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Statistical distribution of the order parameter in spontaneously ordered $Ga_{0.52}In_{0.48}P$ alloys

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The spontaneously ordered $Ga_{0.52}In_{0.48}P$ alloy comprises domains, each of which is characterized by an order parameter η. We have used the low-temperature near-field photoluminescence technique with a high spatial resolution ($\leqslant 2500$ Å) to study the statistical distribution of the order parameter η of single-variant ordered alloys. We have found that for large-domain samples, η varies only slightly between domains and the line width broadening of the excitonic photoluminescence peak comes mainly from alloy scattering within a single domain rather than from a broad distribution of η. [S0163-1829(98)52416-2]

Spontaneous $CuPt_B$-type long-range ordering in $Ga_{0.52}In_{0.48}P$ alloys[1] has been the subject of intense studies in recent years. $Ga_{0.52}In_{0.48}P$ (written as $GaInP_2$ for simplicity) alloys, grown lattice matched to a (001) GaAs substrate by organometallic vapor phase epitaxy (OMVPE), exhibit ordering of cations on the group-III sublattice along [111] or [111], which are the two $[111]_B$ directions, depending on the growth conditions and the substrate misorientation. The ordered alloys consist of monolayer superlattices of $Ga_{(1+\eta)/2}In_{(1-\eta)/2}P/Ga_{(1-\eta)/2}In_{(1+\eta)/2}P$ along the $[111]_B$ directions,[2] where the order parameter η can have values between 0 and 1. Transmission electron microscopy (TEM) measurements reveal that the ordered $GaInP_2$ alloy is not spatially homogeneous.[3] It was inferred,[4] from experimental evidence, that an ordered alloy comprises domains characterized by a function $F(\eta)$ describing the statistical distribution of the order parameter η, where

$$\int_0^1 F(\eta)\,d\eta = 1. \tag{1}$$

Since most optical measurements use probes with spot sizes (typically >50 μm) that are much larger than typical domain sizes (<2000 Å), a physical property P_M of an ordered alloy measured using such macroscopic techniques represents an ensemble average

$$P_M = \int_0^1 P(\eta)F(\eta)\,d\eta, \tag{2}$$

where $P(\eta)$ is the property representing a microscopic domain characterized by an order parameter η. The ''order parameter'' of the alloy determined using such macroscopic techniques would be the ensemble average

$$\eta_{avg} = \int_0^1 \eta F(\eta)\,d\eta. \tag{3}$$

This model was invoked in order to explain the observed line shapes of photoluminescence excitation (PLE) and modulated-reflectivity spectra of ordered alloys.[4,5] However, this model has not been directly tested due to the difficulty in optically probing single domains whose sizes are usually much smaller than the diffraction limit of the probing laser spot. Recently, improvement in sample quality has made available samples with average domain sizes exceeding 5000 Å. This, combined with near-field optical spectroscopic techniques that overcome the diffraction limit,[6] has finally made it possible to investigate the optical properties of ordered $GaInP_2$ alloys with a spatial resolution comparable to the average domain size. In this paper we report a direct measurement of the spatial distribution of the order parameter η using low-temperature near-field photoluminescence (PL) measurements on large-domain ordered $GaInP_2$ samples.

We studied two samples whose PL spectra show an excitonic peak that is well resolved from the defect-related below-gap luminescence peak. Since we use the energy of the excitonic peak as a measure of the band-gap energy, and thus the order parameter η,[7] it is imperative that we use samples with a well-resolved excitonic peak. These samples have a 10-μm-thick $GaInP_2$ epilayer grown by OMVPE on a (001) GaAs substrate. Sample 1 was grown at 690 °C on a Si-doped GaAs (001) substrate misoriented 4° toward $[111]_B$. Sample 2 was grown at 680 °C on a semi-insulating GaAs (001) substrate misoriented 6° toward $[111]_B$. A growth rate of 4 μm/h and a V/III ratio of 70 were used for both the samples. The substrate misorientation toward $[111]_B$ results in single-variant ordering.[8] To obtain a below-diffraction-limit spatial resolution, 700-Å-thick aluminum aperture masks were fabricated by a liftoff process using a mask of polymethylmethacrylate (PMMA) patterned by electron-beam lithography. Since PMMA is a positive resist, the GaInP under the holes did not receive any primary electron dose. On sample 1, the mask has a series of apertures with varying diameters ranging from 5 μm to 2000 Å. On

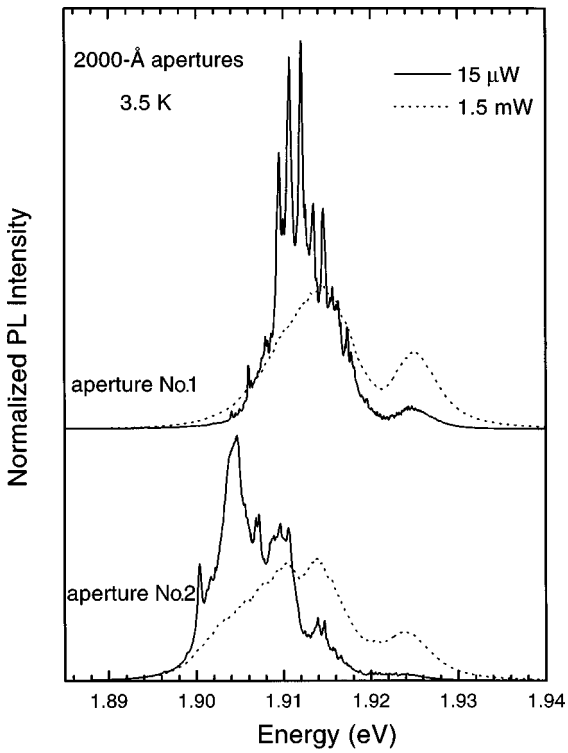

FIG. 1. Near-field PL spectra taken from sample 1 through two 2000-Å apertures. The spectra are normalized to the integrated total PL intensity. Low-excitation-power (15 μW) spectra show sharp peaks at lower energies. At higher excitation power (1.5 mW), the sharp peaks disappear and the excitonic peak at $\sim$1.925 eV gets relatively stronger.

sample 2, the mask has six 10×10 arrays (10-μm spacing) of 2500-Å apertures. The dark-field transmission-electron microscopy measurements[9] on sample 2 and one similar to sample 1 show that the lateral dimensions of ordered domains near the sample surface are about 0.3–1 μm. The sample was mounted on a cold finger of an Oxford Microstat helium cryostat with a 500-μm-thick window, and the PL measurements were performed at 3.5 K. The 5145-Å line of an Ar-ion laser was used as the excitation source. The laser was focused with a long-working-distance microscope objective (N.A.$=$0.55) to a spot size of 4–5 μm. Since the spot size is significantly smaller than the spacing between the apertures, luminescence from only one aperture was collected for each spectrum measured. The PL signal was collected by the same objective, dispersed by a SPEX 1877 0.6-m triple spectrometer, and detected with a high-resolution CCD detector array. The spectral resolution was 0.25 meV.

Figure 1 compares near-field PL spectra from two 2000-Å apertures on sample 1. The spectra are normalized to their integrated total intensity. At low excitation power (15 μW), the PL spectrum from aperture no. 1 consists of an excitonic peak at 1.9248 eV and a series of closely spaced defect-related features at lower energies. These sharp peaks at low energies are due to localized transitions associated with the domain boundaries.[10] A close inspection of this spectrum reveals that there are also sharp features on the lower energy side (1.920–1.924 eV) of the excitonic peak. These sharp features were not observed in the previous near-field optical microscopy study on thinner (and therefore smaller-domain) samples.[11] We interpret these sharp features as due to excitons bound to shallow impurities. Because there are only a limited number of impurities within a small volume that contribute to the near-field PL, the atomiclike transitions from these excitons appear as sharp features in the near-field PL spectra. This is analogous to the case of single quantum dot transitions is observed in GaAs quantum wells.[6] A measurement of the temperature dependence of these sharp features reveals that they have an ''activation energy'' of 3.5 $\pm$0.5 meV, which is consistent with this interpretation. However, unlike the case of GaAs quantum wells,[6] these features do not become isolated sharp peaks even when the excitation power is lowered to the detection limit of our system. Also shown in Fig. 1 is a near-field PL spectrum taken from the same aperture but with a 100 times higher excitation power. As the excitation power is increased, the defect-related transitions are saturated and thus the sharp features disappear. Also, the excitonic peak grows in relative strength with increased excitation power and shows a slight blue shift ($\sim$0.3 meV) due to the band-filling effect. On the other hand, the low-power spectrum from aperture no. 2 is dominated by the defect-related low-energy luminescence. Here, even at 1.5-mW excitation the excitonic peak is relatively weak and is not fully resolved. Based on the recent observation that the relative intensity of the excitonic peak increases with decreasing density of domain boundaries,[9,12] we interpret that the area beneath aperture no. 1 is entirely enclosed within a single ordered domain while aperture no. 2 covers one or more domain boundaries. It is worthwhile to note here that the excitonic peak in the spectrum from aperture no. 1 is still fairly broad with a full-width at half-maximum (FWHM) of 3.7$\pm$0.2 meV.

Figure 2 shows a similar comparison for sample 2. All three spectra were taken with the same excitation power of 15 μW. The top spectrum was taken from an unmasked area of the sample. In this case the signal comes mostly from an area with a diameter of $\sim$4–5 μm defined by the laser spot size. Similar macro-PL spectra were taken from different positions in the area (radius $\sim$250 μm) that encompasses all six array patterns, and they were identical within experimental uncertainties. This indicates that *macroscopic* inhomogeneity is negligible within this area. In this macro-PL spectrum, the excitonic peak at 1.8988 eV is well resolved and has a FWHM of 4.9$\pm$0.2 meV. The spectrum taken through aperture no. 1 has a strong excitonic peak with a FWHM of 3.8$\pm$0.2 meV, while that from aperture no. 2 shows a very weak excitonic peak. The sharp transitions at lower energies due to defect-related localized transitions, as well as the sharp features on the lower-energy side of the excitonic peak due to the localized excitons, are also seen just as in the case of sample 1. In order to study the statistical distribution of η, we measured the energetic position of the excitonic peak in the PL spectra taken from 247 apertures on sample 2. Because of a very slight variation in the electron beam dose we found that not all apertures were open. We could determine the excitonic peak energies for 242 of the 247 spectra measured, and a histogram of the excitonic peak energies is plotted in Fig. 3(a). A Gaussian fit gives a mean value of the excitonic peak energy as 1.8974 eV and a FWHM σ_F as 2.1 meV.

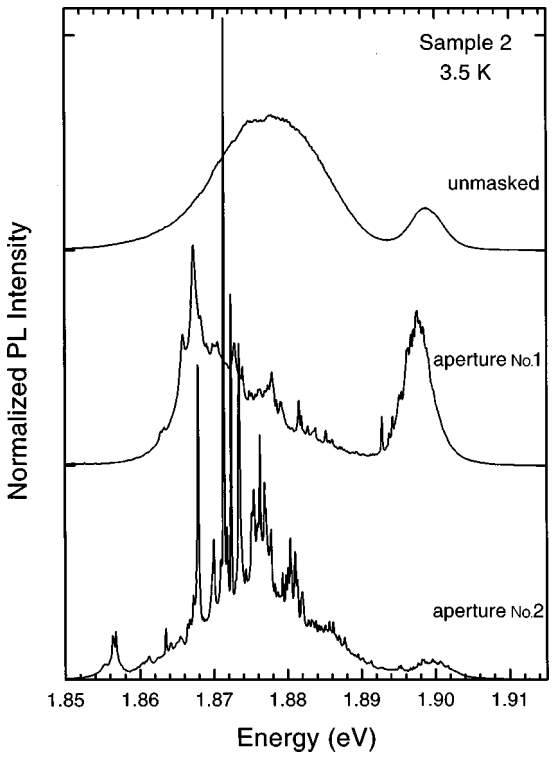

FIG. 2. Comparison of a macro-PL spectrum with near-field PL spectra taken through two 2500-Å apertures on sample 2. All three spectra were taken with the same excitation power (15 μW). The macro-PL spectrum on the top was taken from an unmasked area of the same sample.

The band-gap energy $E_g(\eta)$ of ordered $GaInP_2$ is a quadratic function of η,[13,14] given by[7]

$$E_g(\eta)=E_g(0)-\eta^2[E_g(0)-E_g(1)]$$
$$=2.005-0.471\eta^2\ (\mathrm{eV}). \qquad (4)$$

Using Eq. (4) and ignoring the small Stokes shift or the exciton binding energy, we can convert the excitonic PL peak energy into the order parameter η, and a histogram of η thus obtained is shown in Fig. 3(b). A Gaussian fit of this histogram gives a mean value of the order parameter η as 0.478 and a FWHM as 0.0048.

From the above results we can make several observations. First, the microscopic order parameter η varies by only about 1% within an area of radius $\sim 250\ \mu$m. This means that for large-domain samples like the ones measured in this study, the distribution of the order parameter is very narrow. It is possible that the distribution is broader for samples with smaller domains, but since those samples generally do not show excitonic PL peaks,[12] it is impossible to repeat similar measurements on them. Second, the linewidth of the excitonic peak from a single domain is not much smaller than that from a macroscopic ensemble average as measured in a macro-PL spectrum. In near-field PL spectra that can be interpreted to be from a single domain (e.g., aperture no. 1 of sample 2), the linewidth of the excitonic peak is $\sim 3.8-4.2$ meV.[15] The source of this broadening is alloy scattering due to partial ordering ($\eta<1$). In the ideal case of perfect ordering ($\eta=1$), the ordered alloy is a monolayer superlattice of pure GaP and InP, and hence the excitonic PL

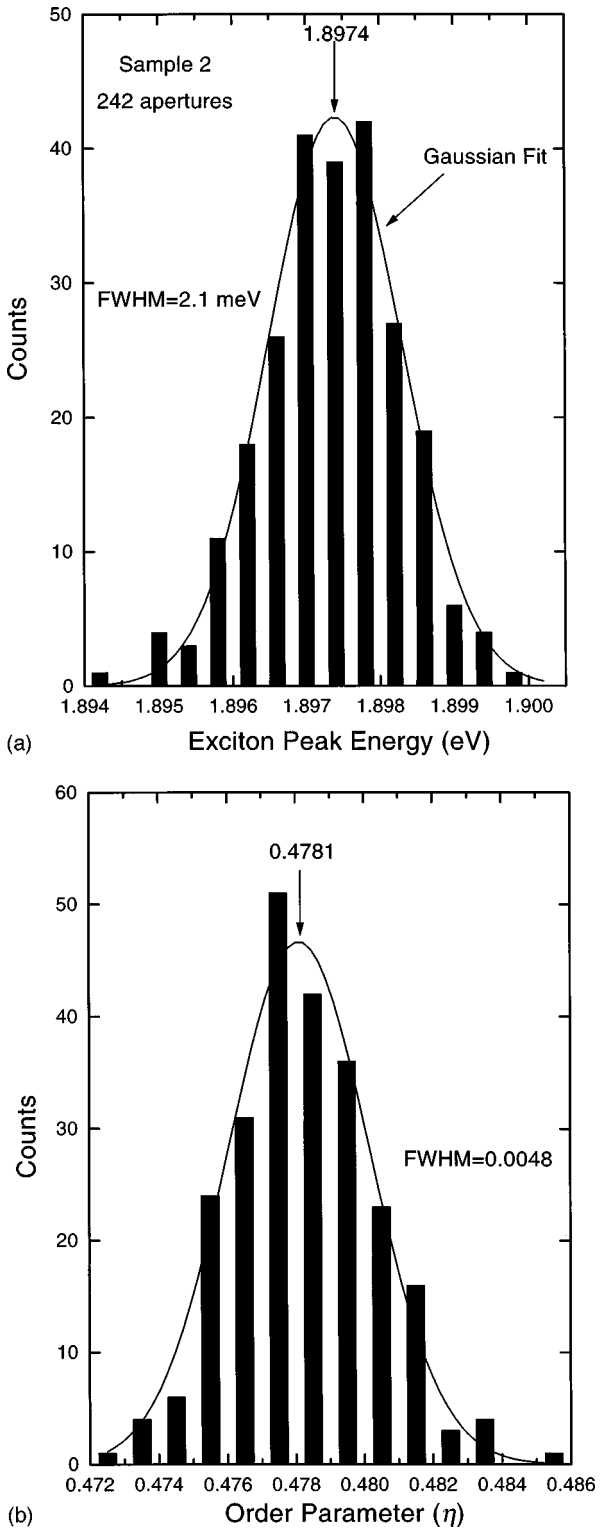

FIG. 3. Histograms of (a) the excitonic peak energy and (b) the order parameter, measured from 242 2500-Å apertures on sample 2. The curves are Gaussian fits to the histograms. The mean values and the FWHM values of the fits are shown.

peak should be much narrower than that of a random alloy [typical FWHM ≥ 5 meV (Ref. 16)]. However, since the ordering is only partial, the monolayers consist of $Ga_{(1+\eta)/2}In_{(1-\eta)/2}P$ or $Ga_{(1-\eta)/2}In_{(1+\eta)/2}P$ alloys. In this case, the alloy broadening[17,18] arises due to the statistical randomness of the cation distribution within each monolayer. If we

take the FWHM σ_s of an excitonic peak from a single domain as 4.0 ± 0.2 meV and use the $\sigma_F = 2.1$ meV from Fig. 3(a), the FWHM σ_M of the excitonic PL from a macroscopic ensemble of ordered domains should be $\sigma_M = (\sigma_s^2 + \sigma_F^2)^{1/2} = 4.5 \pm 0.2$ meV. This compares well with the measured FWHM $\sigma_M^{measured}$ of the macro-PL 4.9 ± 0.2 meV. From this analysis, we conclude that the broadening of the excitonic peak in the macro-PL spectrum is mainly due to the alloy scattering within an ordered domain, and not a result of a broad distribution of η. This contrasts with the case of quantum dots where most of the PL linewidth broadening comes from the distribution of the quantum dot sizes.[19]

In summary, we have used low-temperature near-field PL with a spatial resolution of 2500 Å to study the statistical distribution of the order parameter η of ordered $GaInP_2$ alloys. We have found that for large-domain samples, η varies only slightly between domains and the linewidth broadening of the excitonic PL peak comes mainly from alloy scattering within a single domain rather than from a broad distribution of η.

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