Alloy broadening in photoluminescence spectra of $Al_xGa_{1-x}As$

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The origins of line broadening in photoluminescence spectra of $Al_xGa_{1-x}As$ are analyzed. Thermal broadening, the influence of macroscopic inhomogeneity, and alloy broadening due to random cation distribution are investigated. Quantitative models for the linewidths of the bound exciton and the band-to-acceptor transition are developed, based on compositional fluctuations within the crystal volumes which are characteristic of the two transitions. The linewidths are calculated without any fitting parameter and agree with experimental results. Alloy clustering can be definitely excluded for samples grown (1) in (100) orientation and (2) under optimum conditions. The investigation of alloy broadening in $Al_xGa_{1-x}As$ leads to a quantitative understanding of low-temperature photoluminescence spectra of ternary and also of quaternary III-V semiconductors.

I. INTRODUCTION

Interest in ternary and quaternary III-V semiconductors increased rapidly during the last decade, because their band-gap energies and lattice constants can be varied systematically by appropriate choice of alloy composition.[1] This degree of freedom provides new electronic and optoelectron devices, such as the high-electron-mobility transistor[2] and quantum-well lasers.[3]

The random distribution of atoms in ternary as well as in quaternary alloy systems, however, implies new phenomena not found in elemental group-IV and binary III-V semiconductors. The electron and hole mobilities in ternary and quaternary semiconductors are reduced by alloy scattering.[4] This scattering mechanism is caused by potential fluctuations induced by the random distribution of the different group-III or group-V elements in the crystal. The calculation of the alloy scattering mobility[5] involves a free parameter, usually called the "alloy scattering potential." A calculation without a fitting parameter has not yet been performed.

Deep-level transient spectroscopy (DLTS) measurements made on GaP_xAs_{1-x} (Ref. 6) reveal a significant broadening of the capacitance change—versus—temperature peaks. The broadening was assumed to be caused by the random distribution of the anions in this material. The calculation of the DLTS spectra was performed by means of a Gaussian distribution with the standard deviation used as a fitting parameter.[6] The largest broadening was expected at an alloy composition of $x=0.5$.

In $Al_xGa_{1-x}As$, the random distribution of Al and Ga atoms on the group-III sites not only strongly influences the electrical properties of the material, but also its optical properties, most sensitively in terms of photoluminescence (PL) spectra. The full width at half maximum (FWHM) of the photoluminescence lines are much broader at low temperatures than expected from the customary thermal broadening, which should be on the order of the thermal energy, kT. Tsang *et al.*[7] investigated photoluminescence line broadening caused by low substrate temperature and high arsenic to gallium flux ratio in $Al_xGa_{1-x}As$ grown by molecular-beam epitaxy.

In this work we have developed a quantitative model for the linewidth of the excitonic and the band-to-acceptor recombinations, which we describe in Sec. II. This model is based on the fact that the occupation of the cation (group-III) sites of the ternary semiconductor by Al and Ga occurs randomly. Experimental details are given in Sec. III. Experimental results and their comparison with the model are discussed in Sec. IV.

Our model in principle is not only applicable to $Al_xGa_{1-x}As$ but also to other ternary and quaternary III-V semiconductors where the distribution of atoms is random. The quantitative model gives a new understanding of the optical properties of semiconductor alloys.

II. THEORETICAL MODEL OF PHOTOLUMINESCENCE LINE BROADENING IN $Al_xGa_{1-x}As$

Our model assumes that Al and Ga atoms are distributed randomly on the group-III sites in an *ideal* crystal. The probability of finding an Al atom on any group-III site is given by the alloy composition x. We do not take into account macroscopic inhomogeneities in lateral as well as in growth direction of the epitaxial layer. Broadening mechanisms are not analyzed, if they are due to inferior crystal quality, defects, or alloy clustering. We thus calculate the *minimal* theoretical linewidth of an ideal alloy semiconductor. A hydrogenlike impurity is assumed for the acceptor, making effective-mass theory applicable.

Only a limited volume, V, of the semiconductor determines the energy of the photon emitted during the excitonic as well as band-to-acceptor radiative transition. A finite number, KV, of group-III elements, where K is the density of cations in the crystal, is within this volume. The cation density in a zinc-blende lattice is given by

$$K=4a_0^{-3} \tag{1}$$

because there are four cations in the unit cell of the crys-

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tal with lattice constant a_0. The lattice constant a_0 does not change significantly with the Al mole fraction, and therefore $K=2.21\times10^{22}$ cm^{-3} in the entire composition range $0\leq\times\leq1$ of $Al_xGa_{1-x}As$. The probability of finding n Al atoms within a volume V is given by the binomial distribution (Bernoulli distribution)

$$p(n)=\begin{bmatrix}kV\\n\end{bmatrix}x^n(1-x)^{KV-n}\ . \tag{2}$$

This distribution has the mean value $\mu=xKV$ and the variance $\sigma^2=KVx(1-x)$. The linewidth (FWHM) of photoluminescence lines is much larger than kT at low temperatures and results from the scatter of the band-gap energy, which in turn is caused by the statistical distribution of the two kinds of group-III elements (Al and Ga). The broadening of photoluminescence lines in ternary and quaternary III-V semiconductors, which we call alloy broadening, is most easily investigated at low temperatures where thermal broadening effects are negligible. In the next two sections the linewidth of the excitonic as well as the band-to-acceptor recombination will be calculated.

A. Linewidth of excitonic recombination

A number of publications on photoluminescence have demonstrated that high-quality material of $Al_xGa_{1-x}As$ displays a high-energy peak due to bound excitonic (BE) recombination.[8–10] In elemental or binary III-V or II-VI semiconductors the linewidth of the bound exciton is smaller than kT, since the bound exciton has no kinetic energy. The theoretical line shape of the bound exciton can therefore be approximated by a Lorentzian function in all nonalloy semiconductors. In the ternary semiconductor $Al_xGa_{1-x}As$, statistical effects must also be considered. The excitonic volume V_{exc} results from the hydrogen model and is

$$V_{exc}=\frac{4}{3}\pi\left[\frac{\epsilon_r}{m_r/m_0}a_B\right]^3, \tag{3}$$

where a_B is the Bohr radius, m_r is the reduced mass given by

$$m_r=(m_{\Gamma e}^{-1}+m_{\Gamma hh}^{-1})^{-1}\ . \tag{4}$$

$m_{\Gamma e}$ and $m_{\Gamma hh}$ are the electron- and heavy-hole effective masses, respectively. In the excitonic volume there are $V_{exc}K$ cations, i.e., approximately 1.6×10^5 for GaAs. In $Al_xGa_{1-x}As$ the *average* number of Al atoms within the excitonic volume is xKV_{exc}. The actual number, however, varies due to the statistical distribution of atoms. The standard deviation of the alloy composition within the excitonic volume is given by the binomial distribution

$$\sigma_x=\left[\frac{x(1-x)}{KV_{exc}}\right]^{1/2}. \tag{5}$$

Using the data of Casey and Panish for the band gap E_g versus alloy composition x [$dE_g/dx=1.247$ eV for $0\leq x\leq0.45$ (Ref. 11)], we obtain the standard deviation of the band-gap energy

$$\sigma_E=\frac{dE_g}{dx}\left[\frac{x(1-x)}{KV_{exc}}\right]^{1/2}. \tag{6}$$

From Eqs. (5) and (6) we see that the line broadening due to statistical distribution is 0 at $x=0$ (GaAs) and grows with increasing Al alloy content. If x is increased beyond the direct-indirect crossover at $x=0.45$, the line broadening should become smaller again and approach 0 at $x=1.0$ (AlAs). The present study is restricted to the composition range of the direct semiconductor where the Γ-point minimum is lower in energy than the X-point minimum. Close to the direct-indirect crossover point, the vicinity of the Γ-, X-, and L-point minima impose further complications on the theoretical treatment of alloy broadening not considered here. The binomial distribution can be approximated by a Gaussian distribution for the sake of simplicity since the necessary condition $KV_{exc}x(1-x)\gg10$ is fulfilled in nearly the entire composition range $0.01\leq\times\leq0.45$. The full width at half maximum of a Gaussian distribution is 2.36 times of its standard deviation. Consequently, the linewidth of the bound-exciton recombination is given by

$$\Delta E_{exc}=2.36\sigma_E\ . \tag{7}$$

We next try to estimate quantitatively the fluctuation of the band gap exerted upon the exciton. If there are two excitons at a distance of $2r_{exc}$, the local-alloy compositions within the volumes may be considered to be independent. Thus the average change of the gap energy versus the spatial coordinate z is given by

$$\frac{dE_g}{dz}=\tfrac{1}{2}\sigma_E r_{exc}^{-1}\ . \tag{8}$$

The fluctuation of the gap energy, which implies an average electric field of magnitude

$$F=\tfrac{1}{2}q^{-1}\sigma_E r_{exc}^{-1}\ , \tag{9}$$

raises the question whether the binding of the exciton to the impurity may be overcome by the electric field due to the Poole-Frenkel effect. A simple calculation yields, however, that this field is insufficient to release the exciton from the impurity, if the binding energy of an exciton bound to a carbon acceptor in GaAs [3.5 meV (Ref. 12)] is used.

B. Linewidth of the electron-to-acceptor recombination

An electron in the conduction band (CB) recombines with a hole bound to an acceptor in the free-to-bound transition, also called (e,A^0) transition. The scatter of the alloy composition x changes the energies of the conduction- and valence-band (VB) edge. According to Dingle's rule[13] (DR) for $GaAs/Al_xGa_{1-x}As$ heterostructures, 85% and 15% of the band-gap change affects the CB- and VB-edge energies, respectively. Consequently, we must treat the fluctuations of the VB and CB separately. The fluctuations of the VB and CB are calculated by the Bohr radius of the acceptor and the mean free path of electrons, respectively.

The Bohr radius of the acceptor, r_A, is

$$r_A=\frac{\epsilon_r}{m_{\Gamma hh}/m_0}a_B\ , \tag{10}$$

where a_B is the Bohr radius of the hydrogen atom. The standard deviation of the energy is then given by

$$\sigma_E^A=0.15\frac{dE_g}{dx}\left[\frac{x(1-x)}{KV_A}\right]^{1/2}, \tag{11}$$

where 0.15 results from Dingle's rule, and V_A is the volume of the sphere determined by the Bohr radius of the acceptor.

The fluctuations of the electron energy in the conduction band is determined by the mean free path of electrons

$$\lambda_e=v_{\rm th}\tau\ , \tag{12}$$

where $v_{\rm th}$ is the thermal velocity of electrons and τ is the momentum relaxation time usually estimated on the order of 10^{-13} sec.[14] This time gives a free path of electrons of about 70 Å if the electron temperature is 10 K. The value agrees with the mean free path in GaAs estimated by other authors to be 100–200 Å.[15] The energy standard deviation of electrons in the conduction band is

$$\sigma_E^e=0.85\frac{dE_g}{dx}\left[\frac{x(1-x)}{KV_e}\right]^{1/2}, \tag{13}$$

where the factor 0.85 results from Dingle's rule (DR), and V_e is the volume of the sphere determined by the mean free path of electrons λ_e.

In the band-to-acceptor transition the energy fluctuations of electrons and holes add up according to

$$\sigma_t^2=(\sigma_E^A)^2+(\sigma_E^e)^2\ . \tag{14}$$

The linewidth of the luminescence line ΔE_{eA} of Gaussian shape is then 2.36 times the standard deviation given by Eq. (14):

$$\Delta E_{eA}=2.36\sigma_t\ . \tag{15}$$

The thermal linewidth of the band-to-acceptor transition amounts to 1.8 kT for Maxwell-Boltzmann statistics.[16] At low temperatures ($T=2$ K), however, the thermal broadening can be neglected, since it is much smaller than the contribution of alloy broadening. At higher temperatures ($T\simeq 10$ K), where thermal broadening of photoluminescence lines occurs, the line shape of the band-to-acceptor transition is given by the convolution of the line shapes of thermal and alloy broadening

$$I(\hbar\omega)\sim\int_{-\infty}^{+\infty}[\hbar\omega^*-(E_g-E_a)]^{1/2}\times\exp\left[-\frac{\hbar\omega^*-(E_g-E_a)}{kT}\right]\times\exp\left[\frac{\hbar\omega^*-\hbar\omega}{\sigma_E}\right]^2 d(\hbar\omega^*)\ . \tag{16}$$

The calculated linewidths of the bound exciton $\Delta E_{\rm exc}$ and the free-to-bound transition ΔE_{eA} are depicted in Fig. 1 as a function of alloy composition x. For the free-to-bound transition only alloy broadening but no thermal broadening is assumed; therefore, this linewidth only applies to *low*-temperature photoluminescence. Both the excitonic and the band-to-acceptor linewidth mainly show a square-root dependence on the alloy composition. However, the dependences of the effective masses and the dielectric constant on the alloy composition slightly change the square-root behavior.

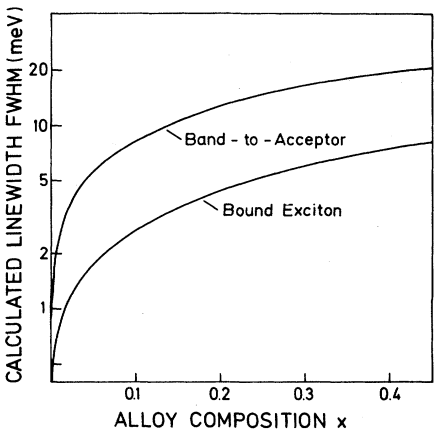

FIG. 1. Theoretical linewidths of bound exciton (BE) and band-to-acceptor transition (e,A^0) in photoluminescence spectra of $Al_xGa_{1-x}As$ versus alloy composition x at a lattice temperature of 2 K according to Eqs. (7) and (15).

In previous theoretical work, primarily the modification of the density of states was considered to be the origin of alloy broadening. Baranovskiĭ and Efros[17] assumed that the square-root behavior of the density of states versus energy is obliterated in alloy semiconductors. Sayakanit[18] suggested a modification of the density-of-states function due to a Gaussian random potential. Goede *et al.*[19] investigated the influence of disorder effects on excitons in $CdS_{1-x}Se_x$. However, the approaches of those authors yielded an expected theoretical band-edge smearing which is much smaller than the observed linewidths. Binomial statistics have not been used in previous investigations.

The simple model proposed in this section also applies to ternary III-V semiconductors other than $Al_xGa_{1-x}As$ by modifying the material parameters. For quaternary semiconductors of the type $A_xB_{1-x}C_yD_{1-y}$ and $(A_xB_{1-x})_yC_{1-y}D$ the line broadening due to x- and y-fluctuations should add up, so that the resulting standard deviation is given by

$$\sigma_Q=(\sigma_{xQ}^2+\sigma_{yQ}^2)^{1/2}\ . \tag{17}$$

Thus in quaternary III-V semiconductors one expects even broader PL lines from the model, compared to ternary semiconductors.[16] However, the distribution of atoms in alloy materials might not be completely random under unusual growth conditions such as extremely low growth rates, or if the formation energies of the constituent molecules are very different. The linewidths of the excitonic and the band-to-acceptor recombination will next be compared with experimental linewidths after a description of some experimental details.

III. EXPERIMENTAL

The $Al_xGa_{1-x}As$ epitaxial layers, typically $2-3$ μm thick for this study, are grown by molecular-beam epitaxy (MBE) on (100)-oriented undoped semi-insulating GaAs substrates at substrate temperatures ranging from 590 to 670 °C in different growth runs. The substrate is continuously rotating azimuthally during growth to provide excellent compositional and thickness homogeneity over the whole substrate area. Typical growth rates are 1 μm/h for deposition of GaAs at 580 °C and 1.2 μm/h for deposition of $Al_{0.25}Ga_{0.75}As$ at 650 °C. Further details of the growth procedure using As_4 as arsenic source have been described elsewhere[20] and hence are not repeated here. However, we would like to emphasize the importance of the *growth temperature* T_S which must be a compromise between the requirements for AlAs growth (higher T_S of about 700 °C) and for GaAs growth (lower T_S of about 580 °C), and of the effective As- to (Al + Ga)-*flux ratio* on the growing surface which has to be kept within a rather narrow range that clearly provides As-stabilized growth conditions even at high-growth temperatures.

During photoluminescence measurements, the sample is mounted on a Cu block and placed either in a liquid-He bath cryostat pumped to temperatures below 2 K or in a variable-temperature continuous-flow cryostat. For excitation we use the 647-nm ($\hbar\omega_{exc}=1.916$ eV) line of a cw Kr^+ laser or the 488 nm ($\hbar\omega_{exc}=2.540$ eV) line of a cw Ar^+ laser. The excitation energy of the laser does not exhibit any significant effect on the PL spectra. The excitation power density is varied between 10^{-1} and 10^2 W/cm^2 using neutral density filters. The luminescence light is analyzed with a 1-m single-pass grating monochromator and detected by a cooled GaAs photocathode photomultiplier (RCA model no. C 31034A) attached to a photon-counting system controlled by a desk-top computer. The detector has a relatively flat response for the wavelengths between 300 and 880 nm which is the range of interest for $Al_xGa_{1-x}As$.

IV. RESULTS AND DISCUSSION

The nominally undoped $Al_xGa_{1-x}As$ films used for our investigations exhibit p-type conductivity in the high 10^{14} cm^{-3} range at 300 K due to residual carbon acceptors. The total impurity content amounts to approximately 1×10^{15} cm^{-3}. It is well established from GaAs layers having similar impurity concentrations that the random electric fields due to the corresponding ionized impurities do not result in a significant line broadening. High-quality $Al_xGa_{1-x}As$ layers of composition below the direct-to-indirect band gap crossover point at $x=0.45$ show two principal near-band-edge luminescence features, as indicated in the inset of Fig. 2. The high-energy line arises from BE recombination. The prominent low-energy band in the spectrum results from carbon-related band-to-acceptor (e,A^0) recombination yielding a carbon-acceptor binding energy of approximately 30 meV for this alloy composition.

We first discuss the effect of extrinsic parameters, including growth temperature and macroscopic inhomogeneities, on the line broadening to evaluate the minimum

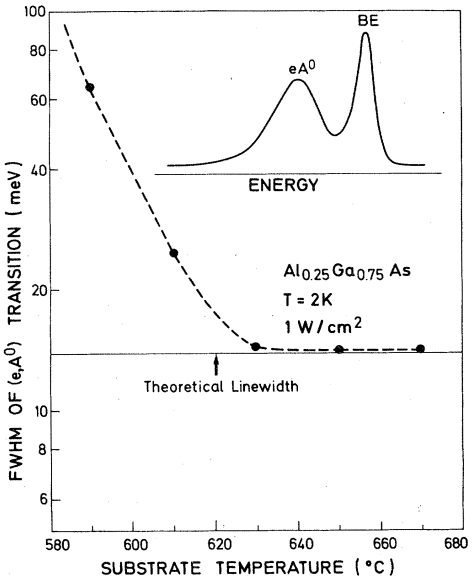

FIG. 2. Linewidth of the band-to-acceptor transition in photoluminescence spectra of $Al_xGa_{1-x}As$ as a function of substrate temperature T_S. The solid curve gives the theoretical linewidth for the alloy composition of $x=0.25$. The inset shows a typical photoluminescence spectrum obtained from a sample grown under optimized conditions.

half width achievable at optimum growth conditions. Subsequently, we discuss the intrinsic effect of alloy broadening owing to random distribution of Al and Ga in $Al_xGa_{1-x}As$ and the influence of thermal broadening upon luminescence linewidth, and we compare the experimental results with our model of Sec. II.

A. Influence of extrinsic effects on line broadening

Several authors have shown[7,10,21] that substrate temperatures in excess of 630 °C during MBE growth are required to obtain $Al_xGa_{1-x}As$ layers of good luminescence quality from tetrameric arsenic (As_4) species. The substrate temperature determines surface diffusion velocities and reevaporation rates of adatoms on the growing surface. Low substrate temperatures thus favor the incorporation of defect like vacancies resulting in a deterioration of the crystal quality. In Fig. 2 we demonstrate that the linewidth of the band-to-acceptor (e,A^0) transition in the luminescence spectra of $Al_xGa_{1-x}As$ decreases drastically with increasing substrate temperatures for $T_S\leq630$ °C. At growth temperatures higher than 630 °C only slight variation of the linewidth is observed. In the range $630\leq T_S\leq670$ °C the linewidth has approached a saturated value which is given by the theoretical linewidth derived from Eq. (15) of our model. The observed saturation indicates that in $Al_xGa_{1-x}As$ samples grown at substrate temperatures $630\leq T_S\leq670$ °C the (e,A^0) linewidth is apparently no longer determined by this extrinsic parameter but by fundamental physical properties of the ternary alloy. With further enhancement of the substrate temperature ($T_S\geq670$ °C) little change is observed at first,

until at $T_S \simeq 700\,^\circ C$ the linewidth becomes broader again.

At this point we must recall two important aspects of MBE growth of $Al_xGa_{1-x}As$. First, the effective As to (Al + Ga)-flux ratio on the growing surface is a very important additional extrinsic parameter for growth of high-quality $Al_xGa_{1-x}As$ (Ref. 7). (The term "effective" arsenic flux means that amount of As_4 actually available for incorporation on the growing surface, taking into account the reevaporation and the second-order growth mechanisms for As_4 interaction.[22]) This As to (Al + Ga)-flux ratio must be adjusted within a rather narrow range that clearly ensures As-stabilized growth conditions at all chosen substrate temperatures.[20] Second, difficulties may be encountered with an accurate determination of the actual temperature of the growth surface during MBE at $T_S \geq 630\,^\circ C$ either by a thermocouple embedded in the Mo heating block on which the GaAs substrate is mounted with In, or by a calibrated optical pyrometer through a special UHV (ultrahigh vacuum) viewport directed normal to the substrate surface. Therefore, favorable growth temperatures reported in most experiments are strictly valid only for the specific MBE-growth system used, and differences up to 100 °C occur between values reported from systems in different laboratories. In addition, we must take into account that the most favorable growth temperature is also correlated to the growth rate in that to a first approximation a higher rate requires a slightly higher temperature T_S.

In analogy to the (e,A^0) linewidth, the growth temperature has also a strong impact on the peak intensity ratio of the band-to-acceptor to bound-exciton recombination line in the photoluminescence spectra of $Al_xGa_{1-x}As$. If we plot the intensity ratio $I_{e,A^0}/I_{BE}$ versus substrate temperature T_S, as shown in Fig. 3, we observe a strong increase of the peak intensity of the bound-exciton line (i.e., a steep decrease of $I_{e,A^0}/I_{BE}$) with increasing T_S, particularly when $T_S \leq 630\,^\circ C$. In the range $630 \leq T_S \leq 670\,^\circ C$ the ratio $I_{e,A^0}/I_{BE}$ begins to saturate, and the optimum values are achieved at 670 °C, indicating a superior crystal quality. At $T_S \leq 580\,^\circ C$ the BE peak reaches noise level of our experimental setup. The recombination probability of the (e,A^0) transition is proportional to the free-electron concentration n, while the probability of the excitonic recombination is proportional to the product np. Consequently, the high $I_{e,A^0}/I_{BE}$ ratio is observed for $Al_xGa_{1-x}As$ samples grown at low substrate temperatures which, together with the experimental observation that the overall luminescence intensity is lower in these samples, indicates that an increasing number of carriers are involved in a Shockley-Read—type nonradiative recombination process.

In addition to the growth temperature, a lateral macroscopic variation of the alloy composition due to the cosine distribution of the effusion cell flux[23] could also affect the linewidth detected in $Al_xGa_{1-x}As$ luminescence spectra. We have studied macroscopic lateral deviation of the alloy composition x across the whole substrate area carefully, and the results from a representative sample are depicted in Fig. 4. We observe a very small linear dependence of the BE peak energy on the lateral coordinates y and z. Quantitatively the change of the bound-exciton energy with lateral dimensions is evaluated to be rather small (≤ 1 meV/cm), assuming that the variation of the BE energy corresponds to a variation of the band-gap energy. The corresponding change of the band-gap energy implies a variation of the alloy composition x of less than 0.001 per cm. With the use of a spot diameter of 300 μm for the exciting laser light, the variation of the band-gap energy within this area is less than 30 μeV. This result clearly demonstrates that the minor macroscopic fluctuations of the alloy composition in the investigated samples are too small to give rise to the observed linewidth in the photo-

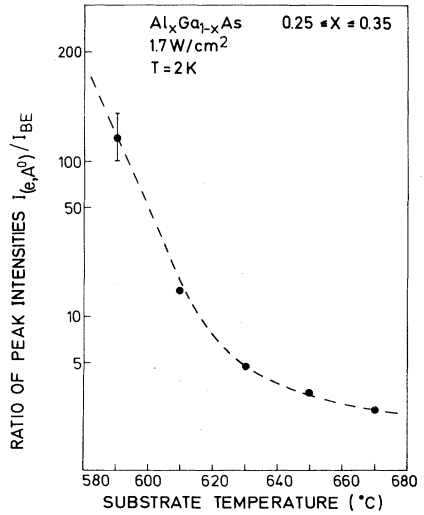

FIG. 3. Ratio of peak intensities of the bound exciton I_{BE} and of the band—to—neutral-carbon-acceptor transition I_{e,A^0} in photoluminescence spectra of $Al_xGa_{1-x}As$ as a function of substrate temperature T_S.

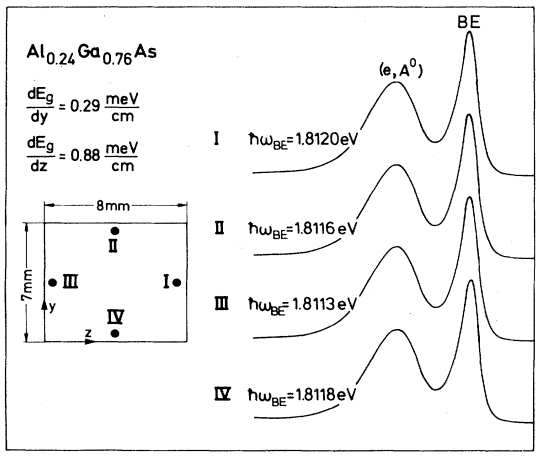

FIG. 4. Variation of photoluminescence spectra taken at four different points of the samples area as indicated. The energy of the bound-exciton line depends linearly on the probing site. During growth, the middle of the rotating substrate holder was at the upper-left angle of the sample.

luminescence spectra. Even for samples prepared with carefully optimized extrinsic parameters the measured linewidths are much broader than expected from the binary constituents of the ternary material.

B. INFLUENCE OF INTRINSIC PROPERTIES ON LINE BROADENING

The lowest achievable linewidth in the photoluminescence spectra of $Al_xGa_{1-x}As$ is limited by statistical fluctuations of the alloy composition caused by the random distribution of the group-III elements on the cation sites of the crystal. This important intrinsic broadening effect due to statistical fluctuations, i.e., alloy broadening, has been analyzed theoretically in Sec. II. In this section we compare experimental and theoretical results and we discuss the influence of lattice and electron temperature on the photoluminescence spectra.

In $Al_xGa_{1-x}As$ the exciton is bound to carbon, which is the dominant residual impurity in material grown by molecular-beam epitaxy and by metalorganic chemical-vapor deposition (MO CVD).[9,10,20,24,25] Free excitons have never been clearly resolved in this ternary alloy. In Fig. 5 we compare the measured and calculated photoluminescence spectrum obtained from $Al_xGa_{1-x}As$ of composition $x=0.24$. The full width at half maximum is 5.2 and 15 meV for the bound-exciton line and the band-to-acceptor line, respectively. The shape of the calculated spectrum consists of two superimposed Gaussian curves having a different standard deviation. The excitonic line is narrower than the band-to-acceptor line. This result is consistent with the model of Sec. II (see also Fig. 1). A good agreement of experiment and theory can be verified in the spectrum of Fig. 5, except at the low-energy shoulder of the excitonic and of the band-to-acceptor transition. The observed small deviations from theory are probably caused by excitons bound to impurities deeper than carbon and by band-to-acceptor transitions of acceptors deeper than carbon (e.g., beryllium and silicon). The energetic separation between the bound-exciton line and the free-to-bound transition in Fig. 5 is measured to be 20.6 meV. With the use of an exciton binding energy of 8.9 meV, which follows from the sum of the free-exciton binding energy (=5.4 meV) plus the impurity binding energy (=3.5 meV), the ground-state energy of the carbon acceptor can be estimated to be 29.5 meV below the conduction band. This energy is in good agreement with the results reported by other authors.[8,20] Finally, the superior material quality of the ternary $Al_xGa_{1-x}As$ layers used for the present investigation is demonstrated by the occurrence of the phonon replica of the bound exciton at 1.7683 eV in Fig. 5.

When we increase the power density of the incident laser beam during photoluminescence measurements on $Al_xGa_{1-x}As$, the electron temperature is evaluated so that thermal broadening effects become significant. In Fig. 6 the linewidth (FWHM) of the band-to-acceptor recombination is shown as a function of the power density of the exciting laser for the sample of Fig. 5. The linewidth increases by 2.5 meV from rather low- to high-power densities. The peak energy, however, does not significantly shift with the laser intensity, as expected for band-to-acceptor transitions. The electron temperature can be obtained by numerically solving Eq. (16) and fitting the calculated to the experimental linewidth. In this case, the observed broadening corresponds to an electron temperature as high as approximately 57 K. The linewidth of the bound exciton, on the other hand, is not affected significantly by a variation of the excitation intensity.

The observed variation of the excitonic linewidth as a function of the alloy composition is not unique to MBE-grown $Al_xGa_{1-x}As$ but is a general property of the material. This result is illustrated in Fig. 7, where the theoretical variation of the excitonic linewidth is compared with experimental data points of this work and obtained by other authors. The observed linewidths increase strongly with alloy composition, in accordance with our model of Sec. II. Furthermore, an excellent agreement between experimental data obtained from MBE as well as MO CVD-grown $Al_xGa_{1-x}As$ layers and theory is evident.[26] A maximum value of $x=0.45$ is used for the alloy composition in the present study. At this alloy composition the direct-to-indirect crossover occurs.

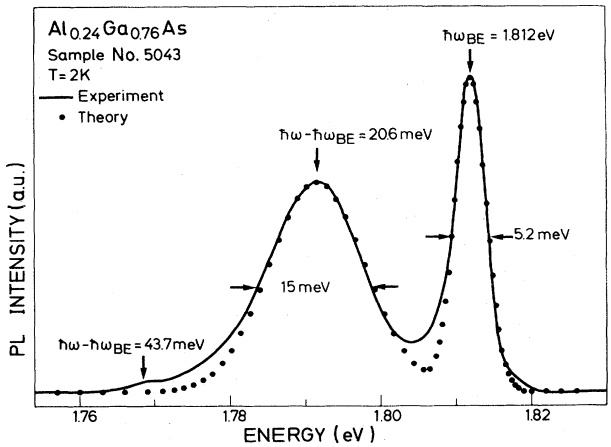

FIG. 5. Comparison between experimental (solid curve) and theoretical (dots) lineshape of the BE and (e,A^0) transition in the photoluminescence spectrum obtained from $Al_{0.24}Ga_{0.76}As$.

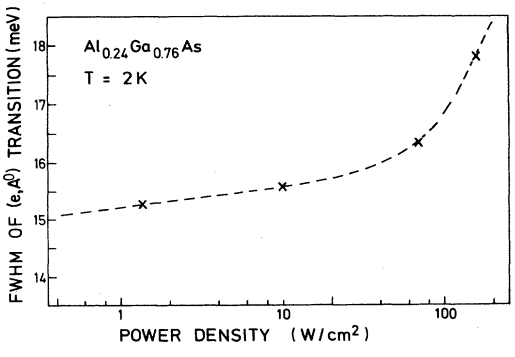

FIG. 6. Linewidth of the band-to-acceptor recombination versus power density of the exciting laser line. Electron heating at high-power densities leads to additional broadening.

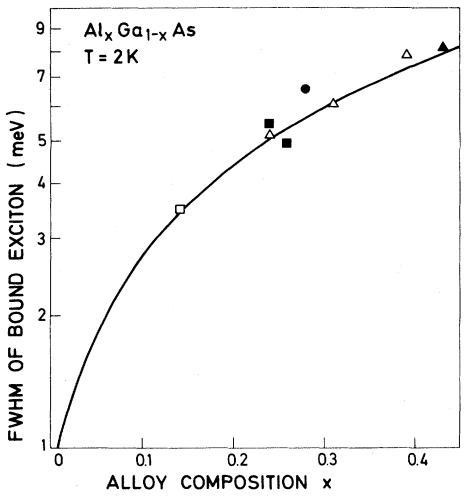

FIG. 7. Comparison of theoretical excitonic linewidth versus alloy composition with experimental data obtained in the present work and reported by other authors. (Closed circle, sample A-118 of Ref. 9, Fig 3; open square, Ref. 25; closed squares, Ref. 24; open triangles, from this work; closed triangle Ref. 20.)

Finally, we must take into account the influence of the lattice temperature on the luminescence linewidths and intensities. The *excitonic* linewidth does *not* change with lattice temperature and remains at 5.2 meV for $x=0.24$ in the whole temperature range investigated ($2 \leq T \leq 35$ K). Furthermore, the peak energy of the exciton does not change with temperature. The peak intensity of the bound-exciton transition, on the other hand, decreases with enhanced temperature. An Arrhenius plot of the peak intensity versus $1/T$ yields an estimate of the binding energy of the exciton to the impurity of approximately 3.0 meV,[27] which differs slightly from the value found in GaAs.[8] The linewidth of the *band-to-acceptor* transition depends on lattice temperature as it does on electron temperature. As indicated in Fig. 8, a moderate broadening of the line is observed from 2 to 35 K. The linewidth calculated from Eq. (16) is included in the plot. This linewidth takes into account alloy broadening as well as the thermal broadening. A comparison of the experimental data with the expected theoretical linewidth clearly reveals that thermal broadening is most probably the origin of the lattice temperature dependence of the linewidth.

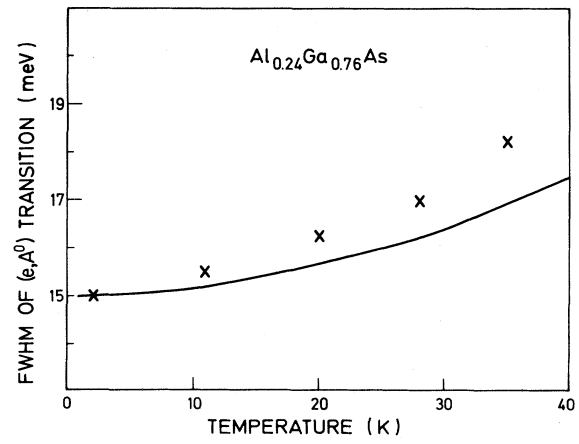

FIG. 8. Lattice temperature dependence of the linewidth of the free-to-bound (e,A^0) recombination in photoluminescence spectra of $Al_{0.24}Ga_{0.76}As$. The calculated linewidth (Eq. 16), which takes into account alloy and thermal broadening, is included in the plot (solid curve).

At a measuring temperature of 2 K and under moderate excitation conditions, however, the most important broadening mechanisms for the excitonic and the band-to-acceptor transition are statistical compositional fluctuations within the crystal volumes that are characteristic of the two luminescence transitions and are well described by our theoretical model. Alloy broadening is an inherent material property of ternary and quaternary III-V semiconductors.

V. CONCLUSION

Linewidths of photoluminescence spectra in the ternary semiconductor $Al_xGa_{1-x}As$ grown by molecular-beam epitaxy have been investigated. At low temperatures the photoluminescence lines due to excitonic as well as free-to-bound transitions are much broader in $Al_xGa_{1-x}As$ as compared to GaAs. The dependence of the linewidth on the crystal-growth temperature is only weak in the range $630 \leq T_S \leq 670$ °C. In this temperature range the linewidths of the photoluminescence spectra are determined by inherent properties of this alloy material. Besides thermal broadening due to the Maxwellian velocity distribution of electrons, we took into account macroscopic as well as statistical fluctuations of the alloy composition during our analysis. Macroscopic fluctuations play a minor role in samples grown on a rotable substrate holder under optimized growth conditions. Statistical fluctuations of the alloy composition, which are caused by the random distribution of Al and Ga on the cation sites of the crystal, are responsible for photoluminescence line broadening at low temperatures. The linewidths of the bound-exciton and band-to-acceptor transitions are determined quantitatively without a fitting parameter. The good agreement of the experimental and theoretical excitonic linewidth clearly demonstrates that no alloy clustering is present in the samples investigated. For the band-to-acceptor transition the two decisive mechanisms are thermal broadening and alloy broadening.

Alloy broadening not only affects homogeneous alloy materials but also quantum-well heterostructures with a ternary material as active layer. Broader lines for spontaneous emission as compared to quantum wells with a binary as an active layer are expected from our investigations.

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