Effects of spontaneous ordering and alloy statistical fluctuations on exciton linewidth in $Ga_xIn_{1-x}P$ alloys

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We experimentally demonstrate an intrinsic statistical effect of the phenomenon of spontaneous ordering in semiconductor alloys: the reduction of alloy fluctuations as a function of the order parameter, as reflected in the exciton linewidth. A theoretical model is presented to qualitatively describe the dependence of the exciton linewidth on the order parameter.

Spontaneous ordering in $Ga_xIn_{1-x}P$ and other III-V alloys has been studied extensively for over a decade. The most frequently observed ordered phase in $Ga_xIn_{1-x}P$ is the CuPt structure, which is a monolayer superlattice consisting of alternating layers of $(Ga_{x+\eta/2}In_{1-x-\eta/2}P)/(Ga_{x-\eta/2}In_{1-x+\eta/2}P)$, along the [111] direction, where η is the order parameter that can vary from 0 to a maximum value of $\min[2x,2(1-x)]$, depending on growth conditions. A majority of the previous studies have focused on ordering induced changes in the crystal structure,[1] electronic and optical properties (e.g., band-gap reduction,[1,2] valence-band splitting,[3–5] optical anisotropy,[3] pyroelectricity,[6] birerefringence,[7] second harmonic generation,[8] conductivity anisotropy,[9] and Raman scattering[10]), and the functional dependence of these phenomena on the order parameter.[11–15] Many of these properties are sensitive to the change in the crystal symmetry caused by ordering. However, there is another aspect of this phenomenon that has been relatively unexplored, which concerns its influence on properties governed by the statistical mechanics of the alloy. The statistical effects referred to are those intrinsic to ordering and which are unrelated to imperfections in sample growth. For example, phenomena associated with the macroscopic spatial variations of the alloy composition or the order parameter[16,17] are considered to be growth related imperfections that can in principle be eliminated or minimized by improving the growth technique. It is well known that the influence of alloy statistical fluctuations on many physical properties is a function of the alloy composition x, that is frequently described by a simple function $x(1-x)$. For a spontaneously ordered alloy, the effects of alloy fluctuations will not only be a function of the average composition x but also of the order parameter η. For a given value of composition x, one expects that the fluctuations decrease with increasing order parameter η.

In this article, we demonstrate that the phenomenon of spontaneous ordering results in a reduction of alloy fluctuations, by investigating the excitonic linewidth as a function of the order parameter η, and present a theoretical model that takes into account the statistical fluctuations of both x and η in determining the linewidth.

All the $Ga_xIn_{1-x}P$ samples used in this study were grown by organometallic vapor phase epitaxy. Benefiting from recent advances in sample growth, for a limited range of order parameters, we are able to obtain spontaneously ordered samples with ordered domain sizes of the order of 1 μm, which is much larger than the exciton Bohr radius.[12] For samples of this type, the band-edge excitonic transition can be clearly observed in the low temperature photoluminescence (PL) spectrum.[12,13] PL was measured at 10 K with the sample mounted in a closed-cycle cryostat. A typical laser spot size was $\sim$50 μm and the excitation density was $\sim$4 W/cm^2. The PL linewidth was found to change very little with either increase or decrease of the excitation density by one order of magnitude. The spectral resolution was typically 0.2 meV. For any given sample, the order parameter as well as the sample quality depends on various growth parameters. During the past decade, there has been a major advance in understanding and controlling the growth of spontaneously ordered $Ga_xIn_{1-x}P$: from samples characterized by a broad statistical distribution function $F(\eta)$ of the order parameter η,[16] to samples characterized by a very narrow statistical distribution function $F(\eta)$.[17] During this same period, several techniques have been used to characterize the order parameter of spontaneously ordered $Ga_xIn_{1-x}P$.[12,14,15] From the large set of samples that we have measured, we carefully selected a set of samples each of which yielded the smallest possible PL linewidth corresponding to its particular value of order parameter η. The linewidth thus obtained is close to the intrinsic linewidth for each particular η value. The sample composition was kept the same, being $x=0.52\pm0.003$ (lattice-matched to the GaAs substrate at $T\sim0$ K).

Figure 1 shows the PL spectra of a spontaneously ordered alloy with $\eta=0.44$ and a disordered sample with $\eta=0$. In the PL spectra, the peak at high energy is due to the band-edge excitonic transition, and the peak at low energy is related to defects and/or impurities whose identities are still unclear.[12,17,18] In addition to the band-gap reduction that results from ordering, it is clear that the linewidth (i.e., the full width at half maximum) of the ordered sample is significantly reduced in the spontaneously ordered alloy.

There are various mechanisms that contribute to the inhomogeneous broadening of the exciton linewidth. These are, (1) statistical fluctuations of x and η that occur on a microscopic spatial scale, (2) macroscopic spatial variations of x and η, and (3) exciton scattering due to potential fluctuations at defects such as those encountered even in disordered alloys, and domain boundaries which are characteristically found in spontaneously ordered alloys. The first contribution is intrinsic and is the main focus of this work. The last two

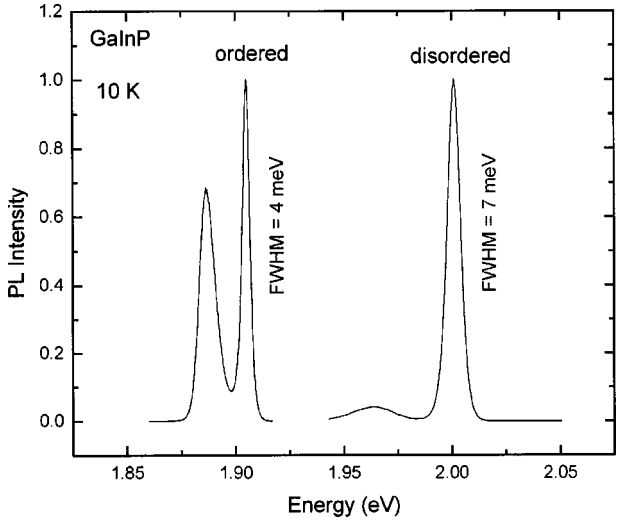

FIG. 1. Photoluminescence spectra for an ordered (left) and a disordered (right) $Ga_xIn_{1-x}P$ sample.

contributions usually coexist with the first. The second contribution can be examined by using a spatially resolved PL technique, as for example in the study performed in Ref. 17. As indicated there, it is possible to obtain samples for which the spatial variation in x and η is rather small. The third effect can be eliminated by using samples with large ordered domains, but this is not possible for samples with η exceeding a value of about 0.45. This is because of the fact that for this range of order parameters, samples with large domain sizes cannot yet be obtained.[19]

Figure 2 is a plot of the linewidth versus the energy E_g of the excitonic transition (or the order parameter η) for a set of samples of spontaneously ordered GaInP. The correlation between E_g and η has been determined experimentally as mentioned earlier.[15] From the plot of the data a trend can be clearly established which is that the linewidth decreases with increasing order parameter for $\eta<0.45$. This effect directly results from the reduction in alloy fluctuations due to spontaneous ordering of the cations. However, the trend reverses roughly at $\eta=0.45$ and this change is attributed largely to the third mechanism mentioned earlier. The linewidths

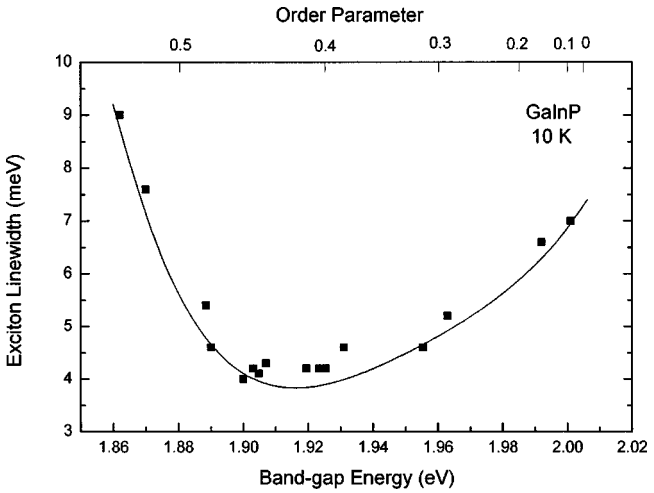

FIG. 2. The excition linewidth as a function of the band-gap energy or the order parameter. The curve is a guide to the eyes.

shown in Fig. 2 are consistent with best reported data for $Ga_xIn_{1-x}P$ alloys. Ref. 17 found a linewidth of 4.9 meV for an ordered sample with a band gap of 1.925 eV at 3.5 K. Reference 20 found a linewidth of 4.3 meV for an ordered sample with a 1.976-eV band gap and 6 meV for a nearly disordered sample with a 1.990-eV band gap at 1.4 K. Note that the results of Fig. 2 were obtained at a somewhat higher temperature than that of these two references (a thermal broadening about $kT=0.86$ meV for 10 K is expected in our data).

There have been many previous theoretical studies of the exciton linewidth in semiconductors.[21–26] Intuitively, inhomogeneous broadening can be visualized as arising from the fact that the alloy composition within one exciton volume is different from that within another exciton volume. If the center of mass motion of an exciton is assumed to be localized, the exciton density of states can be described by a Gaussian line shape[22–24]

$$f(E,x)=\frac{1}{\sqrt{2\pi\sigma(x)}}\exp\left\{-\frac{[E-E_g(x)]^2}{2\sigma(x)^2}\right\}, \tag{1}$$

and

$$\sigma(x)^2=\left[\frac{dE_g(x)}{dx}\right]^2 x(1-x)\frac{V_0(x)}{V_{\rm ex}(x)}, \tag{2}$$

where $E_g(x)$ is the excitonic band gap, $V_0(x)$ is the volume of the unit cell, and $V_{\rm ex}(x)$ is the volume of the exciton. The main difference amongst Refs. 22–24 is in the determination of the exciton volume. The exciton linewidth is given as

$$W(x)=2\sqrt{2\ln 2}\,\sigma(x). \tag{3}$$

For a CuPt ordered $Ga_xIn_{1-x}P$ alloy with order parameter η, the compositions of the Ga-rich and In-rich layers are $x_1=x+\eta/2$ and $x_2=x-\eta/2$, respectively. The size of the unit cell is now double that of the cubic alloy. The composition and order parameter dependence of the band-gap energy near $x=0.5$ can be approximately described by $E_g(x,\eta)\approx E_g(x,0)-\delta E(\eta_{\max})\eta^2$, where $\eta_{\max}$ is the maximum possible order parameter for a specific x.[11] Since η^2 is the leading term, the local expansion of $E_g(x,\eta)$ is performed with respect to variables x and $\theta=\eta^2$. Following the same procedure of Ref. 24 and treating the two layers independently, we obtain

$$\sigma^2(x,\theta)=\left\{\frac{1}{2}E_x^2\left[x(1-x)-\frac{1}{4}\theta\right]+2E_\theta^2\left[x(1-x)+\frac{1}{4}\theta(1-4\sqrt{\theta}+2\theta)\right]+E_xE_\theta(1-2x)\sqrt{\theta}\right\}\frac{V_0(x,\theta)}{V_{\rm ex}(x,\theta)} \tag{4}$$

where $E_x=\partial E/\partial x$ and $E_\theta=\partial E/\partial\theta$. For $\eta=0$, Eq. (2) is recovered. When $x=0.5$, Eq. (4) reduces to

$$\sigma^2(\theta)=\left\{\frac{1}{8}E_x^2(1-\theta)+\frac{1}{2}E_\theta^2[1+\theta(1-4\sqrt{\theta}+2\theta)]\right\}\times\frac{V_0(x,\theta)}{V_{\rm ex}(x,\theta)}, \quad (5)$$

This model gives the functional dependence of the exciton linewidth for the order parameter in a spontaneously ordered alloy. However, the numerical results of Eq. (5) for either the linewidth or its variation with the order parameter are somewhat smaller than the experimental results shown in Fig. 2, with $E_x=700+1520x$ (meV), $E_\theta=-498$ (meV),[15] and the exciton parameters given in Ref. 27 for ordered $Ga_xIn_{1-x}P$ alloys with $x=0.52$. For instance, this model yields a line width change of 11% when η varies from 0 to 0.5, as shown in Fig. 3 (The contribution of the homogeneous linewidth is not included). Such a discrepancy is not a surprise, since for III-V alloys in general this type of model tends to yield a linewidth and its composition dependence significantly smaller than that of the experiment[23] even with a more recent and improved theory.[26] A shortcoming of this conventional theory[22–24,26] is that, as pointed out in Ref. 25, only the exciton relative motion is considered. As the electron and hole are perturbed by the alloy fluctuations independently, the contribution to the linewidth should include three parts:[25] the electron, the hole and the combination of both. Such a model becomes mathematically rather complex, but it does yield an exciton linewidth closer to the experimental result.[25]

In summary, we have demonstrated an intrinsic statistical property of the phenomenon of spontaneous ordering which is that the exciton linewidth of ordered $Ga_xIn_{1-x}P$ alloys decreases with increasing order parameter. Other extrinsic effects that also contribute to the inhomogeneous broadening of the exciton linewidth are discussed. A theoretical model is presented to describe qualitatively the order parameter and composition dependence of the exciton linewidth.

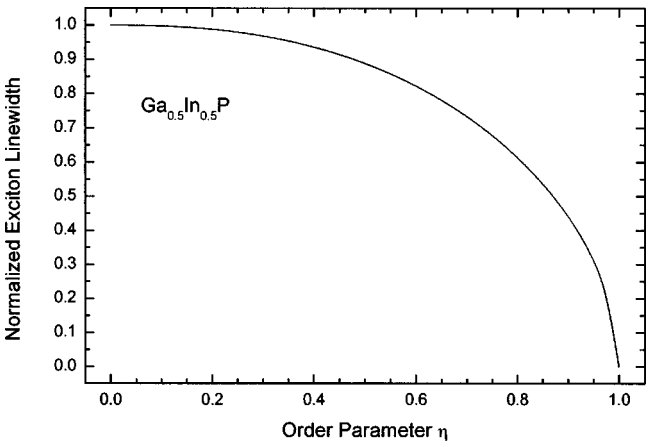

FIG. 3. The excition linewidth, normalized to its value at $\eta=0$, as a function of the order parameter calculated using Eq. (5).

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