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Atomic ordering and bond relaxation in optical spectra of self-organized InP/GaInP₂ Wigner molecule structures.

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We used transmission electron microscopy, Raman and photoluminescence (PL) spectroscopy to identify the effect of CuPt-type GaP-InP atomic ordering (AO) on the structural and emission properties of self-organized (SO) InP/GaInP₂ Wigner molecule (WM) quantum dot (QD) structures. We found that correlation of AO and SO growth results in the formation of InP/GaInP₂ QD/AOD-domains (QD/AODs) core-shell composites. This observation shows that intrinsic WMs in this system emerge due to a strong piezo-electric field generated by AODs, which induces QD doping and a built-in magnetic field. We found that the bond relaxation of AODs leads to a decrease in the emission energy of WMs of 80 meV. Photoluminescence spectra of single WMs having an emission energy ~1.53 eV are here presented, the lowest one reported for this system.

From a variety of self-organized (SO) semiconductor quantum dot (QD) systems realized up to date, which include III-V, II-VI and III-N (nitride), materials³, the phosphide III-V QDs grown on GaAs substrates are the only ones which can provide weak quantum confinement and accumulation of up to 20 electrons in situ³, ⁴ similar to that realized in electrostatically controlled, nano-fabricated QDs⁴, ⁵, ⁶. Moreover, strong built-in magnetic fields⁶, ⁷ can exist in these QDs, creating a quantum Hall regime at zero external magnetic field. Thus, these QDs represent natural two-dimensional electron/quantum Hall puddles and/or electron/composite fermion⁸ Wigner molecules (WMs)⁹ and are interesting for fundamental and applied research in quantum physics, nano-electronics, conventional⁹ and fault tolerant topologically protected¹⁰ quantum computing. Moreover, due to a very strong photoluminescence (PL) intensity and efficient cavity-mode-QD coupling these WM QDs provide the lowest lasing threshold of optical micro-resonators¹¹ and are interesting for nano-photonic applications.

These natural WM structures are n-type lens shape InP islands obtained using SO metal-organic vapor phase epitaxy (MOVPE) by deposition of few monolayers (MLs) of InP on Ga₀.₅₃In₀.₄₇P, or, simply, GaInP₂, lattice-matched to GaAs. The islands have lateral size 80-180 nm, height 5-25 nm, Ga content 0.0-0.25 and density 2-10 μm⁻². It was found that optimal SO InP/GaInP₂ WM QD structures, in terms of electron occupation, size distribution and density, are obtained using substrate having exact [001] orientation or 2° misorientation towards [110] direction, deposition of 3 ML of InP, growth temperature T₉=720° and III-V ratio 120, as reported previously⁹.

An intrinsic property of GaInP₂ lattice-matched to GaAs is atomic ordering (AO)¹², ¹³ which appears as a GaP-InP monolayer superlattice along one of the two <111>ₐ, zinc blende diagonals, known as CuPt₈-type crystal structure. In epitaxial GaInP films this is represented by the [T11] or [T̅11] oriented AO domains (AODs) and antiphase boundaries having size 5-500 and 1-40 nm and occupying up to 50% and 10% of material volume, respectively, depending on growth conditions¹⁴-¹⁶. Strong AO (i.e. large and dense AODs) lowers the band gap of GaInP₂ by up to 150 meV¹⁷, generates a piezo-electric field of up to ~200 kV/cm¹⁸ and creates a symmetry misfit strain¹⁹. The AODs can be strained or relaxed, i.e. have GaAs cubic or [111]-GaP/InP rhombohedral in-plane atom positions¹⁹. Thus, AO can strongly affect doping, confinement potential, optical properties and formation of WMs; however, previous reports on the growth of InP/GaInP₂ structures²⁰ did not consider this effect. On the other hand, growth of InP QDs should affect AO and it was found that ordered GaInP₂ islands can be formed on top of SO InP QDs grown at 8°C²⁰.

Here we used transmission electron microscopy (TEM), Raman and temperature dependent μ-PL spectroscopy measurements, including near-field scanning PL, to study the effect of CuPt₈-type AODs on the structural and emission properties of InP/GaInP₂ SO QDs structures grown by low pressure MOVPE²¹. Using cross-section TEM imaging to monitor the location of AODs we report the formation of InP/GaInP₂ QD/AODs core-shell composites consisting of InP QD core surrounded by a few GaInP₂ AODs having lateral size and height of 20-50 and 2-15 nm, respectively. By low-temperature μ-PL spectra we observed a set of narrow emission lines and peaks in the range 1.92-1.52 eV. In this set we identified QD-type excitonic lines related to GaInP₂ AODs and excitonic/WM lines/peaks related to coherent and incoherent InP QDs. We found an 80 meV decrease in the emission energy of the WM QDs due to bond relaxation (BR) of AODs and we

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demonstrate that the emission spectra of single WMs can have the emission energy as low as 1.53-1.55 eV.

The QD WM structure discussed here, sample number A2389 and henceforth denoted as R1, was grown using following conditions: $T_g=680$ C, III-V ratio 400 and substrate misorientation (SM) 0.2° towards [111]a. This growth differs from somehow optimal conditions described in Ref. 9. Thus, the data for R1 were compared with sample AIX2421 (denoted as U2 from this point forward), which was grown under the conditions described in ref. 9. Furthermore, PL spectra of these samples were compared with sample ii from Ref. 2, grown at lower $T_g$ (650 C) and with a thicker InP deposition (8 ML), denoted here as U0.

Raman spectra were excited by the 532 nm line of a solid-state laser from the (001) plane and measured in backscattering geometry using a CCD and a 0.5 m focal length spectrometer in two parallel configurations (XX) and (YY), where X[[110] and Y[[110]. We should point out, that Raman technique is the only one we can think of capable of addressing the strain/relaxation status of AODs. Plan-view TEM samples were prepared by conventional mechanical polishing using a Gatan simpler grinder, followed by Ar+ milling in a PIPSII. Cross-section TEM samples were prepared through a conventional mechanical polishing using Model 590 Tripod Polisher followed by Ar+ milling in a PIPS 691. TEM specimens were characterized using a JEOL 2100F and a FEI G2 Talos microscopes operating at an accelerating voltage of 200 kV. $\mu$-PL measurements were conducted at different temperatures in the range 10-300 K. Single dot measurements were performed using ozone plasma treatment, quenching the emission of the major part of the dots. Full details of room temperature near-field scanning optical microscopy (NSOM) and ensemble/single dot $\mu$-PL spectroscopy are described in Ref. 9.

In Raman spectra (see Fig. 1(a)) we observed the difference in the intensity of the (XX) and (YY) configurations for the GaP-type longitudinal phonon (LO$_1$) at 382 cm$^{-1}$ and an anti-phase boundary vibrational mode (Y’) at 355 cm$^{-1}$ in both R1 and U2 samples, which are the signatures of AO in GaInP$_2$ layers$^9$. In the R1 sample the LO$_1$ phonon has stronger intensity in the (XX) configuration indicating relaxation of AODs (see insert in Fig. 1(a)). The LO$_1$ phonon in the U2 sample has two components: one, near 379 cm$^{-1}$, which is stronger in the (XX) configuration and similar to that of R1, and the other, near 383 cm$^{-1}$, which is stronger in the (YY) configuration, indicating unrelaxed (strained) AODs. BR gives a mismatch of -1.5% for the [110] direction and +1.7% for the [110] direction corresponding to the frustration of Ga-P and the compression of In-P bonds. Thus, changing SM, $T_g$ and III-V ratio results in switching between unrelaxed and relaxed states of AODs.

Selected area electron diffraction (SAED) of sample R1 in Fig. 2(a) reveals superstructure reflections along with the fundamental zinc-blende spots. The [110]-pole SAED pattern contains superlattice spots at $\frac{1}{2}$[111] with pronounced streaking along the [001] axes which are typical features of CuPt-type ordering on both (111) and (111) planes$^{12,13}$. Therefore, two types of domains with ordering on two mirror planes and anti-phase boundaries are present, confirming the Raman observations of AO. Similar SAED patterns indicating AO were obtained for U2, U0 and other samples.

The 002 dark-field (DF) cross-section images clearly revealed the InP QDs as nm-sized islands within the 140 nm thick GaInP$_2$ film. Most islands were observed to be flat with $h$ =3-5 nm, lateral dimensions of 100-150 nm, and

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**FIG. 1.** Raman spectra of sample R1 measured in backscattering configurations XX and YY – (a) and comparison of (YY)-(XX) difference spectra of samples R1 and U2. Insert – strained arrangement of Ga, In, and P atoms in (001) plane (dashed lines show distortion due to bond relaxation, i.e. CuPt-type bond lengths).

**FIG. 2.** [110]-pole electron diffraction pattern of sample R1- (a); 002 dark-field cross-section image (b); [110]-zone bright-field TEM micrograph of the sample R1 (c and d - top), a combined picture comprising two overlaid (c – bottom) or separated (d - middle and bottom) dark-field micrographs taken with $\frac{1}{2}$[111] and $\frac{1}{2}$[111] extra-reflections (circled in a) from the same region of the sample. The dashed lenticular shape in d outlines the QD.
a density of approximately 50 µm$^{-2}$. These are type A QDs (see Ref. 2). Among them thicker quantum dots having $h$~20 nm (type B QDs) rarely occur. We also observed few defected regions having sizes of ~150 nm and $h$~40 nm, which can be attributed to C-type dots$^2$. An example of 002 DF cross-section image showing one A- and one B type QD is represented in Fig. 2(b).

The upper part of Fig. 2(c) provides a [110]-zone bright-field (BF) micrograph showing the general view of ~1 µm area of the GaInP$_2$ epitaxial layer. In the bottom part of Fig. 2(c) a combination of two overlaid DF micrographs taken with $\frac{1}{2}$(TT1) and $\frac{1}{2}$(TT3) extra-reflections from the same region of the sample is presented. The overlaid micrographs are false-colored; the AODs having [TT1] or [TT3] direction are shown in blue and red, respectively. The domains at the bottom of the GaInP$_2$ layer are seen as lamellae with a lateral size of 10-100 nm and a thickness of few nm. The domains in the cap GaInP$_2$ layer become thicker and occupy the whole 40-50 nm thick cap, their lateral size being 150-200 nm.

In the upper image of Fig. 2(d) we show the 200 nm area [110]-zone BF TEM micrograph of an InP QD having lateral size of 110 nm and height 9 nm, appearing as a dark lenticular island. In the same region, AODs with [TT1] or [TT3] directions are marked as red and blue contrast in the central and bottom parts of Fig. 2(d), respectively. We observed one [TT1] and three [TT3] AODs having lateral size of ~20 nm, adjacent to the bottom, as well as two large (~50 nm) and one small (~15 nm) [TT1] AODs adjacent to the top of the QD. Thus, the full structure of the QD is characterized as an InP/GaInP$_2$ QD/AODs core-shell composite. This indicates a correlation between the AO and SO growth, which agrees with the observation in Ref. 20. We should point out that in the upper image in Fig. 2d there are light-grey areas coinciding with AODs. Thus, the total height of the composite is ~20 nm, which could indicate that B-type dots are represented by these composites.

AODs generate a strong piezo-electric field of ~200 kV/cm along [TT1] or [TT3] directions leading to formation of WMs. In-plane inhomogeneity of this field can generate a build-in magnetic field. Thus, the formation of QD/AODs composite is a key feature for existence of natural InP/GaInP$_2$ WMs.

In the plan-view TEM image (see Fig. 3(a)) the InP QDs appear as grey and dark-grey spots having a size of 120-80 and 150-200 nm, and density ~2 µm$^{-2}$ for both sizes, respectively. We attribute the changes in grey contrast to the changes in dot thickness and, accounting for the small density observed, we assign these to B- and C-type dots, respectively. A-type dots are not observed in plan-view due to their small height. C-type dots, having size >150 nm show defect boundaries, suggesting incoherent relaxation of strain, as observed in cross-section TEM.

Figures 3(b) show the NSOM images acquired at a power density of 50 kW/cm$^2$ with spectral ranges of 740-780 and 640-680 nm, related to the ranges of InP QD and GaInP$_2$ emission, respectively (see single dot NSOM PL spectrum in the insert in upper Fig. 3(b)). In the image taken for 740-800 nm range, the QDs appear as bright spots having density ~2 µm$^{-2}$, i.e. the same as in the plan-view TEM image in Fig. 3(a). The size of the emission area (dashed circles) estimated from the image is ~90 nm and thus, they are related to B-type dots. On the other hand, in the image taken for the 640-680 nm range, the QDs appear as dark-grey and grey spots, which arise due to absorption of GaInP$_2$ emission by the QD material. The grey spots are related to B-type dots and their position coincides with the position of bright spots of the QD emission image. The size estimated from the absorption profile is ~120 nm, and is larger than the emission area due to partial filling of QD states by the photoexcited carriers involved in the emission process. At the same time the absorption images of B-type dots show a slight decrease of the absorption at the center, due to band filling, i.e. bleaching. The dark-grey spots have sizes of 150-200 nm and related to C-dots. These appeared dark at room temperature due to non-radiating defects.

Lateral size probability distribution function (PDF) of the sample R1 has two maxima, at 85 and 150 nm, having a FWHM of ~40 nm (see Fig. 3(c)). While, the sample U2 has its maxima at larger sizes, 130 and 170 nm, which indicates a decrease in the adatoms diffusion length for [111]$_a$ SM. For sample U0 PDF has one maximum at
180 nm and large FWHM of ~100 nm, which is due to Ostwald ripening.

The comparison of the 77 K PL spectra for R1, U2 and U0 samples shows an increase of the emission wavelength of InP QDs due to BR of AODs. For sample R1 A- and B-type dots were found to have an emission wavelength of ~720 and 800 nm, while for samples U2 and U0 the dots have an emission wavelength of 700-710 and 730-750 nm, respectively. In sample U0, the emission bands overlap with the bands of sample R1, indicating some fraction of relaxed AODs. Moreover, Raman spectra in Fig.1(b) indicate existence of some fraction of relaxed AODs in the U2 sample. For unrelaxed AODs the emission energy of InP QDs, neglecting In-Ga intermixing, is 1.61 eV\(^2\), which has a ~200 meV blue shift compared to bulk InP due to the strain arising from the 3.8% lattice mismatch with GaInP\(_2\). For relaxed AO GaInP\(_2\), the decrease in emission energy is 80 meV, i.e. ~0.4 of total shifts. This value agrees very well with the 0.4 change of the lattice mismatch due to BR.

In the ensemble \(\mu\)-PL spectra of sample R1 measured at temperatures T= 250, 200, 150, 100, 50, 20 and 10 K, (see Fig. 4(a)) only the band related to the B-type dots is observed for T=200-300 K. At T=250 K it has a maximum at 820 nm and a FWHM of ~30 nm. At T=150 K, another band having a FWHM of ~30 nm related to A-type dots appears at 740 nm. When the temperature further decreases, the A-band shifts to lower wavelengths reaching ~700 nm at 10 K. It starts revealing a fine structure at 20 K. At T=50 K a shoulder of A-band related to C-dots appear at 740 nm and two shoulders related to the HE and LE bands of AO GaInP\(_2\), reported previously\(^{23-25}\), appear at 650 and 685 nm, respectively. The LE band reveals a fine structure at T=20 K. Also, at 20 K two GaAs substrate peaks having a FWHM of ~5 nm appear at 820 and 830 nm. We should point out that the wide spectral range (50-90 nm) of the emission of A- and B-type InP QDs indicate Ga-In intermixing\(^2\), which can reach values up to 0.25 and thus the emission at lower wavelengths of these ranges originate from In(Ga)P QDs.

In the 10 K \(\mu\)-PL spectra of the specimen having reduced dot density all bands, except HE, decay on sharp emission lines (FWHM<1 meV). This is related to QD-type excitonic transitions of AODs of GaInP\(_2\)\(^{26,27}\) and InP and In(Ga)P QDs, as well as broader peaks (FWHM ~1-5 meV) related to InP and In(Ga)P WMs.

In Fig. 4b we show a set of selected single dot spectra of five B-type dots having emission energies 1.53-0.155 eV and different electron occupation (\(N\)). One dot has \(N=0\) and shows a single s emission exciton peak. While, the rest of the dots are WMs, having \(N=1-10\) and \(h\omega_0 =1.5-3\) meV, revealing features previously reported for unrelaxed AO WMs having emission energies of 1.7-1.8 eV\(^9\). For \(N=1\), the spectrum has a broad Stokes feature indicating a formation of 2 electrons (2e) WM in photo-excited state; for \(N=2\) and 5, anti-Stokes peaks related to p electrons of 3e- and 6e-WMs in photo-excited state, and Stokes peaks related to rotational (\(\alpha_0,\alpha_1\)) and translational (\(\alpha_2\)) modes of 2e- and 5e-WMs in initial states, are observed; for \(N=10\), an additional anti-Stokes peak related to d electrons of 11e-WM appears\(^8\).

In conclusion, we report the effect of CuIn\(_2\)-type AO on structural and emission properties of InP/GaInP\(_2\) SO QW WMs. We observed a formation of InP/GaInP\(_2\) QD/AODs core-shell composites and found that AODs can be relaxed. In low-temperature \(\mu\)-PL spectra we observed a set of emission lines related to excitons of QD-like GaInP\(_2\) AODs and exitons/WMs of coherent and incoherent InP QDs. PL spectra of single WMs having number of electrons \(N=2-10\), quantum confinement \(h\omega_0 =1.5-3\) meV and emission energy as low as 1.53 eV, resulting from AODs BR, were identified in \(\mu\)-PL spectra. Our observations elucidate the existence of natural WM as a result of correlation of AO and SO growth and strong piezo-electric fields generated by AODs.

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(a) Raman intensity (arb. units)

(b) $I_{YY} - I_{XX}$ (arb. units)

Raman shift (cm$^{-1}$)

$X \parallel [1\bar{1}0]$
$Y \parallel [110]$

TO$_2$
LO$_1$
LO$_2$
Y'

Ga
In
P
P

R1
U2