Compositional disorder anomalies in Ga(N,P,As)/GaP quantum well structures

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Abstract. Photoluminescence (PL) in many-component semiconductor heterostructures is strongly affected by disorder potential caused by compositional fluctuations. Our experimental study of the temperature-dependent PL in Ga(N,P,As)/GaP QW indicates the intriguing feature that the scale of disorder potential decreases with increasing concentration of the fluctuating compositional component (nitrogen). We claim that this effect strongly indicates that the dependence of the band structure on the concentration of the fluctuating compositional component weakens and the effective mass decreases with increasing concentration (in 2% ÷ 4% domain). This conclusion is supported by theoretical estimates within the analytical theory of compositional fluctuations in mixed crystals.

1. Introduction

The application of QW structures in optoelectronic devices requires detailed knowledge of their optical quality. Being grown at extreme non-equilibrium conditions the QW structures inevitably possess a certain degree of disorder due to their alloy structure and/or to imperfect interfaces. The disorder gives rise to carrier localization that dramatically affects optical properties. Measurements of the photoluminescence (PL) response have become a standard tool for characterizing the quality of the sample. In many situations, depending on various microscopic parameters, the Coulomb interaction between the photo-excited electrons and holes can be treated by considering excitons moving in an effective disorder potential [1]. Because of exciton localization, the PL peak energy and the PL linewidth demonstrate non-monotonous temperature dependencies shown schematically in Fig.1. The main experimentally observed trends of temperature-dependent PL spectra are (i) an anomalous redshift of the PL peak energy in the range of intermediate temperatures, so-called S-shape behavior; (ii) a peak of the PL linewidth within a narrow temperature range. Experimental study of the PL properties supplied by kinetic Monte-Carlo simulations gives valuable information about the energy scale of the disorder, and hence about the quality of the QW structure.

The experimentally observed effects of disorder on the dynamics of recombining carriers can be reproduced within a model where spatially localized excitons hop between localized states distributed randomly in space and energy [2]. The important input of the model is the density of states (DOS) in the band tail. The model can be applied to any kind of disordered systems,
though the results are rather sensitive to the shape and to the energy scale of the DOS. Therefore the correct determination of the DOS is the task of crucial importance. While single energy and spatial scales of disorder were necessary to explain experimental data in ZnCdSe/ZnSe, (GaIn)(NAs)/GaAs, (GaIn)(NAs)/GaNAs, Ga(NAs)/GaAs QW structures [1, 3], disorder with several scales was assumed to interpret experiments in (Al,In,Ga)N and Ga(As,Bi) material systems [4]. Another interesting example that evidences two, short- and long-ranged scales of disorder is Ga(N,P,As)/GaP QW structure recently studied in Ref. [5]. The long-range disorder was attributed to the variation of QW thickness due to the interface imperfections while the short-range disorder was attributed to the compositional fluctuations inherent in any compound material. Monte-Carlo simulations using this model reveal the exponential distribution of both, short-range and long-range disorders with characteristic energies $E_0$ and $\varepsilon_0$, respectively, as well as several universal relations giving the possibility to extract these energy scales from the experimentally observed PL features.

In the present paper we show another interesting and intriguing feature of Ga(N,P,As) compound. Intuitively one can suggest that the higher the nitrogen content in the compound gets, the high the energy scale of disorder should be since the absolute deviation of the composition from the average one increases with increasing concentration of the fluctuating compositional component (nitrogen in our case). Our experimental results evidence however the opposite effect: Both $E_0$ and $\varepsilon_0$ energy scales of the short-range and the long-range disorders decrease with increasing nitrogen concentration. We give a theoretical explanation of this “anomalous” effect using the analytical theory [1, 6] that allows one to determine the energy scale of compositional disorder from the structural and energy parameters of the compound. Further we focus our attention on the variation of short-range disorder since this kind of disorder is conditioned by the compositional fluctuations of the alloy [5]. The variation of long-range disorder is reserved for separate study.

Prior to presenting our experimental and theoretical results we briefly discuss the analytical theory of compositional disorder as well as the basics of the band-anticrossing (BAC) model [7] giving the compositional-dependent energy structure of the compound necessary for our theoretical considerations.

2. Analytical theory for compositional disorder

The short-range disorder in nitride III-V QW structures is conditioned by the compositional fluctuations inherent in the compound [5, 8]. Therefore, it is important to reveal the compositional dependent parameters determining the energy scale of the disorder potential. The corresponding analytical theory has been developed in Refs. [1, 6]. The basic idea of this theory is the following.

Let us assume that certain lattice sites may contain atoms of either type A or B. Let the concentration of such sites be $M$ and the mean fraction of A sites be $x$. The mean number of A atoms in a volume $R \times R \times R$ is $xMR^3$, and the typical excess number is of the order of
\[(xMR^3)^{1/2}\]. The fluctuational change in the fraction of A atoms in this volume is then
\[\Delta x \simeq \frac{(xMR^3)^{1/2}}{MR^3}.\] (1)

For small values \(\Delta x\) the compositional dependent energy \(E_c(x)\) corresponding to the bottom of the conduction band may be expressed as
\[E_c \simeq E_c(x) + \alpha \Delta x,\] (2)
where \(\alpha = (\partial E_c/\partial x)_{\Delta x=0}\). Thus, in the considered volume, a potential well (or hump) is formed, with the depth (or height) of the order
\[V \simeq \alpha \frac{(xMR^3)^{1/2}}{MR^3}.\] (3)

If \(V\) and \(R\) satisfy the inequality \(V >> \hbar^2/mR^2\), where \(m\) is the effective electron mass, such a well has an electronic level close to \(V\). If the opposite inequality is valid, the well contains no level at all. It is seen from Eq.(3) that the energy \(V\) increases with decreasing \(R\). Consequently, the most effective of the wells having levels are those with small \(R\). The most important wells are therefore those with the lowest value of \(R\) that generate a level [6]. This value is determined by the equation \(V = \hbar^2/mR^2\), i.e.,
\[R \simeq \frac{h^4 M}{\alpha x m^2}.\] (4)

Substituting Eq.(4) in Eq.(3), we find that the smearing of the band edge is of the order of
\[E_0 \simeq \frac{\alpha^4 m^3 x^2 (1-x)^2}{\hbar^6 M^2},\] (5)

We use Eq. (5) to estimate the energy scale of compositional disorder \(E_0\) in the samples under study. In our case the more precise definition of content \(x\) is necessary. We study the fluctuation disorder in quaternary Ga(N,P,As) compound where the content of both phosphorous and nitrogen components may fluctuate. However, the conduction band edge \(E_c\) is much more sensitive to the variation in the nitrogen rather than in the phosphorous content because of the extremely strong anticrossing interaction [7] between the localized nitrogen states and the extended states of the semiconductor matrix. Hence, \(\alpha_N = \partial E_c/\partial x_N\) for nitrogen is much larger than \(\alpha_P = \partial E_c/\partial x_P\) for phosphorous and concomitantly the disorder energy scale \(E_0\) given by Eq. (5) is mainly determined by fluctuations of the nitrogen content. Therefore we imply under \(x\) the nitrogen content. Accordingly, \(M\) is the concentration of sites for group V elements in the compound.

The important input of Eq. (5) is the compositional dependence of the band gap in QW compound \(\alpha\). This parameter can be estimated from simple two-level band-anticrossing model [7]. The basics of this model are given in next Section.

3. Band-anticrossing (BAC) model

It is well known that even a small amount of incorporated nitrogen leads to a strong reduction of the band gap energy of III-V semiconductor compounds. In BAC model [7] the modification of the conduction band is described as an anticrossing interaction between highly localized states of the substitutional nitrogen atoms and the extended states of the host semiconductor matrix. According to this model the newly formed lowest \(E_c\) subband position can be estimated as
\[E_c(x) = \frac{1}{2} \left[ (E_T + E_N) - \sqrt{(E_T - E_N)^2 + 4C^2 x} \right],\] (6)
Table 1. Compositional and geometrical Characteristics of studied Ga(N,P,As)/GaP QW structures

| Sample  | $X_N$ (%) | $X_P$ (%) | $X_{As}$ (%) | QW width (nm) |
|---------|-----------|-----------|--------------|---------------|
| sample1 | 2         | 14        | 84           | 5.6           |
| sample2 | 3         | 5         | 92           | 5.6           |
| sample3 | 4         | 7         | 89           | 5.4           |

where $E_\Gamma$ is the $\Gamma$ conduction band edge in the host semiconductor matrix, $E_N$ is the energy of the N level and $C$ is the coupling parameter.

Originally Eq. (6) has been applied in order to parameterize the strong band gap bowing of GaAs or GaP-based material systems such as Ga(N,As), (Ga,In)(N,As) and Ga(N,P). Recently the BAC model has been adopted for As-rich Ga(N,P,As) mixed compounds [9] by extrapolation of $E_N$ and $E_\Gamma$ energy levels from Ga(N,As) and Ga(N,P) ternary endpoints. Furthermore, the modification of these energy levels as functions of the macroscopic strain inherent in QW structure was also taken into account. We use the adopted BAC model to estimate the band gap variation $\alpha$ in studied Ga(N,P,As)/GaP QW structures. The estimated values of this material characteristic are then exploit to determine the energy scale of compositional disorder $E_0$ according to Eq. (5).

This program is performed in Section 5 to provide the theoretical explanation of the experimentally observed anomalous trends in the compositional-dependent energy scale of disorder in Ga(N,P,As)/GaP QW structures.

4. Experimental results

We study the photoluminescence behavior of three Ga(N,P,As)/GaP QW structures with different compositional and geometrical characteristics gathered in Table 1. The experimental results presented in Fig. 2 show the following tendencies with increasing nitrogen content: (i) the linewidth of the PL spectra decreases, (ii) the temperatures corresponding to the minimal peak energy and to the maximal linewidth of the PL spectra decrease. According to Ref. [2], the temperatures corresponding to the minimal peak energy and to the maximal linewidth of the PL spectra ($T_1$ and $T_2$, respectively. See also Fig. 1a,b) are related with the energy scale of the short-range disorder $E_0$ by the following universal relations

$$k_B T_1 = (0.75 \div 0.80) E_0,$$
$$k_B T_2 = (1.10 \div 1.15) E_0.$$  

Eqs. (7) give the possibility to extract the energy scales of compositional disorder in studied Ga(N,P,As)/GaP QW structures from the experimentally observed PL features presented in Fig. 2. The corresponding nitrogen content dependence of the energy scale $E_0$ shown in Fig. 3a (open circles) evidences the significant reduction of the compositional disorder with the increase of nitrogen concentration resulting in decreasing linewidth of the PL spectra.

In the next Section we exploit the analytical theory of compositional disorder and the band-anticrossing model in order to estimate the energy scale of compositional disorder $E_0$ in Ga(N,P,As)/GaP QW structures with different nitrogen contents $x$ and compare the obtained $E_0(x)$ dependence with that extracted from our experimental studies.
5. Calculation results and comparison with experiment

The analytical theory presented in Section 2 gives the possibility to relate the energy scale of compositional disorder with important material characteristics such as the composition-dependent band-structure and the effective mass. To determine the band-structure we use the BAC model (see Eq. (6) of Section 3) adopted to Ga(N,P,As) quaternary compounds [9]. The calculated nitrogen content dependencies of the variation of the conduction band edge $\alpha$ is presented in Figs. 3b. The resulting dependence of the relative $E_0$ scale of compositional disorder on the nitrogen content calculated according to Eq. (5) assuming the constant effective mass is shown in Fig. 3a (solid circles). The comparison of the calculated energy scales of compositional disorder with those extracted from PL features observed in our experimental studies (open circles in Fig. 3a) evidences that the analytical theory of compositional disorder gives the qualitative explanation of the observed anomalies in Ga(N,P,As)/GaP QW structure, i.e. the energy scale of disorder decreases with increasing nitrogen content. However, there still exists the quantitative discrepancy between the calculated and the experimental results. We account for this discrepancy with the assumption of the constant effective mass used in our calculations. The values of the effective mass are not known so far for Ga(N,P,As) material system. The situation is not completely clear even for Ga(N,As) and Ga(N,P) ternary compounds (see for example Ref. [10]). An analytical theory of compositional fluctuations [1, 6] opens the opportunity to determine the compositional variation of the effective mass in As-rich Ga(N,P,As) quaternary compounds. The relative values of the effective mass as a function of the nitrogen content (see Fig. 3c) are estimated as the values providing the exact agreement between the experimentally observed and the calculated energy scales of compositional disorder. According to our estimations, the effective mass decreases with increasing nitrogen concentration, which is a common feature of dilute III-V nitride compounds with comparatively high nitrogen
content [10, 11].

6. Conclusions
The experimental investigation of the photoluminescence behavior in Ga(N,P,As)/GaP QW structures reveals the anomalous compositional dependence of the disorder parameters. In particular, the energy scale of disorder decreases with increasing nitrogen content.

Using the theory of compositional fluctuations in mixed crystals it is shown that the reason for reducing disorder is the reducing effective mass and the specific dependence of the conduction band edge on the nitrogen content in Ga(N,P,As)-material systems. This dependence becomes weaker with increasing nitrogen content.

Acknowledgments
Financial support of the Fonds der Chemischen Industrie and that of the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

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