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Optical properties of a high-quality (311)-oriented $GaAs/Al_{0.33}Ga_{0.67}As$ single quantum well

O. Brandt,* K. Kanamoto,* Y. Tokuda,* and N. Tsukada*
Central Research Laboratory, Mitsubishi Electric Corporation, 1-1, Tsukaguchi-honmachi 8-chome, Amagasaki, Hyogo 661, Japan

O. Wada and J. Tanimura
Materials and Electronic Devices Laboratory, Mitsubishi Electric Corporation, 1-1, Tsukaguchi-honmachi 8-chome, Amagasaki, Hyogo 661, Japan

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We analyze the photoluminescence and photoluminescence-excitation spectra of a 10-nm-thick (311)-oriented $GaAs/Al_{0.33}Ga_{0.67}As$ single quantum well of state-of-the-art optical quality. The ground-state ($1S$) heavy-hole exciton transition is coincident in emission and absorption and has a linewidth of 0.86 meV. We observe the first excited state ($2S$) of the heavy-hole as well as of the light-hole exciton, allowing accurate determination of their binding energies. Having determined, in addition, both the quantum-well width and the barrier composition by independent means, we can thus deduce from the experimental transition energies the heavy-hole and light-hole masses along the [311] direction. The measured values of 0.460 and 0.092 for the heavy-hole and light-hole masses, respectively, are consistent with results derived from refined sets of Luttinger parameters proposed recently.

As a manifestation of the band-structure anisotropy of bulk GaAs, most of the electronic properties of $GaAs/Al_xGa_{1-x}As$ quantum wells (QW's) such as, e.g., the interband transition energies and oscillator strengths, are predicted to be sensitive to the crystallographic direction of epitaxial growth.[1,2] The optical properties of non-(100)-oriented $GaAs/Al_xGa_{1-x}As$ QW's thus represent a unique tool for studying direction-dependent phenomena and to thereby gain insight into the underlying band-structure anisotropy of GaAs. However, there has been only a few reports[3–11] of non-(100)-oriented $GaAs/Al_xGa_{1-x}As$ quantum wells having the optical quality required for a meaningful study of such phenomena. It has, in fact, been stated many times that the growth of these structures is inherently more difficult than that of the standard (100)-oriented structures.[12] In contrast, it has been suggested by Sangster that the epitaxial growth of compound semiconductors should proceed particularly well on (m11) surfaces because of their high step density compared to the atomically flat (100) surface.[13] These steps, composed of (100) terraces and (111) risers, are expected to favor surface planarity and thus the formation of well-defined interfaces. In addition, if the steps expose the nonreactive single dangling bonds of the group-III atoms [(m11)A-orientation] they are also expected to minimize the incorporation of impurities.[14] In light of these considerations, the (311)A surface seems to be particularly attractive since it provides the maximum step density among all (m11) surfaces and, therefore, promises to be the optimum orientation for epitaxial growth.

In this paper we show that it is actually possible to obtain (311)-oriented $GaAs/Al_xGa_{1-x}As$ QW's of the same quality as the best available (100)-oriented ones. We concentrate on the photoluminescence (PL) and photoluminescence excitation (PLE) spectra of a 10-nm-thick (311)-$GaAs/Al_{0.33}Ga_{0.67}As$ single QW grown by solid-source molecular-beam epitaxy (MBE). The ground-state heavy-hole (hh) exciton transition is coincident in PL and PLE and has a linewidth of 0.86 meV. Pronounced $2S$ exciton features are detected in excitation as well as in emission, allowing accurate determination of the exciton binding energies. This direct measurement of the exciton binding energy, together with the knowledge of both the well width and the barrier composition [determined by high-resolution electron microscopy (HREM) and double-crystal x-ray diffractometry (HRDXD), respectively] allows us to reliably deduce the (311)-hole masses from the experimentally observed transition energies. The values obtained are inconsistent with the most commonly used sets of Luttinger parameters (LP's) but in good agreement with refined sets recently proposed.

The sample under consideration is grown by MBE on an exactly (311)A-oriented ($<0.05°$ off) Si-doped GaAs substrate. The layer sequence consists of 255 nm of GaAs, a 30-period GaAs/AlAs superlattice buffer with an individual layer thickness of 2.5 nm, 265 nm of GaAs, and a nominally 10-nm-thick GaAs QW clad by 380-nm-thick $Al_{0.33}Ga_{0.67}As$ barrier layers. An As cracker cell providing As_2 dimers was used as the As source. All temperatures mentioned are measured by an IR pyrometer calibrated to the desorption temperature of the native GaAs oxide. The growth process is monitored *in situ* by reflection high-energy electron diffraction (RHEED) along the perpendicular $[01\bar{1}]$ and $[\bar{2}33]$ azimuths using a 17-keV electron beam. The results of this investigation have motivated the choice of the growth conditions and will be reported in detail elsewhere. We point out, however, that we observe RHEED oscillations with a (311)-monolayer (ML) period (0.1705 nm) that reveal that growth takes place in a layer-by-layer fashion. In addition, for both GaAs and AlAs the use of growth interrup-

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tions at temperatures above about 580°C is found to lead to a complete recovery of the RHEED specular spot intensity towards the one of a well-annealed static surface, indicating a corresponding recovery of the growth front. To favor smooth interfaces, the substrate temperature is thus set to 600 °C, and at both interfaces growth is interrupted for 2 min. The Ga and Al deposition rates are set by RHEED intensity oscillations to 0.83 and 0.415 (311)-ML/s, respectively. The As_2/Ga ratio is set to about 5. The as-grown structure is examined by HRDXD [using the symmetric (311)-reflection] and HREM (in [$\bar{2}$33] projection), the former providing the barrier composition x of (0.335 ± 0.005) and the latter the well width of (59 ± 1) ML (10.1 nm). PL and PLE measurements are performed with the sample mounted in a bath-cryostat held at 4 or 77 K by using an Ar^+ laser operating in the multiline mode and an Ar^+ laser-pumped Ti-sapphire laser as excitation source, respectively. The excitation density is adjusted by means of neutral density filters to 500 mW/cm^2 in the case of PL and to 50 W/cm^2 in the case of PLE. The emitted light is dispersed by a 0.75-m monochromator and detected by a GaAs photomultiplier connected to a lock-in amplifier. The spectral resolution is better than 0.1 nm (0.2 meV).

Before focusing on the optical experiments, we comment on a recent paper by Nötzel *et al.*[15] in which it was reported that the ideal (311) surface is actually unstable developing a periodic corrugation under typical MBE growth conditions. Since this corrugation was shown to significantly affect the optical properties of the investigated structures it is important to consider this point. Our RHEED and HREM measurements showed that this corrugation was actually absent in our case. First of all, we did not observe the characteristic vertical splitting of the main streak in the RHEED pattern during growth that is indicative of the corrugation. Second, and even more important, the observation of RHEED intensity oscillations reveals that, despite nominally almost identical growth conditions (except for the use of different As species, namely, As_2 in our work but As_4 in theirs), the growth mode of GaAs and AlAs in our experiments differed obviously from that in the work of Nötzel *et al.* Finally, the HREM images—particularly of the GaAs/AlAs superlattice buffer of the sample investigated—conclusively demonstrate the absence of the corrugation. The reason for this discrepancy between our results and those of Nötzel *et al.* is not yet clear and remains under investigation. A detailed report of our RHEED and HREM results will be postponed until a consistent explanation has been established. Here, it is important to bear in mind that the optical properties of our sample, such as the transition energy and the exciton binding energy, are not affected by the interface corrugation reported in the work of Nötzel *et al.*

In Fig. 1 we show the 4-K PL spectrum of the sample under investigation. The dominant transition at 800.1 nm stems from the recombination of hh excitons associated with the first electron and hh subbands in the QW. At slightly lower energy a donor-bound exciton is resolved, which is a typical feature in the PL spectra of high-quality QW's.[16,17] The linewidth of the intrinsic transition is 0.86 meV, which is to our knowledge, by far the narrowest reported for any non-(100)-oriented QW and is amongst the best values for (100)-oriented QW's of this thickness.[17] In the spectral region between 818 and 824 nm four transitions originating from free, neutral donor, neutral acceptor, and defect-complex bound excitons from the GaAs buffer layer are visible. The dominance of the free exciton transition and the total absence of the usual free-to-bound transition around 830 nm, even at this low excitation density, is remarkable and evidences the high purity of this sample. This result is in accordance with the theoretically expected low affinity of the specific dangling-bond configuration of the (311)A surface to impurity incorporation.

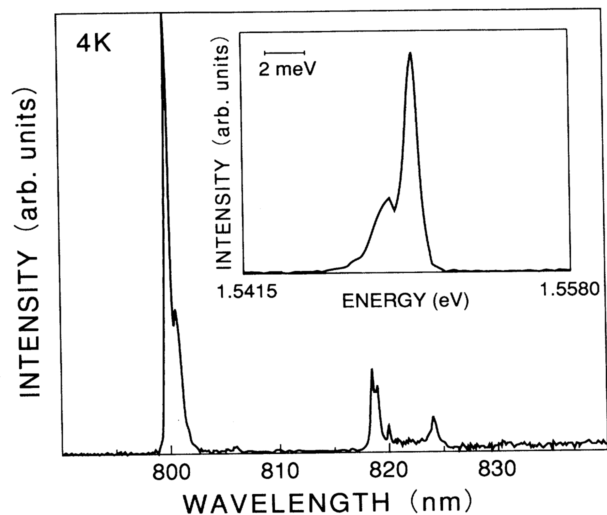

FIG. 1. PL spectrum at 4 K of the 10-nm (311)-oriented GaAs/$Al_{0.33}Ga_{0.67}$As QW under consideration. The high-energy transitions stem from the QW, the lower-energy transitions from the GaAs buffer layer. The inset shows the QW transitions on an expanded energy scale.

Figure 2 shows the PL and PLE spectra taken at 4 K in the spectral region of the QW transitions related to the lowest QW subbands. The 1S hh exciton resonance ($E_{\rm hh}^{1S}$) at 800.1 nm is exactly coincident with the corresponding transition in the PL spectrum. The very narrow linewidth and the absence of a Stokes shift implies a very high interface quality, i.e., those interface perturbations giving rise to exciton localization and line broadening (i.e., mainly vertical interface fluctuations) are absent in this sample. The second distinct resonance at 792.4 nm in the spectrum stems from the 1S light-hole (lh) exciton ($E_{\rm lh}^{1S}$) associated with the first electron and lh subbands. Note that the 1S lh exciton is degenerate with the hh continuum for this well width, which leads to the observed Fano broadening of the lh resonance. The two features ($E_{\rm hh}^{2S}$ and $E_{\rm lh}^{2S}$) at 795.8 and 787.6 nm originate from the first excited states (2S) of hh and lh exciton, respectively. The measured 1S-2S splitting energies are 8.4 meV for the hh and 9.6 meV for the lh exciton. Finally, we note that we found the spectra (within experimental uncertainty) to be unpolarized with respect to a rotation

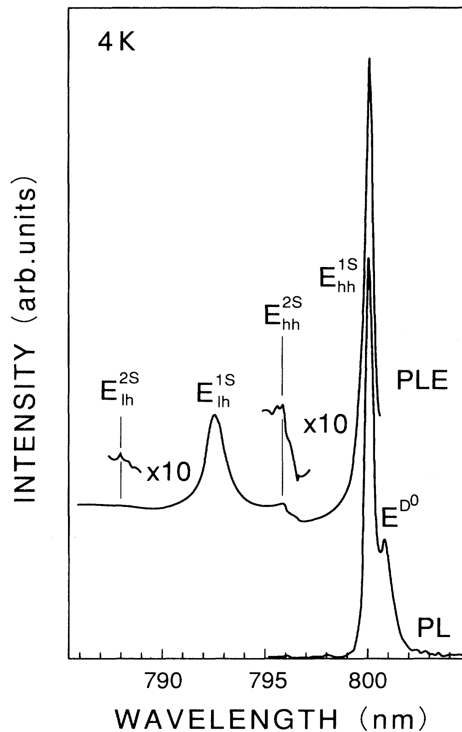

FIG. 2. PL and PLE spectra at 4 K of the 10-nm (311)-oriented $GaAs/Al_{0.33}Ga_{0.67}As$ QW under consideration. The peaks are labeled according to the discussion in the text.

of the polarization vector in the plane of the QW. This finding again confirms the absence of the interface corrugation reported in Ref. 15.

In Fig. 3 we present the PL and PLE spectra taken at 77 K. The same main transitions (E_{hh}^{1S} and E_{lh}^{1S}) as in the 4-K spectra shown in Fig. 2 are observed. The $2S$ features are now absent in the PLE spectrum, which is caused by the thermal broadening and consequent spectral overlap of the participating transitions.[18] However, in the PL spectrum two additional features at the high-energy side of the E_{hh}^{1S} transition are visible. Their spectral position agrees with the one expected for the onset of the hh exciton continuum (E_{hh}^{C}) and for the $1S$ lh exciton (E_{lh}^{1S}), both of which become thermally populated at 77 K. As discussed by Koteles and Chi,[18] only the exciton continua can be observed at 77 K as the $2S$ excitons are already thermalized at this temperature. The energy difference between the $1S$ resonance and the continuum onset observed in the 77-K PL spectrum (9.4 meV) is, therefore, slightly larger than the $1S$-$2S$ splitting energy.

The observation of the $2S$ states in PLE is known to allow the most reliable determination of the exciton binding energies. We point out that there are so far only two measurements of the exciton binding energies of non-(100)-oriented QW's and these contradict each other.[4,6] To obtain the exciton binding energy, we have to add the binding energies of the $2S$ excitons to the measured $1S$-$2S$ splitting energies. An accurate calculation of both $1S$ and $2S$ exciton binding energies, taking into account

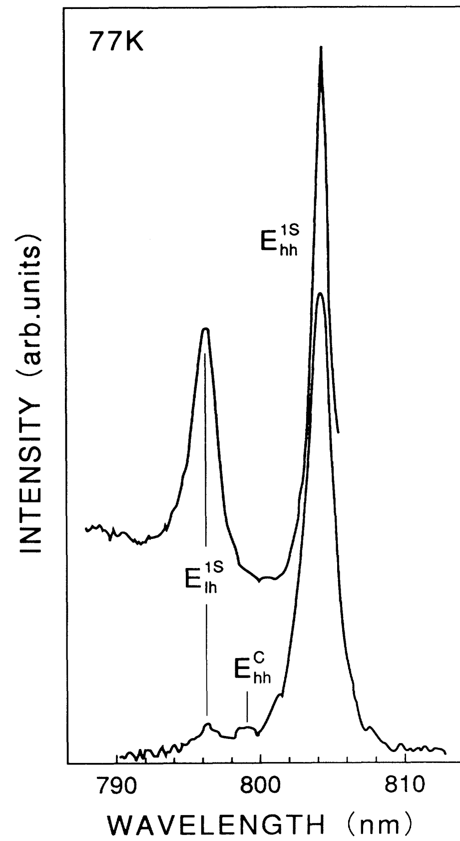

FIG. 3. PL and PLE spectra at 77 K of the 10-nm (311)-oriented $GaAs/Al_{0.33}Ga_{0.67}As$ QW under consideration. The peaks are labeled according to the discussion in the text.

Coulomb coupling, bulk nonparabolicity, and the dielectric mismatch, has been presented by Andreani and Pasquarello.[19] Taking their values for a GaAs QW of the given width and depth, we obtain binding energies of 10 and 12.3 meV for hh and lh excitons, respectively. These values are in very close (± 0.2 meV) agreement with both calculated[19] and experimental[20,21] binding energies for (100)-oriented $GaAs/Al_{0.33}Ga_{0.67}As$ QW's of this width. This finding confirms the results of Ref. 6 which suggest that the exciton binding energies are rather insensitive to the crystal orientation.

The direct measurement of the exciton binding energies and the independent and accurate determination of both well width and barrier composition now allows us to deduce the (311)-hole masses from our experimental data. The transition energies are calculated by an envelope function model, taking into account both electron and lh subband nonparabolicity, employing the 14×14 $\mathbf{k}\cdot\mathbf{p}$ formalism presented by Braun and Rössler[22] for the electron subband and the 8×8 $\mathbf{k}\cdot\mathbf{p}$ formalism presented by People and Sputz[23] for the lh subband. The electron mass (0.0665) (Ref. 24) is a well-established parameter for this material system. The band offset ratio is not known with the same degree of accuracy, but all the recent studies we are aware of suggest values between 60:40 (Refs. 11 and 25) and 68:32.[5,26] The hole masses—the remaining adjustable parameters in our model—are used to match the

observed transition energies. Closest agreement between calculation and experiment is obtained for a hh and lh mass of 0.460 ± 0.06 and 0.092 ± 0.006. The uncertainty denoted results almost exclusively from the uncertainty in well width of ±0.2 nm, whereas, the above denoted variation of the band offset is found to introduce only a minor change of the transition energies. This result demonstrates the very high degree of accuracy in measuring the well width which is necessary for a reliable determination of the hole masses.

Finally, we compare our effective hole masses with those derived from the LP's proposed in the literature.[27] The two most commonly used sets of LP's are the one suggested by Lawaetz[28] on theoretical grounds and the one derived by Hess *et al.*[29] from magneto-optical experiments. The former set results in values of 0.514 and 0.075 for the hh and lh masses, respectively, while the latter one yields 0.546 and 0.084. These values are clearly inconsistent with our data. Among the studies relying, like the present work, on the energy position of interband transitions, we found (within experimental uncertainty) good agreement using the LP's reported by Molenkamp *et al.*[5] and Gershoni *et al.*,[11] yielding hh masses of 0.482 and 0.487, respectively, and a lh mass of 0.087. Though the uncertainty in well width in these works is larger than our figure of 0.2 nm, the reported values were derived from simultaneous fits for sets of different samples which results in an statistical uncertainty as small as for the present experiment. The closest agreement is obtained, however, with the LP's proposed by Shanabrook *et al.*,[7] resulting in a hh mass of 0.466 ± 0.05 and a lh mass of 0.088 ± 0.005. In fact, we consider these values to be particularly reliable since they were derived from *intersubband* transitions, which are firstly very sensitive to small changes of the effective mass, and secondly, are neither influenced by excitonic effects nor by conduction subband nonparabolicity. Even more important, the well width sensitivity is greatly reduced compared to the case of *interband* transitions. Note, however, that despite the recently achieved convergence of the values for the hole masses of GaAs the obtained degree of accuracy is still far from that reached for the electron mass. This fact underlines the need for further theoretical and experimental studies of the valence-band anisotropy of GaAs.

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*Present address: Semiconductor Research Laboratory, Mitsubishi Electric Corporation, 1-1, Tsukaguchi-honmachi 8-chome, Amagasaki, Hyogo 661, Japan.

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