample 5.

The high-field data from sample 1 are summarized in Fig. 2(c). Squares indicate the PL features associated with X_S^-, circles with X^0, and triangles with the X_T^-. The lower (upper) component of the X_S^- is due to recombination with $-\frac{3}{2}$ ($+\frac{3}{2}$) heavy holes.[7] The X_T^- that is unbound at $B=0$ T is not observed at zero-magnetic field. The application of a magnetic field results in the binding of X_T^- the lowest component of which becomes observable at 5 T. The lowest component of X_T^- (solid triangles) crosses the upper component of X_S^- (open squares) at 12 T. Up to 25 T the X_S^- lowest component (solid squares) is the ground state of the charged exciton complex.

We emphasize the importance of the reflectance spectra in distinguishing between X^- and D^0 (barrier)- X. In Fig. 1, which shows a very strong X^- PL feature, there is an equally strong reflectance feature at the same energy. In a previous work it was shown that impurity bound excitons provide no signature in the reflectance spectra.[16,17] Thus, the suggestion by Volkov *et al.* that this feature conventionally attributed to X^- is due to a barrier donor-bound exciton is not supported by our data.

Finally, since the charged excitonic complex is formed by an excess electron and an electron-hole pair created by the incident photon, it follows that the absence of an X^- signature in the reflectance spectrum suggests that there are no excess electrons confined in the wells. Thus, the comparison between the PL and reflectance spectra in the vicinity of the excitonic features becomes a powerful tool that allows us to explore the possible mechanisms involved in the creation of X^-.

B. "Top"- and "bottom"-doped samples

The results from samples 2 and 3 are presented in this subsection. In Fig. 3, the PL spectra from these structures are shown; the reflectance spectrum from sample 2 is included also [Fig. 3(a)] for comparison. The PL spectra contain features at 1524.6, 1523.3, and 1522.9 meV. These are attributed to the neutral exciton (X^0), negatively charged exciton (X^-), and donor-bound exciton (D^0X), respectively. While the first two of these features have a corresponding signature in the reflectance spectrum, the donor-bound exciton does not.[16,17] The fact that the X^- feature appears in the reflec-

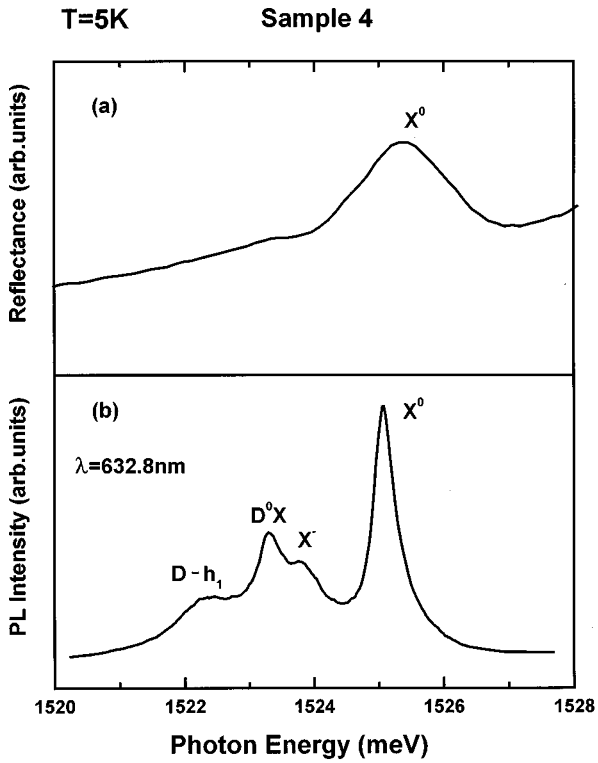

FIG. 4. (a) Reflectance spectrum from sample 4. (b) PL spectrum from sample 4, excitation wavelength = 632.8 nm.

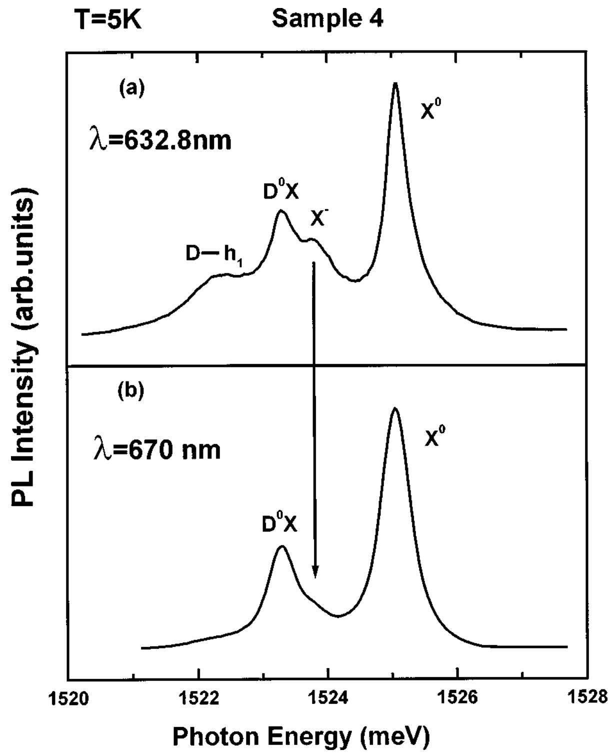

FIG. 5. PL spectra from sample 4. (a) Excitation wavelength = 632.8 nm. (b) Excitation wavelength = 670 nm.

tance spectrum indicates that the requisite excess electrons for the formation of X^- are present in the wells. The remaining electron-hole pair is generated by the incident photon. This observation provides an explanation for the appearance of X^- in samples 2 and 3 which are doped at the ''bottom'' and ''top'' one third of the well, respectively. We attribute the presence of excess electrons in the wells to donors that diffused from their original position in the well into the $Al_xGa_{1-x}As$ barriers during growth (bottom-doped sample) or have propagated along with the growth front into the barrier (top-doped sample). The energy states of such donors lie just below the bottom of the conduction band in $Al_xGa_{1-x}As$ and release their electrons into the wells. One expects growth front propagation to be more effective in sample 3 and diffusion to be the mechanism in sample 2. This difference should manifest itself in the relative intensity of the PL features associated with X^-. Indeed the intensity of the X^- PL feature in sample 3 is much stronger than the corresponding feature in sample 2 (all other conditions such as temperature, excitation wavelength, and power density being the same). The alternative explanation[13,14] in terms of neutral-barrier donor-bound excitons is not supported by the presence of a strong reflectance feature at 1523.3 meV in Fig. 3(a).

C. Well-center-doped and not-intentionally doped samples

In this section, we present the results from samples 4 and 5 and propose a mechanism to explain the formation of the negatively charged exciton in these structures. This mechanism is distinct from the mechanism at work in samples 2 and 3. The PL and reflectance spectra from sample 4 in the vicinity of the band gap are shown in Fig. 4. This sample is doped n-type in the central one third of the 210 Å wells (barrier thickness = 125 Å). The PL spectrum has four features at 1525.1, 1523.8, 1523.3, and 1522.3 meV. The identification of these features is as follows: the neutral exciton X^0, the negatively charged exciton X^-, the well-center donor-bound exciton D^0X, and the donor-to-valence-band transition $D\text{-}h_1$, respectively.[18] In contrast to samples 2 and 3 the reflectance spectrum of sample 4 does not have a significant signature of the X^- complex thus indicating that there are few electrons in the absence of above gap illumination. This is not surprising, since the donors are placed at the center $\frac{1}{3}$ of the GaAs wells from where it is unlikely that they reach in any significant numbers into the $Al_xGa_{1-x}As$ barriers by diffusion or growth-front propagation. A similar situation is observed for the undoped sample 5, in which the PL spectrum contains the X^0 and X^- features [see Fig. 6(a)] while the reflectance spectrum (not shown) contains only one feature associated with the neutral exciton X^0. The results from samples 4 and 5 can be summarized as follows: neither structure contains any significant excess electron density, and thus the X^- feature is not present (or is very weak) in the reflectance spectra. Under laser illumination with photon energy larger than the barrier band gap on the other hand, the negatively charged exciton X^- is formed as witnessed by the corresponding feature in the PL spectra.

We propose a possible mechanism which can explain the presence of X^- in samples 4 and 5 and discuss the supporting evidence. Illumination with photons whose energy is above the $Al_xGa_{1-x}As$ barrier gap results in the excitation of equal number of electrons and holes. Under the influence of an electric field with a nonvanishing component along the growth axis the electrons and holes will drift in opposite directions. The presence of these electric fields is almost unavoidable due to surface states.[19] Thus there are wells in

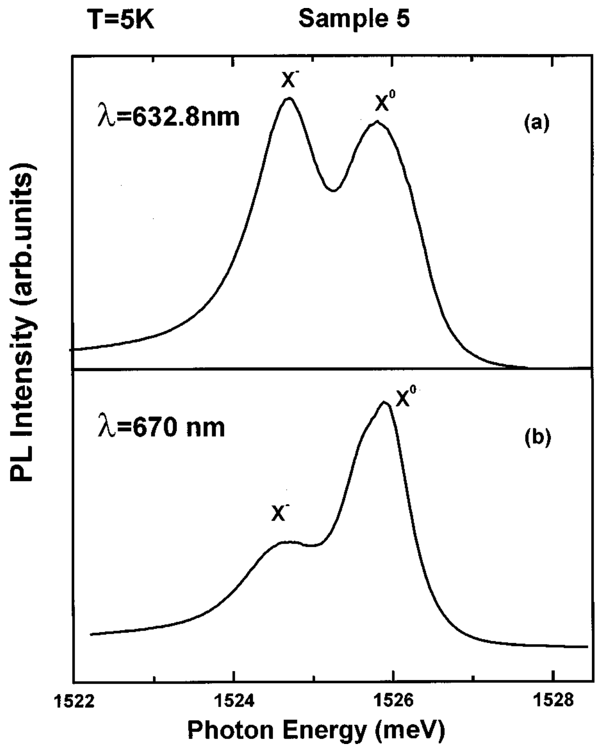

FIG. 6. PL spectra from sample 5. (a) Excitation wavelength $=632.8$ nm. (b) Excitation wavelength $=670$ nm.

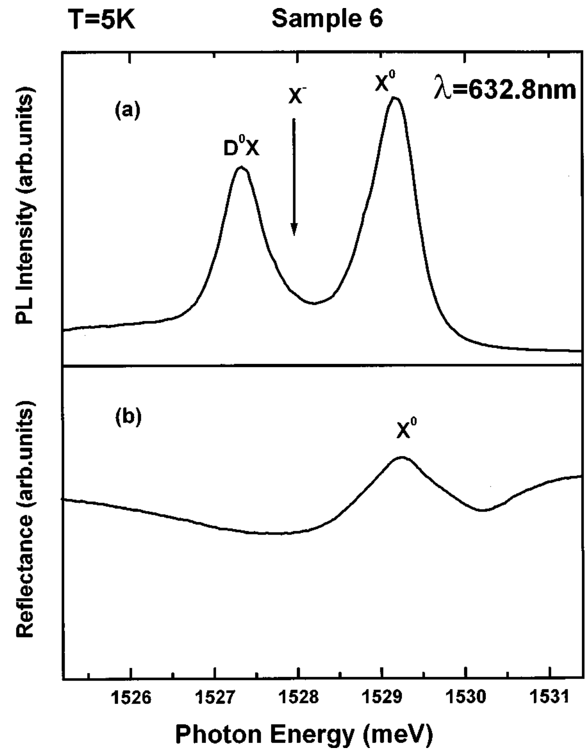

FIG. 7. (a) PL spectrum from sample 6. (b) Reflectance spectrum from sample 6. $T=5$ K, PL excitation wavelength $=632.8$ nm. The vertical arrow indicates the expected position of the X^- PL feature.

which the number of electrons will exceed the number of holes and it is in these wells that negatively charged excitons X^- can form and have a signature in the PL spectrum. The reflectance spectra are recorded in the absence of any above-gap photons, and therefore in samples 4 and 5 no excess electrons are generated in the wells. As a consequence there is no X^- feature in the reflectance spectra from these samples as was the case in samples 1, 2, and 3.

Additional supporting evidence is provided by a comparison of the PL spectra of samples 4 and 5 that were excited with photons above the barriers band gap (632.8 nm or 1.96 eV) with those excited with photons having energy below the $Al_xGa_{1-x}As$ gap (670 nm or 1.85 eV). The results are shown in Fig. 5 for sample 4 and Fig. 6 for sample 5. In both samples the relative intensity $I(X^-)/I(X^0)$ decreases significantly under excitation by the 670-nm laser. We note here that no difference in the relative intensities of the X^- and X^0 PL features from samples 1, 2, and 3 was observed when excitation was switched from 632.8 to 670 nm. Further (negative) evidence is provided by sample 6, which like sample 4 is doped n type over the central one third of the wells, but its barriers have a width of only 40 Å. The thin barriers allow tunneling of electrons from wells into which there is an excess electron population towards wells in which there is electron deficit. As a result there are equal electron and hole populations inside the wells and thus no negatively charged excitons can form. This is clearly shown in Fig. 7. The PL spectrum contains two features at 1529.2 and 1527.3 meV, which are attributed to the X^0 and D^0X recombination channels, respectively. The vertical arrow in Fig. 7(a) indicates where the X^- PL feature is expected.

IV. CONCLUSION

We have carried out a systematic study of negatively charged excitons, X^-, in several GaAs/$Al_xGa_{1-x}As$ quantum well structures using photoluminescence and reflectance spectroscopies. The X^- was detected in samples doped n type in the wells as well as in undoped samples in which no charged excitons were expected. In all cases the creation of X^- is attributed to the presence of excess electrons in the wells. We found that in samples doped at the edge, the X^- formation is due to donors that diffuse or are propagated along the growth front into the $Al_xGa_{1-x}As$ barriers. In samples doped in the well center, as well as unintentionally doped structures, an X^--associated feature appears in the PL spectra under excitation with photons having energy higher than the barrier gap. In this case, the excess electrons are provided by built-in electric fields associated with surface states. Excitation with photons having below-barrier energies leads to greatly reduced intensity in the X^- PL features.

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