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Photoluminescence properties of $Al_xGa_{1-x}As$ and an investigation of a new 1.951 eV transition

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Abstract. A detailed study of the photoluminescence properties (5 K) of $Al_xGa_{1-x}As$ with an interpretation for both the direct and indirect bandgap regions is presented. Linear relationships for the excitonic and acceptor related peak energies as a function of composition in both regions are given. In the indirect region phonon replicas of the indirect exciton recombination are observed. The measured energies and strengths of these phonon replicas are presented and compared with data from the literature. In the indirect region a new transition at 1.951 ± 0.001 eV has been measured, which has a peak energy that is independent of the Al content of the material. Its relative intensity increases strongly near the $Al_xGa_{1-x}As$/GaAs interface. This transition originates from either an indirect excitonic transition in the GaAs underneath the $Al_xGa_{1-x}As$ or an interface effect.

1. Introduction

The fact that GaAs is a direct bandgap semiconductor makes it very suitable for use in electro-optical devices. The almost perfect lattice match when combined with $Al_xGa_{1-x}As$ makes it possible to use $Al_xGa_{1-x}As$/GaAs heterojunctions and superlattices as light-emitting devices. Many photoluminescence (PL) measurements on GaAs have been performed and have given much information about excitonic, (e, A^0)† and (D^0, A^0)‡ direct Γ_{1c}–Γ_{15v} transitions.

The PL properties of $Al_xGa_{1-x}As$ have also been investigated extensively [1–14]. The fact that $Al_xGa_{1-x}As$ becomes an indirect semiconductor around $x = 0.40$ complicates the interpretation of the PL spectra above this value. Another complicating factor arises from the fact that the methods used to determine the Al fraction of the material such as electron x-ray microprobe analysis [1–4], nuclear reaction profiling (Rutherford backscattering) [6], Auger electron spectroscopy sputtering [11] and elastic recoil detection [15] are not very accurate. Therefore, there is no unanimity in the literature concerning the direct bandgap–composition relationship and the composition at which the direct-to-indirect bandgap transition occurs.

In the indirect region the uncertainties are even larger. Accurate values for the low-temperature indirect bandgap are not available. The interpretation of the PL

† (e, A^0) refers to a band-to-acceptor transition $e + A^0 \rightarrow A^- + h\nu$.
‡ (D^0, A^0) refers to a donor-to-acceptor transition $D^0 + A^0 \rightarrow D^+ + A^- + h\nu$.

spectra in the indirect region is still ambiguous. Most authors agree on the fact that the main transitions are the phononless indirect exciton recombination and the donor–acceptor pair recombination. Dingle [11] claimed that around the cross-over point the difference in photon energy between the peak energies of these two transitions shows a maximum as a result of the increasing donor binding energy because of mixing of the Γ, X and L donor states. This maximum in donor binding energy was confirmed by Hall measurements [16–18] and by PL experiments on pressure-induced indirect GaAs [19]. The exact values for the donor binding energy, however, differed a lot.

Phonon replicas of indirect exciton recombinations were reported by several authors [4–10], but there exists some discrepancy as to the nature of the participating phonons. The reported strengths of the phonon replicas also show many discrepancies as will be shown in this report.

In this paper we present a study of the PL properties of $Al_xGa_{1-x}As$ from which the linear relationships for the excitonic- and acceptor-related PL energies as a function of the Al fraction are derived. In addition, we report a new transition in the indirect region at 1.951 ± 0.001 eV which has a peak energy that does not depend on the Al fraction of the material. This transition is related to either an indirect excitonic transition in the GaAs underneath the $Al_xGa_{1-x}As$ or an effect at the $Al_xGa_{1-x}As$/GaAs interface. Several experiments to reveal the origin of this transition will be discussed.

2. Experimental details

The epitaxial layers used in this study were grown in a conventional atmospheric pressure MOVPE reactor described in an earlier publication [20]. The deposition parameters were: growth temperature 745 °C, group V/group III ratio 24, growth rate ~ 55 nm min^{-1}. Trimethylgallium (TMG), trimethylaluminum (TMA) and arsine were the source materials. The epitaxial structures consisted of an $Al_xGa_{1-x}As$ layer 2 μm thick grown on top of a thin buffer layer of 30 nm GaAs. These layers were grown on (100)- and (110)-oriented semi-insulating Cr-doped GaAs substrates. The (100) substrates were misoriented 2° off towards the (110) direction. The Al fraction x of the $Al_xGa_{1-x}As$ layer was varied between 0 and 0.84. The relation between x and the TMA/(TMA + TMG) input ratio was extensively investigated by van Sark *et al* [15]. We used their relationship to calculate x using the values for the growth temperature and the TMA/(TMA + TMG) input ratio. The *CV* measurements indicated that all the samples were n-type with net carrier concentrations of approximately 2×10^{17} cm^{-3}. Hall measurements at 293 K using the van der Pauw [21] method on a cloverleaf-shaped sample with $x = 0.47$, yielded a Hall carrier concentration of $(4.6 \pm 0.3) \times 10^{17}$ cm^{-3} and a Hall mobility of (975 ± 13) cm^2 V^{-1} s^{-1}. PL measurements were performed with the 2.41 eV (514.5 nm) line from an Ar^+ laser with the sample in He exchange gas at 5 K. For standard PL measurements an excitation power of 100 mW was used with a spot size of 3.8×10^{-2} cm^2 (irradiance $E = 2.6$ W cm^{-2}). The luminescence was dispersed by means of a 0.6 m double monochromator and detected with a cooled photomultiplier with a S1 response. The gratings of the monochromator were holographically ruled to 1200 lines mm^{-1} without blaze. Therefore, the spectral response of the system was almost constant, so that no corrections on the PL spectra were made. The optical resolution of the system was 0.1 nm.

3. Results

3.1. The $Al_xGa_{1-x}As$ transitions

The PL spectra of several samples with increasing Al fraction x are shown in figure 1. In the direct bandgap region ($x \leqslant 0.42$) a high energy peak is seen which is related to donor–bound exciton (D^0_Γ, X) recombinations and a low energy peak which is related to donor–acceptor pair transitions involving the C_{As} acceptor: (D^0, C^0_{As}). Because of the alloy-broadening of the PL linewidth in $Al_xGa_{1-x}As$ it is not possible to resolve the (e, C^0_{As}) transition. In the indirect bandgap region ($x \geqslant 0.42$) the assignment of the peaks is more complicated. In order to distinguish between the several peaks, the PL spectra were measured as a function of irradiance. In this paper we will focus our attention on the near-bandgap peaks between 1.9 and 2.2 eV. The broad peaks between 1.6 and 1.9 eV which are also visible in the material for $x \geqslant 0.48$ (figure 1), and are related to complex defects, will be left out of the consideration.

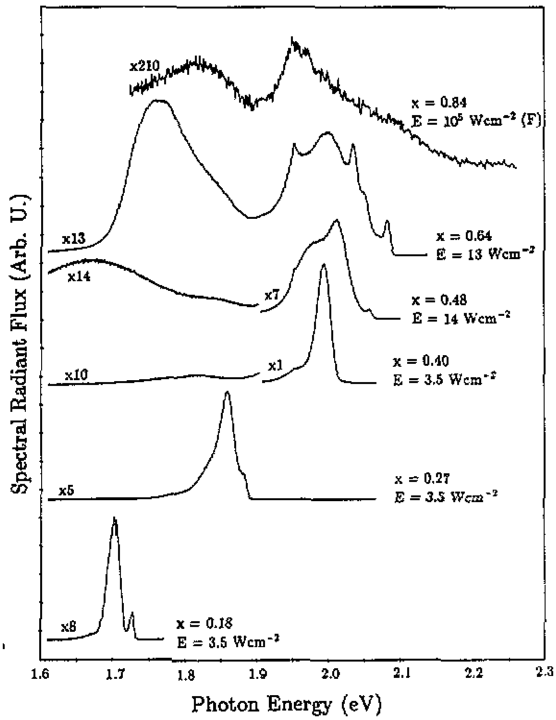

Figure 1. Photoluminescence spectra (5 K) of $Al_xGa_{1-x}As$ as a function of the Al fraction x. The relative gain used to record each spectrum is given to the left. The Al fraction x and the irradiance E are given to the right. The spectrum at $x = 0.84$ was measured with the laser beam focused (F) to a spot size of 5×10^{-6} cm^2.

A typical set of spectra with different irradiances is shown in figure 2 for a sample with $x = 0.64$. At high irradiances a narrow peak arises at the high energy side of the spectrum. Dingle *et al* [10] related this peak to zero-phonon donor–bound exciton (D^0_X, X) annihilation. Sturge *et al* [9], however, argued that the exciton line in undoped $Al_xGa_{1-x}As$ ($n \simeq 1\text{–}3 \times 10^{16}$ cm^{-3}) is related to recombinations of localized indirect excitons scattered by alloy fluctuations. Since in our samples the carrier

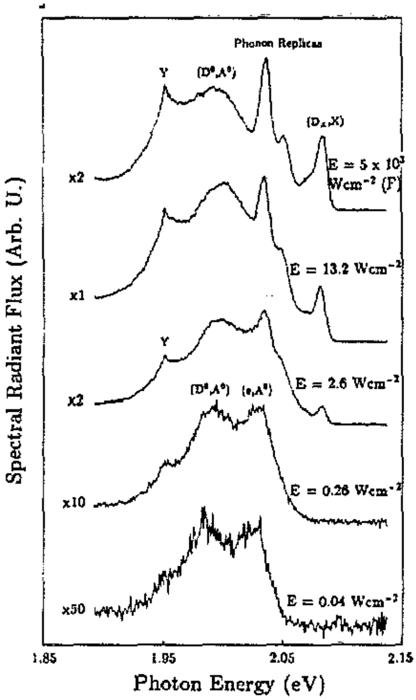

Figure 2. Photoluminescence spectra (5 K) of $Al_{0.64}Ga_{0.36}As$ as a function of irradiance E. The relative gain used to record each spectrum is given to the left. The irradiance is given to the right. The highest irradiance (F) was obtained by focusing the laser beam to a spot size of 5×10^{-4} cm^2.

concentrations are significantly higher ($n \simeq 2$–5×10^{17} cm^{-3}), we believe that in our spectra donor–bound exciton (D_X^0, X) recombinations dominate just as in the Te-doped samples measured by Sturge *et al* [9]. In this work, however, knowledge of the exact nature of this excitonic peak is not required.

Two narrow features, located 33.2 ± 1.5 and 47.3 ± 0.5 meV below the exciton peak, are attributed to phonon replicas of this peak [11]. At the highest irradiance a shoulder is visible at the low energy side of the excitonic transition. This shoulder is a TA_X phonon replica [5, 6] with a phonon energy of 13 ± 2 meV. The assignment of the phonons will be discussed in section 4.1.

At low irradiances two broader peaks remain. The peak around 1.994 eV shifts to a higher energy at a rate of 7 meV per decade of increasing irradiance. Such a shift is typical for donor–acceptor pair transitions [22, 23] and is caused by saturation of distant pair transitions with increasing carrier concentrations together with a screening of the fluctuations in the local Coulombic potential [24]. Therefore, we attribute this peak to (D^0, A^0) transitions. The shift in energy is comparable with the measurements of Oelgart *et al* [1] who measured 8 meV/decade at $x = 0.51$.

The second broad peak around 2.030 eV, which is seen at low irradiances, is masked by a phonon replica of the indirect exciton peak at higher irradiances. It is clear that its shift is much less than that of the donor–acceptor pair recombinations. Therefore, we assign this broad peak to band–acceptor (e, A^0) transitions. This peak has not been reported before in the literature, due to the fact that higher irradiances have usually been used. Figure 3 shows the peak energy of the several transitions as a function of the Al fraction x. The results of the linear fits to the data points are listed in the caption to figure 3. These results will be discussed in more detail in section 4.1.

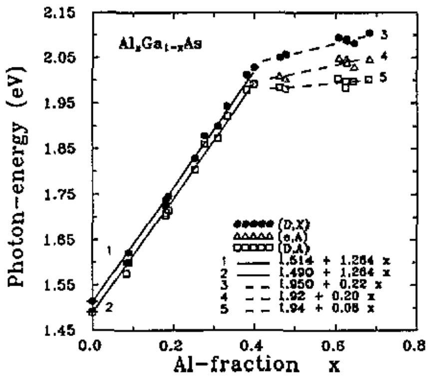

Figure 3. Variation of PL peak energies (5 K) of the excitonic (D^0, X) and acceptor related (e, A^0) and (D^0, A^0) transitions in $Al_xGa_{1-x}As$ as a function of the Al fraction x. In the direct region ($x \leqslant 0.42$) the difference between (e, A^0) and (D^0, A^0) could not be resolved. The full lines represent linear fits to the data points in the direct region while the broken lines represent linear fits to the data points in the indirect region. The results of the fits are listed in the legend.

3.2. The 1.951 eV transition: the Y-peak

The lowest energy peak in figure 2, which is situated at 1.951 ± 0.001 eV, is present in all the spectra in the indirect region and becomes more pronounced with increasing x (figure 1). The most important characteristic of this transition is that its peak energy is independent of the Al content of the $Al_xGa_{1-x}As$ layer. To our best knowledge this transition has never been reported in the literature until now. A thorough check, including measurements at other laboratories, ensured that this peak was not an artificial effect. For convenience we will call this transition Y.

The fact that the Y-peak does not shift as a function of the Al concentration indicates that this peak does not originate from the $Al_xGa_{1-x}As$ layer itself. This implies that this transition is either luminescence from the interface or from the GaAs layer underneath the $Al_xGa_{1-x}As$. Since this peak could not be detected in measurements on GaAs without an $Al_xGa_{1-x}As$ top layer, even under the highest irradiances, it can be concluded that if the latter is true, this peak can only be excited through the $Al_xGa_{1-x}As$. The mechanism that can explain this is the following. The 2.41 eV photons of the Ar^+ laser excite electrons into the conduction band of the $Al_xGa_{1-x}As$. The electrons will thermalize into the Γ_{1c} minimum of that band. Intervalley scattering will transfer most electrons from the Γ_{1c} to the X_{1c} valley. The electrons and the holes are able to diffuse from the $Al_xGa_{1-x}As$ layer to the GaAs layer underneath. This gives a population of electrons in both the Γ_{1c} and X_{1c} bands of the GaAs and luminescence from both bands can occur. In this view the 1.951 eV transition is due to an indirect X_{1c}–Γ_{15v} transition in the GaAs layer underneath the $Al_xGa_{1-x}As$. This explains the necessity of an $Al_xGa_{1-x}As$ top layer to populate the X_{1c} conduction band minimium of the GaAs. The fact that the direct Γ_{1c}–Γ_{15v} GaAs transitions ($1.45 < h\nu < 1.52$ eV) are also detectable for all samples confirms that diffusion indeed occurs.

We have measured the intensity of the Y-peak as a function of the thickness of the $Al_xGa_{1-x}As$ layer. A sample with an Al fraction $x = 0.64$ and a layer thickness of 7.9 μm, was etched under an angle of 0.09° according to a chemical bevel method developed by Huber *et al* [25]. The laser beam was focused to a spot with a diameter of 25 μm with the sample mounted on an insert which could be translated with a resolution of 10 μm. In this way it was possible to measure PL spectra along the bevel direction with a layer thickness resolution of 20 nm. Figure 4 shows that the intensities of both the Y-peak and the (D_X^0, X) transition decreased with decreasing $Al_{0.64}Ga_{0.36}As$ layer thickness. Since the absorption coefficient of $Al_{0.64}Ga_{0.36}As$ at 4 K is approximately 2×10^3 cm^{-1} at the laser photon energy of 2.41 eV [2], the penetration ($1/e$) depth of the laser is approximately 5 μm. Hence, the intensity of the excitonic transition decreases since less laser light will be absorbed in the $Al_{0.64}Ga_{0.36}As$ layer with decreasing layer thickness. From the PL measurements as a function of irradiance (figure 2) it could be concluded that for all the samples the PL intensity of both the excitonic transition and the Y-transition increased linearly with the irradiance. This implies that the ratio between the intensity of the Y-transition and the excitonic transition is expected to be constant. However this ratio, which is also given in figure 4, shows a strong increase near the $Al_{0.64}Ga_{0.36}As$/GaAs interface. This indicates again that the Y-peak does not originate from the $Al_xGa_{1-x}As$ itself.

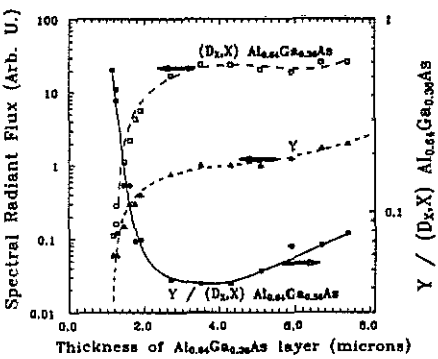

Figure 4. The PL intensity of the donor-bound exciton (D_X^0, X) transition and that of the Y-transition in an $Al_{0.64}Ga_{0.36}As$/GaAs sample as a function of $Al_{0.64}Ga_{0.36}As$-layer thickness are represented by broken curves (left y-axis). The intensity ratio of the Y-transition and the (D_X^0, X) transition is represented by a full curve (right y-axis).

In order to reveal the origin of the Y-peak, PL measurements (4.2 K) were performed with an Ar^+-laser pumped tunable dye-laser with rhodamine 6G as dye. The photon flux density (photons s^{-1} cm^{-2}) was chosen to be equal to that of the Ar^+ laser. The photon energy of the dye laser was chosen in such a way that it was impossible to directly excite the excitonic transitions in the indirect $Al_xGa_{1-x}As$. Its energy, however, was high enough to directly excite the Y-transition ($h\nu_{dye} > 2.0$ eV). Nevertheless the Y-transition could not be detected. This implies that this transition cannot be excited directly, but that it is correlated to the indirect excitonic $Al_xGa_{1-x}As$ transitions.

Temperature-dependent PL measurements showed that the intensity of the Y-peak decreased slowly when the temperature was raised and was still detectable at temperatures up to 160 K. Up to this temperature the Y-peak did not shift by more than

2 meV.

Another characteristic of the Y-transition was that it was always more pronounced if the epitaxial layers were grown on (110)-oriented substrates rather than if they were grown on (100) 2° off towards (110)-oriented substrates. This is shown in figure 5 for samples with $x = 0.55$. Both samples were grown in the same growth run with almost the same substrate position in the reactor. From figure 5 it is also clear that all the $Al_xGa_{1-x}As$ transitions are broader in the sample grown on the (110) substrate than in the sample grown on the (100) 2° off towards (110)-oriented substrate. This implies that the (110) material is less homogeneous.

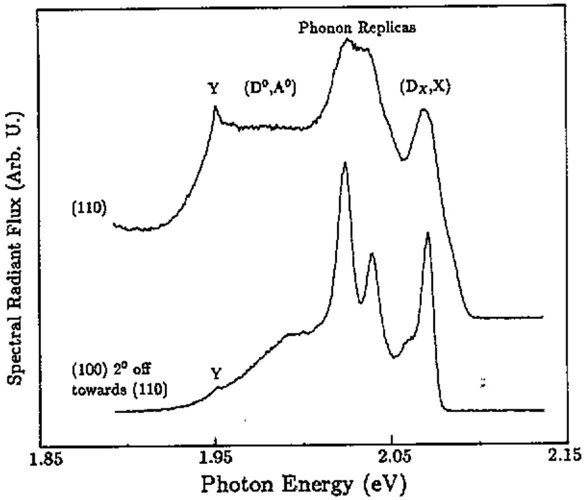

Figure 5. Photoluminescence spectra (5 K) of $Al_{0.55}Ga_{0.45}As$ for two substrate orientations. Both spectra were recorded with an irradiance of 3.8×10^2 W cm^{-2} and with the same gain.

4. Discussion

4.1. The $Al_xGa_{1-x}As$ *transitions*

The values for the peak energies as a function of the Al fraction (figure 3) are fitted using a linear relationship. We found in the direct region that

$$h\nu(D^0_\Gamma, X) = (1.514 \pm 0.001) + (1.264 \pm 0.010)x \text{ eV} \qquad (x < 0.42) \qquad (1)$$

$$h\nu(D^0, A^0) = (1.490 \pm 0.002) + (1.264 \pm 0.012)x \text{ eV} \qquad (x < 0.42) \qquad (2)$$

and in the indirect region

$$h\nu(D^0_X, X) = (1.950 \pm 0.016) + (0.22 \pm 0.03)x \text{ eV} \qquad (x > 0.42) \qquad (3)$$

$$h\nu(e, A^0) = (1.92 \pm 0.03) + (0.20 \pm 0.04)x \text{ eV} \qquad (x > 0.42) \qquad (4)$$

$$h\nu(D^0, A^0) = (1.94 \pm 0.02) + (0.08 \pm 0.03)x \text{ eV} \qquad (x > 0.42). \qquad (5)$$

The relationship for the donor–bound-exciton recombination in the direct region is in good agreement with the relationship given by Stringfellow and Linnebach [12]

($h\nu(D^0_\Gamma, X) = 1.512 + 1.245x$ eV) based on the PL data of Dingle *et al* [11]. For both the (D^0_Γ, X) and the (D^0, A^0) transition, our data yield a linear coefficient equal to 1.264 ± 0.010, where we used the relation of van Sark *et al* [15] to calculate the Al fraction. Recently Kuech *et al* [6] stated that the linear coefficient should be equal to 1.455 ± 0.004.

The transition from direct-to-indirect bandgap occurs at $x = 0.42 \pm 0.02$, which is in agreement with the value of $x = 0.44$ given by Dingle *et al* [11]. Kuech *et al* [6] showed that the (D^0, X) Al fraction relationship bends at $x = 0.370 \pm 0.015$ and concluded that at this value the direct–indirect transition occurs.

For the indirect region the relationship for the (D^0_X, X) exciton recombination (equation 3) is in reasonable agreement with data from the literature measured in the same composition range. Oelgart *et al* [1] obtained $h\nu(D^0_X, X) = 1.986 + 0.16x$ eV whereas Shah *et al* [14] measured $h\nu(D^0_X, X) = 1.948 + 0.29x$ eV. In $Al_xGa_{1-x}As$ a slight deviation of linearity is expected in equation (3) but there is no unanimity on the magnitude of this deviation [26, 27].

Since a maximum in donor binding energy is reported at around $x \simeq 0.4$ with a gradual decrease as x increases [1, 16–18] it is expected that the difference in peak energy between the (e, A^0) and (D^0, A^0) transition decreases above $x \simeq 0.4$. This is in contradiction with our measurements, which can be explained by the fact that the compensation ratio N_A/N_D increases with increasing Al fraction in MOVPE grown $Al_xGa_{1-x}As$ [5, 7, 12]. Since the (D^0, A^0) transition shifts to lower energy values at increasing compensation ratios [23, 24], the rise in compensation with increasing x can thus explain why the (D^0, A^0) transition diverges away from the (e, A^0) transition.

Dingle *et al* [10] proposed that the phonons involved in the phonon replicas of the excitonic transition in indirect $Al_xGa_{1-x}As$ (figure 2) are momentum-conserving LO_X phonons of two optical branches: one of the AlAs mode and the other of the GaAs mode. On the other hand, Kuech *et al* [5, 6] claimed that zone boundary TO_X and LA_X phonons participate in these phonon replicas. To our knowledge, the zone boundary phonon energies in $Al_xGa_{1-x}As$ have not been measured, so that a direct comparison cannot be made. Kim *et al* [28] measured the energies of both the GaAs-like and the AlAs-like TO_Γ and LO_Γ phonons in $Al_xGa_{1-x}As$. From their measurements it can be concluded that TO_Γ phonon energies hardly depend on the Al fraction, whereas the LO_Γ phonons show a relatively strong dependency on the Al fraction x. Furthermore, it can be concluded from their measurements that

$$\text{at } x = 0: \ LO_\Gamma(\text{AlAs-like}) = TO_\Gamma(\text{AlAs-like}) \tag{6}$$

and

$$\text{at } x = 1: \ LO_\Gamma(\text{GaAs-like}) = TO_\Gamma(\text{GaAs-like}). \tag{7}$$

Furthermore, in $GaAs_xP_{1-x}$ [29] it has been found that the TO_L and TO_X phonon energies also hardly depend on the P fraction. For these reasons we assume that the TO_X phonon energies in $Al_xGa_{1-x}As$ are independent of the Al fraction, so that

$$TO_X(\text{AlAs-like}) \approx TO_X(\text{AlAs}) = 41.5 \text{ meV [30]} \tag{8}$$

and

$$TO_X(\text{GaAs-like}) \approx TO_X(\text{GaAs}) = 31.3 \text{ meV}\dagger \text{ [31]} \tag{9}$$

† This value is measured at room temperature, but since phonon energies are almost temperature independent it is possible to use this value.

For the LO_X phonons we assume that their dependence on the Al fraction is similar to that of the LO_Γ phonons. We assume that at $x = 0$:

$$LO_X(\text{AlAs-like}) \approx TO_X(\text{AlAs}) = 41.5 \text{ meV [30]} \tag{10}$$

$$LO_X(\text{GaAs-like}) = LO_X(\text{GaAs}) = 29.8 \text{ meV [32]} \tag{11}$$

and at $x = 1$:

$$LO_X(\text{AlAs-like}) = LO_X(\text{AlAs}) = 50.0 \text{ meV [30]} \tag{12}$$

$$LO_X(\text{GaAs-like}) \approx TO_X(\text{GaAs}) = 31.3 \text{ meV}\dagger \text{ [31]} \tag{13}$$

so that in first order

$$LO_X(\text{AlAs-like}) = 41.5 + 8.5x \text{ meV} \tag{14}$$

and

$$LO_X(\text{GaAs-like}) = 29.8 + 1.5x \text{ meV}. \tag{15}$$

Consequently, at $x = 0.64$ we find that AlAs-like $LO_X = 46.9$ meV which, within error, is equal to the measured value of 47.3 ± 0.5 meV, so that we assign the phonon with the highest energy to AlAs-like LO_X. Furthermore, we find at $x = 0.64$ that GaAs-like $LO_X = 30.8$ meV and GaAs-like $TO_X = 31.3$ meV which are both very close to the measured value of 33.2 ± 1.5 meV. Therefore, it is not clear whether this phonon should be assigned to GaAs-like LO_X or TO_X. On the other hand, it can be stated that Kuech's [5, 6] assignment to LA_X is very unlikely, since it is expected that the phonon energies in $Al_xGa_{1-x}As$ are in between the phonon energies of GaAs and AlAs. For GaAs it was reported that $LA_X = 28.1 \pm 0.2$ meV† [31] whereas for AlAs $LA_X = 27.5 \pm 1.5$ meV [30] and therefore the measured phonon energies are not in between the extrema for LA_X. Hence, we conclude that these phonon replicas should be assigned to AlAs-like LO_X and GaAs-like LO_X or TO_X. This assignment is completely in accordance with phonon energies measured by several authors at different Al fractions (see table 1).

We assign the shoulder visible at the low energy side of the (D_X^0, X) transition at the highest excitation energy (figure 2) to TA_X phonon replicas since its energy (13 ± 2 meV) is in between the TA_X phonon energy of 9.76 ± 0.06 meV for GaAs [31] and 13.5 ± 1.5 meV for AlAs [30]. This assignment is in agreement with Kuech *et al* [5, 6]. The ratios between the intensity of the zero-phonon excitonic line and the intensity of the phonon replicas vary in the literature as is shown in table 1. Shealy [8] compared PL spectra of $Al_{0.43}Ga_{0.57}As$ for undoped and Zn-doped ($p = 5 \times 10^{17}$ cm^{-3}) layers and found that the phonon replicas were relatively stronger in the doped material. This is in contrast with measurements of Sturge *et al* [9] in which the phonon replicas could not be detected in n-type Te-doped $Al_xGa_{1-x}As$ whereas they were clearly visible in the undoped material.

For completeness it should be mentioned that Shealy speculated that these transitions involve excitons bound to deep donor or acceptor species rather than phonon replicas of the (D_X^0, X) line. This speculation seems very unlikely since these transitions have been reported in LPE [4, 9, 11] and MOVPE [5, 6, 8] grown material. It would imply that these background impurities are always present in $Al_xGa_{1-x}As$ independently of the growth method of the material.

† This value is measured at room temperature, but since phonon energies are almost temperature independent it is possible to use this value.

Table 1. Phonon energies, assignments and intensity ratios of phonons involved in replicas of the indirect excitonic transition in $Al_xGa_{1-x}As$ measured by several authors. The intensity ratio is defined as the intensity of the zero-phonon excitonic line divided by the intensity of the phonon replica of the excitonic line. Shealy *et al* [8] compared PL spectra for undoped and Zn-doped ($p = 5\times10^{17}$ cm^{-3}) $Al_{0.43}Ga_{0.57}As$ and measured different intensity ratios, whereas Sturge *et al* [9] reported that in Te-doped n-type indirect $Al_xGa_{1-x}As$ no phonon replicas could be detected. Shealy's intensity ratios are labelled u and z for the undoped and Zn-doped material respectively.

	Alferov [4]	Shealy [8]	Sturge [9]	Kuech [5, 6]	Dingle [10]	This work
Al content	$x = 0.38$ [3]	$x = 0.43$	$x = 0.46$	$x = 0.48$	$x = 0.50$	$x = 0.64$
Growth method	LPE	MOVPE	LPE	MOVPE	LPE	MOVPE
First phonon replica						
Phonon energy (meV)	—	—	—	~ 12	—	13 ± 2
Assignment	—	—	—	TA_X	—	TA_X
Intensity ratio	—	—	—	1.3	—	3.3 ± 0.4
Second phonon replica						
Phonon energy (meV)	30	31	31 ± 1	30.2	33	33.2 ± 1.5
Assignment	—	—	—	LA_X	GaAs-like LO_X	GaAs-like LO_X or TO_X
Intensity ratio	60	6^u 0.9^z	4.2	2.3	20	2.4 ± 0.4
Third phonon replica						
Phonon energy (meV)	45	46	46 ± 1	43.8	47	47.3 ± 0.5
Assignment	—	—	—	TO_X	AlAs-like LO_X	AlAs-like LO_X
Intensity ratio	77	7^u 0.7^z	3.0	1.7	8	0.90 ± 0.15

4.2. The 1.951 eV transition: the Y-peak

We have suggested that the Y-peak at 1.951 ± 0.001 eV could be related to indirect transitions in GaAs underneath the $Al_xGa_{1-x}As$. Emission lines involving indirect X_{1c}–Γ_{15v} transitions in GaAs are not normally observed using PL techniques due to carrier thermalization to the direct Γ_{1c} minimum. Olega and Cardona [35] have observed an X_{1c}–Γ_{15v} transition at 1.935 eV at 100 K in heavily Zn-doped GaAs ($p = 9\times10^{19}$ cm^{-3}) in PL spectra obtained with the 2.71 eV Ar^+-laser line. They state that this observation was possible by an enhancement of the luminescence efficiency caused by the violation of the k selection rule effected by the impurities.

High pressures make it possible to induce a direct-to-indirect bandgap transition in GaAs. From their high-pressure measurements Wolford *et al* [33, 34] extrapolated the (D^0_X, X) transition at 1.975 ± 0.004 eV and the indirect X_{1c}–Γ_{15v} bandgap at 2.010 ± 0.008 eV at atmospheric pressure (5 K). However, from Schottky-barrier reflectance measurements Aspnes [36] obtained a value of 1.986 ± 0.006 eV (2 K) for the X_{1c}–Γ_{15v} bandgap. Using Wolford's value of 35±9 meV difference between the indirect gap and the (D^0_X, X) energy, Aspnes's value would result in a (D^0_X, X) energy of 1.946±0.011 eV, which deviates considerably from the value obtained by Wolford *et al*. Summarizing it can be stated that there is no agreement in the literature on a value for the X_{1c}–Γ_{15v} bandgap and the (D^0_X, X) energy in GaAs. The (D^0_X, X) energies, however, are all very close to the measured value for the Y-transition. This value is also in agreement with the value of 1.950 ± 0.016 eV in equation (3) which is the value for the (D_X^0, X) transition in GaAs extrapolated from the (D_X^0, X) transition in $Al_xGa_{1-x}As$.

The facts that (i) the peak energy of the Y-transition is approximately the same as the reported values for the (D_X^0, X) energy in GaAs and (ii) the peak does not shift as a function of Al fraction of the $Al_xGa_{1-x}As$ layer, are indications which are in favour of assigning the Y-peak to an indirect excitonic transition in GaAs rather than to an interface effect. The key to the fact that this indirect transition can be seen is that carriers diffuse from the X_{1c} minima in the $Al_xGa_{1-x}As$ to the X_{1c} minima in the GaAs. Intervalley scattering in the GaAs from the X_{1c} minima to the Γ_{1c} minimum will appear, but some electrons will still recombine radiatively with holes of the Γ_{15v} valence band. This is the main difference from PL experiments performed directly on GaAs since in that case there will be no population of electrons in the X_{1c} minima.

The PL measurements as a function of the $Al_xGa_{1-x}As$ layer thickness showed that the relative intensity of the Y-peak increased near the $Al_xGa_{1-x}As$/GaAs interface. This can be a confirmation for assigning the Y-peak to indirect transitions in the GaAs underneath the $Al_xGa_{1-x}As$, but it could also imply that the Y-peak is related to an interface effect. Lattice mismatch between the GaAs and the $Al_xGa_{1-x}As$ can cause segregation [37] of the $Al_xGa_{1-x}As$ into GaAs and AlAs. In that case there will be precipitates of GaAs in the $Al_xGa_{1-x}As$ at the interface. Since this segregation is more pronounced in (110)-oriented material than in (100) 2° off oriented material [37], this can explain why the Y-peak is more pronounced in the (110)-oriented material (figure 5).

In this paper we have argued that the Y-peak is related to indirect excitonic transitions in GaAs. The arguments are, however, not firm enough to exclude the fact that the peak originates from an interface effect. Such an interface effect can be caused by an isolated centre in the $Al_xGa_{1-x}As$ near the interface or by a heterojunction like triangular quantum well in the X_{1c} conduction band.

The fact that the Y-peak energy hardly depends on temperature is an argument against the assignment to an indirect transition in GaAs, since it is expected that this transition follows the behaviour of the indirect X_{1c}–Γ_{15v} bandgap as a function of temperature. Aspnes [36] postulated that the Varshni [38] equation

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T + \beta} \tag{16}$$

with estimated values for $\alpha = 4.6 \times 10^{-4}$ eV K^{-1} and $\beta = 204$ K is valid for the indirect X_{1c}–Γ_{15v} bandgap. This implies a decrease in the indirect X_{1c}–Γ_{15v} bandgap of approximately 32 meV between 5 and 160 K, which is much more than the measured shift of the Y-peak. However, since there is no experimental verification of the estimated values for α and β, a firm conclusion cannot be drawn and further experiments will be necessary to give a self-consistent explanation for the origin of the Y-transition.

5. Conclusions

In this paper, a study of the low temperature PL properties of $Al_xGa_{1-x}As$ is presented. With PL spectra as a function of irradiance it is possible to give a reliable interpretation of the spectra. The values reported for the excitonic and acceptor related transitions as a function of alloy composition are in good agreement with the literature. In the indirect region phonon replicas of the (D_X^0, X) transition are measured at 13 ± 2, 33.2 ± 1.5 and 47.3 ± 0.5 meV. These phonon energies are in good agreement with the literature and can be assigned to TA_X, GaAs-like LO_X or TO_X and AlAs-like LO_X phonons.

A new transition at 1.951 ± 0.001 eV is measured. This transition is only detectable if indirect $Al_xGa_{1-x}As$ is present although its position is independent of the Al fraction and irradiance. Its relative intensity increases near the $Al_xGa_{1-x}As/GaAs$ interface. We conclude that this transition is either related to indirect excitonic transitions in the GaAs underneath the $Al_xGa_{1-x}As$ or to an interface effect.

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References

[1] Oelgart G, Schwabe R, Heider M and Jacobs B 1987 *Semicond. Sci. Technol.* **2** 466
[2] Monemar B, Shih K K and Pettit G D 1976 *J. Appl. Phys.* **47** 2604
[3] Alferov Zh I, Amosov V I, Garbuzov D Z, Zhilayev Yu V, Konnikov S G, Kop'ev P S and Tromfin V G 1973 *Sov. Phys.-Semicond.* **6** 1620
[4] Alferov Zh I, Garbuzov D Z, Ninua O A and Tromfin V G 1971 *Sov. Phys.-Semicond.* **5** 982
[5] Kuech T F, Veuhoff E and Bradley J A 1984 *Inst. Phys. Conf. Ser.* **74** 181
[6] Kuech T F, Wolford D J, Potemski R, Bradley J A, Kelleher K H, Yan D, Paul Farrel J, Lesser P M S and Pollak F H 1987 *Appl. Phys. Lett.* **51** 505
[7] Kuech T F, Wolford D J, Veuhoff E, Deline V, Mooney P M, Potemski R and Bradley J 1987 *J. Appl. Phys.* **62** 633
[8] Shealy J R, Schaus C F and Eastman L F 1984 *J. Cryst. Growth* **68** 305
[9] Sturge M D, Cohen E and Logan R A 1983 *Phys. Rev.* B **27** 2362
[10] Dingle R, Logan R A and Nelson R J 1979 *Solid State Commun.* **29** 171
[11] Dingle R, Logan R A and Arthur J R Jr 1977 *Inst. Phys. Conf. Ser.* **33a** 210
[12] Stringfellow G B and Linnebach R 1979 *J. Appl. Phys.* **51** 2212
[13] Sugiyama K and Kawakami T 1971 *Japan. J. Appl. Phys.* **10** 1007
[14] Shah J, Miller B I and DiGiovanni A E 1972 *J. Appl. Phys.* **43** 3436
[15] van Sark W G H J M, Janssen G J H M, de Croon M H J M, Tang X, Giling L J, Arnold Bik W M, Dunselman C P M, Habraken F H P M and van der Weg W F 1988 *J. Appl. Phys.* **64** 195
[16] SpringThorpe A J, King F D and Becke A 1975 *J. Electron. Mater.* **4** 101
[17] Lifshitz N, Jayaraman A and Logan R A 1980 *Phys. Rev.* B **21** 670
[18] Yang J J, Moudy L A and Simpson W I 1982 *Appl. Phys. Lett.* **40** 244
[19] Kobayashi M, Yokoyama T and Narita S 1983 *Jap. J. Appl. Phys.* **22** L612
[20] van de Ven J, Rutten G M J, Raaijmakers M J and Giling L J 1986 *J. Cryst. Growth* **76** 352
[21] van der Pauw L J 1958 *Philips Res. Repts.* **13** 1
[22] Leite R C C and DiGiovanni A E 1967 *Phys. Rev.* **153** 841
[23] Lucovsky G, Varga A J and Schwarz R F 1965 *Solid State Commun.* **3** 9
[24] Nathan M I and Morgan T N 1966 *Physics of Quantum Electronics* ed P L Kelley, B Lax and P E Tannenwald (New York: McGraw Hill) p 478

[25] Huber A M, Laurencin G and Razeghi M 1983 *J. Physique Coll.* C4 **44** 409
[26] Casey H C Jr and Panish M B 1978 *Heterostructure Lasers* (New York: Academic) parts A and B
[27] Lee H J, Juravel L Y and Woolley J C 1980 *Phys. Rev.* B **21** 659
[28] Kim O K and Spitzer W G 1979 *J. Appl. Phys.* **50** 4362
[29] Chen Y S, Shockley W and Pearson G L 1966 *Phys. Rev.* **151** 648
[30] Monemar B 1973 *Phys. Rev.* B **8** 5711
[31] Waugh J L T and Dolling G 1963 *Phys. Rev.* **132** 2410
[32] Fasol G, Tanaka M, Sakaki H and Horikoshi Y 1988 *Phys. Rev.* B **38** 6056
[33] Wolford D J and Bradley J A 1985 *Solid State Commun.* **53** 1069
[34] Mariette H, Wolford D J and Bradley J A 1986 *Phys. Rev.* B **33** 8373
[35] Olego D and Cardona M 1979 *Solid State Commun.* **32** 1027
[36] Aspnes D E 1976 *Phys. Rev.* B **14** 5331
[37] Kuan T S, Kuech T F, Wang W I and Wilkie E L 1985 *Phys. Rev. Lett.* **54** 201
[38] Varshni Y P 1967 *Physica* **39** 149