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Determination of valence-band effective-mass anisotropy in GaAs quantum wells by optical spectroscopy

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We present the first high-resolution excitation spectra of (Al,Ga)As multiple-quantum-well structures grown on substrates with different orientations [(001), (111)*B*, and (310) planes]. The features in these spectra can be consistently assigned by a single set of effective masses in a sophisticated eight-band $\mathbf{k}\cdot\mathbf{p}$ calculation. In this way, we obtain very directly the anisotropy of the valence bands in GaAs. We obtain masses of $0.34m_0$ and $0.094m_0$ for the heavy hole and the light hole in the [001] direction and $0.7m_0$ for the heavy hole in the [111] direction.

The spectroscopy of (Al,Ga)As quantum-well structures has been extensively studied over the last decade. Sample quality has improved greatly in the past few years resulting in, e.g., the observation of "forbidden" ($\Delta n \neq 0$) transitions[1,2] and of 2*s*-excitonic features in both luminescence[3] and excitation[4] spectra. Meanwhile, several $\mathbf{k}\cdot\mathbf{p}$-type theories have been developed (see Ref. 5, and references therein) for the calculation of confinement energies of electrons and holes. However, considerable uncertainty still exists as to the appropriate values of the effective masses and the band offset to be used in such calculations for (Al,Ga)As structures. Moreover, since quantum wells of sufficient quality for optical experiments have so far only been grown on (001)-oriented GaAs substrates, no direct optical information on the anisotropy of the valence band was obtained. In this paper we report the successful fabrication of (001)-, (310)-, and (111)-oriented (Al,Ga)As multiple-quantum-well structures. We characterize these samples by means of photoluminescence excitation spectroscopy and interpret the resulting spectra in terms of the effective-mass anisotropy of the valence bands. Our data allow us to extract directly the band effective mass from the observed hole confinement energies. This is in contrast with mass determinations *via* magnetooptical[6,7] or cyclotron resonance[8] experiments in which an exciton mass or a cyclotron hole mass is measured. These latter quantities result from averaging band effective masses in the plane perpendicular to the applied magnetic field. In general, the effective masses reported in these magnetooptical studies vary from report to report, and differ even more with the values commonly used in the description of the optical spectra of quantum wells.

The (Al,Ga)As multiple-quantum-well samples were grown in a Varian GEN2 molecular-beam-epitaxy machine using an approach described elsewhere.[9] Substrate wafers (*n*-type) of three orientations [(001), (310), and (111)*B* surfaces] were placed side by side on the rotating substrate holder enabling simultaneous epitaxy on the three different substrates. Two sets of multiple-quantum-well structures were grown. In set I the (310) and (111)*B* oriented substrates were misoriented by 4° towards the (001) plane to facilitate nucleation;[10] in set II the misorientation was 2°. All the samples consisted of 60 GaAs wells. The $Al_{0.33}Ga_{0.67}As$ barriers had the same thickness as the wells, which was determined by x-ray diffraction and photoluminescence excitation spectroscopy to be 76 Å for set I and 71 Å for set II. The surface quality of the (001)- and (310)-oriented samples was excellent (no defects), while that of the (111)-oriented samples was fair. Differences in the morphology of the surface between 2° and 4° off-cut samples were negligible. For all samples, clear superlattice-induced satellites of the diffraction spots could be observed.

For the photoluminescence-excitation experiments an argon-ion laser pumped pyridine 2 dye laser served as the excitation source. The samples were kept at a temperature of 6 K in an optical cryostat. The luminescence was dispersed through a double monochromator and detected by a cooled photomultiplier with a GaAs photocathode using photon-counting techniques.

The photoluminescence excitation spectra obtained for the samples of set I in the spectral region of the transitions involving the first confined electron level are shown in Fig. 1. Apart from the well-resolved lines corresponding to the transitions between the first electron and first heavy- (denoted as 1-1*h*) and light-(1−1*l*) hole levels, additional excitonic peaks due to the forbidden 1-2*h* and 1-3*h* transitions show up clearly in the excitation spectra. This is important because the 1-3*h* transition is expected to be the most sensitive to the effective-mass anisotropy of the valence band. Note the well-defined 2*s* excitonic features in the (001)-oriented structure, which are indicative of the high quality of these samples. For further analysis, we must extract from these spectra the electron and hole confinement energies in a consistent manner. Since the 2*s* exciton has a binding energy of around 2 meV,[4] we assume the electron-hole continuum to start at 2 meV higher energy than the peak of the 2*s* lines in the (001) case. For the (310) sample we assume the 2*s* exciton to be situated at the position indicated by the vertical lines in Fig. 1, and again use a value of 2 meV for the binding energy. While the (111) spectrum does not show any sign of

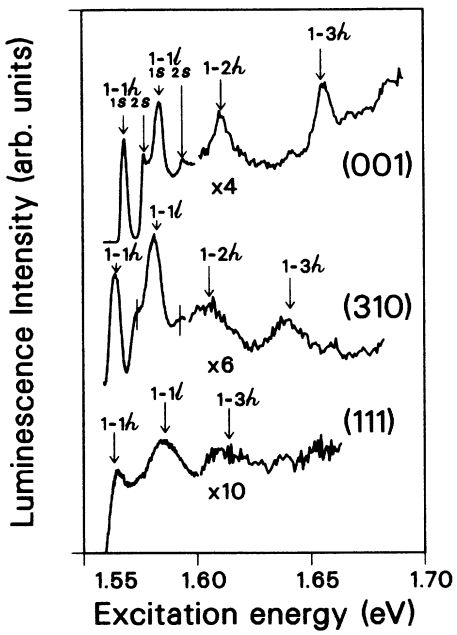

FIG. 1. Photoluminescence excitation spectra at 6 K of the transitions involving the first confined electron level for the first set of samples, with substrate orientation as indicated. The arrows indicate calculated transition energies. The vertical lines in the spectrum of the (310)-oriented sample give the positions assumed for the $2s$ excitations for the 1-1h and 1-1l transitions. The excitation power-density is in all cases 6 W/cm^2. Detection is at the low-energy tail of the 1-1h luminescence.

a $2s$ excitonic feature, a sensible approximation for the binding energy of the $1s$ exciton can be made by using the value obtained from the (310) sample. We have recently verified the validity of this latter procedure by calculating the anisotropy of the exciton binding energy.[11]

For the calculation of electron and hole confinement energies we use the eight-band $\mathbf{k}\cdot\mathbf{p}$ theory described recently,[5] which now incorporates the appropriate rotation of the $\mathbf{k}\cdot\mathbf{p}$ matrix and the corresponding boundary conditions in order to describe quantum wells grown in an arbitrary crystal orientation. Mixing of electron and hole bands, as occurs particularly in low-symmetry crystal directions, is fully taken into account. For an arbitrary direction $\hat{\mathbf{k}}$, where $\hat{\mathbf{k}}$ is a unit vector in $\mathbf{k}$ space, the effective mass $m^*_{h(l)}(\hat{\mathbf{k}})$ of heavy (light) holes, expressed in Luttinger's γ parameters,[12] is given by[5]

$$m_0/m^*_{h(l)}(\hat{\mathbf{k}}) = \gamma_1 \mp [4\gamma_2^2 + 12(\gamma_3^2 - \gamma_2^2) \times (\hat{k}_x^2 k_y^2 + \hat{k}_y^2 \hat{k}_z^2 + \hat{k}_x^2 \hat{k}_z^2)]^{1/2}. \quad (1)$$

Here m_0 is the free-electron mass and the minus (plus) sign applies to heavy (light) holes. As is obvious from Eq. (1), the anisotropy of the effective mass is most pronounced for the heavy holes. The largest mass difference will occur between holes in the [001] and [111] directions. Expressions for cyclotron masses in terms of γ parameters can be obtained using the method originally given by Dresselhaus, Kip, and Kittel[13] [cf. Eq. (74) in Ref. 13 and Eqs. (3) and (4) in Ref. 8].

It should be noted that, as we aim for almost exact fits (within 1 meV) we cannot use spectral features originating from the second confinement level of the electrons. The reason is that the nonparabolicity of the conduction band is not fully incorporated even in our extended theory. A better description of the nonparabolicity of the first conduction band is in principle possible by including more bands explicitly in the $\mathbf{k}\cdot\mathbf{p}$ matrix, but at the moment impractical. For now, we limit ourselves to fits on transitions involving the lowest electron confinement level.

The procedure we use for fitting our experimental data is as follows. First, we only focus on the spectra of the (001)-oriented samples to determine well width (the same for all samples within one set, as supported by the x-ray data) and the appropriate combination of band offset and effective masses in the [001] direction (same for all samples). Using the parameters thus obtained we then fit the data for the (310)- and (111)-oriented samples, allowing only the valence-band anisotropy to vary. The assumptions implied by this procedure (constant well width within one set of samples and an orientation-independent band offset) will be justified below.

Our fitting procedures for the (001)-oriented structures lead to effective masses in the [001] direction of $(0.34\pm0.02)m_0$ and $(0.094\pm0.005)m_0$ for heavy and light holes, respectively, and a band offset $\Delta E_{\text{cond}}/\Delta E_{\text{gap}}$ of 0.68. This latter value is in very good agreement with a recent determination of the band offset from type-II quantum-well structures.[14] The well widths arrived at agree well with those inferred from the x-ray data. We have set the material parameter $(2m/\hbar^2)P^2$, which describes the coupling between the conduction and the valence band over the momentum operator,[5] equal to 28.8 eV.[15] Together with the above heavy- and light-hole masses consistency within our model then requires[5] an effective mass of $0.1788m_0$ for the split-off band. The material parameters used are summarized in Table I. The resulting calculated photon energies for the excitonic transitions are given by the arrows in Fig. 1. The quality of the calculations is apparent. It turns out that our quantum wells are best described using effective masses used previously in studies where forbidden transitions were ex-

TABLE I. The material parameters used in this work and the Luttinger parameters derived from them. All effective masses refer to the center of the Brillouin zone and all but $m^*_{hh}(111)$ are in the [001] direction.

	E_{gap} (eV)	Δ_{so} (eV)	m^*_{el}	m^*_{hh}	m^*_{lh}	m^*_{so}	$m^*_{hh}(111)$	$(2m/\hbar^2)P^2$ (eV)	γ_1	γ_2	γ_3
GaAs	1.519	0.343	0.0665	0.34	0.094	0.1778	0.7	28.8	6.790	1.924	2.681
AlAs	2.766	0.281	0.15	0.752	0.16	0.2882	1.0	28.8	3.790	1.230	1.395

plicitly taken into account.[1,2] Other sets of parameters[7,16] do either not lead to accurate predictions of $1-1h$, $1-1l$, and $1-3h$ transition energies or necessitate the use of unacceptable well widths and band offsets to obtain a reasonable fit of the spectra.

We are now in a position to calculate the confinement energies for the remaining samples as a function of the valence-band anisotropy, which we have parametrized by $m^*_{hh}(111)$, the heavy-hole effective mass in the [111] direction. To account for the effects of anisotropy in the band structure of the barrier material, we have taken $m^*_{hh}(111)$ for AlAs equal to $1.0m_0$. The exact value of $m^*_{hh}(111)$ in AlAs has virtually no (i.e., less than 0.3 meV) influence on the calculated confinement energies for the wells. In Fig. 2 we plot the calculated total confinement energies for the 1-1h, 1-1l, and 1-3h transitions for the (310)- and (111)-oriented samples (solid lines) as a function of $m^*_{hh}(111)$. The hatched areas give the experimentally determined values for the confinement energies and the region of uncertainty. It is immediately evident that the third heavy-hole confinement level is far more sensitive to the valence-band anisotropy than the first heavy- and light-hole levels, as the confinement energy is much larger. From the observed 1-3h transition energies for both series of samples we consistently find a value for $m^*_{hh}(111)$ of $(0.7\pm0.1)m_0$, as depicted by the dotted area in Fig. 2. The Luttinger parameters corresponding to the effective masses given here are also presented in Table I. The fact that it is possible to get a consistent result for the anisotropy from two sets of *three* samples justifies our assumption concerning the orientation independence of the band offset. This latter point is in good agreement with recent experimental and theoretical studies.[17]

Using the parameter sets given by Lawaetz[16] and Hess *et al.*[7] we calculate a much larger valence-band anisotropy than that observed. Where in our case the ratio $m^*_{hh}(111)/m^*_{hh}(001)$ equals 2.06, this number is 2.60 for the Lawaetz set and 2.53 for Hess *et al.*[7] We have already seen that attempts to fit our (001)-oriented samples were not satisfactory when these parameter sets were used. While Lawaetz's set was constructed using mainly theoretical arguments, Hess *et al.* obtained their parameters from fitting magnetoreflection experiments, measuring interband transitions between Landau levels. The relevant parameter in describing such experiments is the (reduced) exciton mass $m_{exc}=(1/m^*_{el}+1/m^*_{hole})^{-1}$. The value of m_{exc} is dominated by the small electron mass and a precise determination of the hole mass becomes difficult. Moreover, as mentioned above, the hole masses involved in magnetooptic experiments are averaged values of the valence-band masses in the plane perpendicular to the applied magnetic field. Similar information, but without interference from electron masses, can be obtained from cyclotron resonance experiments monitoring intraband transitions between Landau levels. The most recent experiments on holes were done by Skolnick *et al.*,[8] who report heavy-hole cyclotron masses of $0.45m_0$ and $0.57m_0$ when the magnetic field is oriented along [001] or [111], respectively. Using our values for the band effective masses, we calculate[8,13] cyclotron masses of $0.44m_0$ and $0.57m_0$,

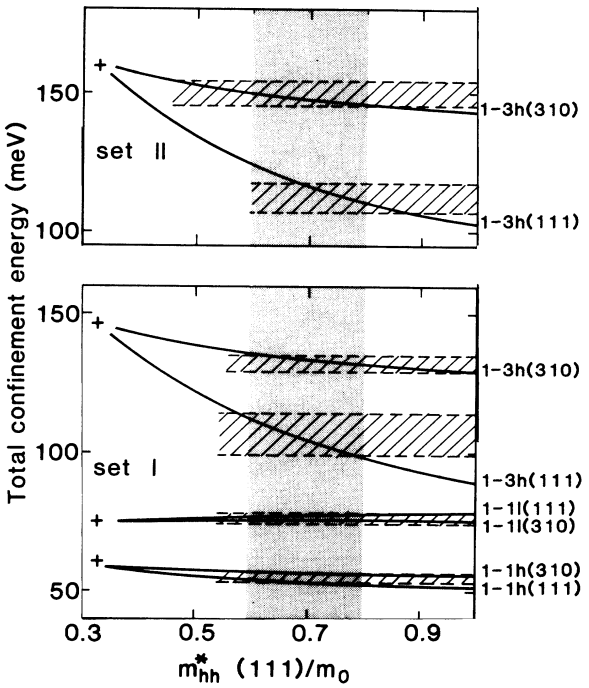

FIG. 2. Calculated confinement energies of the 1-3h transition for both sets of samples. Electron, heavy- and light-hole masses in the [001] direction are those given in Table I, while $m^*_{hh}(111)$ is allowed to vary. Hatched areas give the experimental data with their uncertainty. The 1-1h and 1-1l data for the first set of samples is shown only to illustrate the relative unsensitivity of these transitions to the value of $m^*_{hh}(111)$. Crosses denote the experimentally obtained confinement energies for the various transitions for the (001)-oriented samples.

again for a magnetic field parallel to, respectively, [001] and [111], in very good agreement with the data of Skolnick *et al.* The light-hole cyclotron mass for a magnetic field parallel to [001] that can be calculated from our data is $(0.089\pm0.005)m_0$. This compares reasonably well with the value of $(0.082\pm0.004)m_0$ that Skolnick *et al.* report.[8]

To sum up, we have obtained excitation spectra from quantum-well structures grown on several differently oriented substrates, allowing detailed information on valence-band anisotropy to be obtained in a very direct manner. The observed anisotropy in GaAs is in very good agreement with recent cyclotron-resonance data.[8] In general, a gratifying convergence of band parameters obtained by magnetooptical[18] and all optical experiments has now been obtained.

Note added in proof. After submission of the present work, studies on (111)-oriented (Al,Ga)As quantum wells were also reported in the literature by B. V. Shanabrook *et al.* [J. Phys. (Paris) Colloq. **48**, C5-235 (1987)], and by T. Hayakawa *et al.* [Phys. Rev. Lett. **60**, 349 (1988)].

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[18]We should remark here that the band offset $\Delta E_{\text{cond}}/\Delta E_{\text{gap}}$ of 0.85 that long has been used in the description of (Al,Ga)As quantum-well spectra finds its origin in the effective-mass values used by Dingle *et al.* in their original publication on quantum wells [R. Dingle, W. Wiegman, and C. H. Henry, Phys. Rev. Lett. **33**, 827 (1974)]. Although Dingle *et al.* do give the correct expressions for the hole masses in terms of Luttinger parameters, the mass values quoted in that paper are those of cyclotron masses and not of band effective masses.

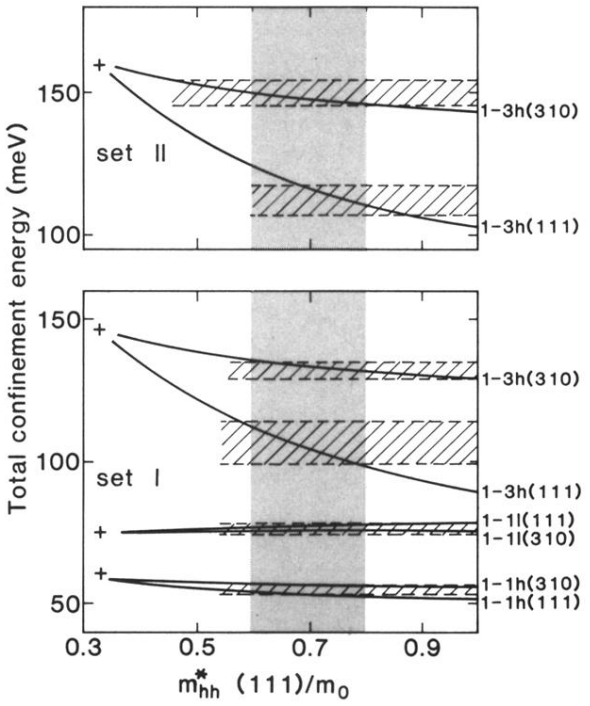

FIG. 2. Calculated confinement energies of the 1-3*h* transition for both sets of samples. Electron, heavy- and light-hole masses in the [001] direction are those given in Table I, while $m^*_{hh}(111)$ is allowed to vary. Hatched areas give the experimental data with their uncertainty. The 1-1*h* and 1-1*l* data for the first set of samples is shown only to illustrate the relative unsensitivity of these transitions to the value of $m^*_{hh}(111)$. Crosses denote the experimentally obtained confinement energies for the various transitions for the (001)-oriented samples.