Electronic Structure of "Sequence Mutations" in Ordered $GaInP_2$ Alloys

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The electronic consequences of layer thickness fluctuations in CuPt-ordered $GaInP_2$ (layer sequence Ga-In-Ga-In...) are investigated. We show that the formation of a "sequence mutated" Ga-In-In-Ga... region creates a hole state $h1$ localized in the In-In double layer, while the electron state $e1$ is localized in the CuPt-ordered region. Thus, the system exhibits electron-hole *charge separation* in addition to spatial localization. This physical picture is preserved when the dimension of the mutated segment is reduced from 2D to 0D, resulting in disklike dot structures. Our theory explains the long-standing puzzle of the origin of the peculiar luminescence properties of ordered $GaInP_2$.

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Surface-reconstruction-induced ordering of (001)-grown III-V semiconductor alloys [1] is manifested by alternate monolayer superlattices $(GaP)_1/(InP)_1$ oriented along $[1\bar{1}1]$ or $[\bar{1}11]$ directions ("CuPt-ordering subvariants"). This spontaneous ordering reduces the band gap relative to the random alloy and splits the valence band maximum, leading to polarized excitonic transitions E_X whose dependence on the degree of long-range ordering is well studied [2]. It has been known for a long time [3,4], however, that 20–50 meV below this excitonic line there exist low-energy (LE) transitions E_{LE} with peculiar properties [3–9]: (i) E_{LE} has a longer photoluminescence (PL) decay time than the excitonic transition E_X [3–5] (this has been observed also in ordered $GaInAs_2$ [10]). (ii) While the luminescence peak from E_X shifts quadratically as a function of external magnetic field, E_{LE} shows a linear dependence [5]. (iii) As the excitation power is increased, the PL peak position of E_{LE} shifts to higher energies [3–6]. (iv) While E_X shows no clear structure in its line shape beyond Gaussian-like broadening, E_{LE} consist of extremely sharp emission lines (typical linewidth ≤ 1 meV over a range of 10–15 meV) [7,8]. Combination of observations (i)–(iii) had led to the conclusion that E_{LE} is a spatially indirect (type-II) band-to-band transition [3–5]. However, despite extensive experimental characterization [3–9] of E_{LE}, the identity of the atomic microstructure that leads to these transitions in ordered $GaInP_2$ alloys has remained unresolved.

In order to explain the slow and spatially indirect optical transitions, it has been postulated [3,9,10] that the samples could contain both ordered and random-alloy domains, and that electrons are localized on the former, while holes live on the latter. However, first-principles calculations [11] have shown that the disordered/ordered interface in $GaInP_2$ does not exhibit type-II band alignment. Later experimental studies [7] have also shown that, in fact, the degree of order is rather uniform in the samples. Furthermore, while structural polytypes, resulting from alternate sliding of (001) planes, were predicted [12] to exhibit type-II band alignment in two-subvariant samples having such stacking faults [3,4], the E_{LE} emission has also been detected [7] in single-subvariant samples, where polytype structures do not exist.

To search for a microstructure that can explain the origin of E_{LE} in *spontaneously* ordered alloys, let us consider first the microstructure of *artificially* ordered superlattices (Fig. 1). While an ideal superlattice consists of a periodic stacking of atomic layers, i.e., $(A)_n/(B)_n$, one can encounter imperfections ("sequence mutations") in this system in the form of layer thickness fluctuations [the thicker bilayer in Fig. 1(a)]. Electronic structure calculations [13] of $(AlAs)_n/(GaAs)_n$ superlattices have shown that such mutations can cause sharp localization of both electron and hole wave functions. However, there is no obvious mechanism to cause *spatial separation* of electrons

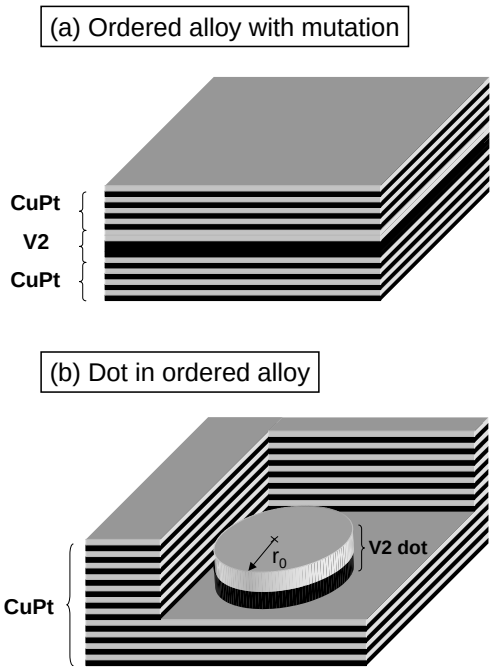

FIG. 1. Structure of sequence mutation in ordered $GaInP_2$: one period of Ga-Ga-In-In ($V2$) inside the Ga-In-Ga-In (CuPt) structure. In (a) the $V2$ region forms 2D quantum well, while in (b) $V2$ is disklike (0D quantum dot with radius r_0).

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from holes if the band alignment of A and B is type I, since effective-mass models would suggest that both electron and hole wave functions will localize in the widest segment of the superlattice. The interesting discovery in the present paper is that sequence mutations in $(GaP)_1/(InP)_1$ [111]-superlattices can induce charge separation in addition to wave function localization despite the fact that band alignment between GaP and InP is type I [14]. This noneffective-mass effect provides a microscopic explanation for the type-II band alignment concluded from the experimental observations (i)–(iii). The effect can be traced back to the presence of a "sequence mutated" In-In layer embedded in the Ga-In-Ga-In-... (CuPt) structure. We will further show that the charge separation persists, if the spatial extent of this sequence mutation is reduced from two dimensions [Fig. 1(a)] to zero dimension [disklike "dot" in Fig. 1(b)]. Such thickness-fluctuation-induced zero-dimensional structures have been observed spectroscopically in ordinary, *artificially* grown superlattices [15]. These experiments show a multitude of sharp and narrow PL lines as well as a blueshift due to "band filling" effect as the excitation power is increased. These features are qualitatively identical with the experimental observations (iii) and (iv) in ordered $GaInP_2$. Thus, our predicted properties of zero-dimensional disklike In-In-double layer structures embedded in CuPt-ordered $GaInP_2$ can explain the peculiar properties [(i)–(iv)] of the E_{LE} transition. This result supports the suggestion by Kops *et al.* [8] that the quantum-dot-like objects exist in these alloys. Recent scanning tunneling microscopy (STM) studies have indeed observed In-In double layers in nominally ordered $GaInP_2$ [16].

To investigate the electronic properties of ordered $GaInP_2$ we use a plane-wave basis generalized empirical pseudopotential method (EPM) [17] which (i) can handle the large system sizes ($>10^4$ atoms) required for the description of dotlike structures and (ii) realistically predicts the electronic structure of these structures. The atomic pseudopotentials are carefully fitted to reproduce the experimental band structure of GaP and InP binaries and the first-principles [local density approximation (LDA)] calculated GaP/InP band offsets [17]. The relaxed atomic positions are obtained using the valence force field [18] method.

Figure 2 shows as solid dots and lines the calculated energies of band edge states in $(GaP)_n/(InP)_n$ [111]-superlattices as a function of period n. The most noteworthy feature is that the conduction band minimum energy does not decay monotonically with period n: the $n = 2$ structure (denoted $V2$) has its conduction band minimum *above* that of $n = 1$ CuPt structure. This is in clear contrast with the monotonic decay (illustrated schematically by dashed lines in Fig. 2) predicted by effective-mass approximation. This anomalous behavior results from strong repulsion effects of folded superlattice states: In [111]-superlattices the L_{1c} and Γ_{1c} zinc-blende states fold into the superlattice $\bar{\Gamma}_{1c}$ state. For $n = 1$, the coupling between the folded L state $\bar{\Gamma}_{1c}(L_{1c})$ and the original

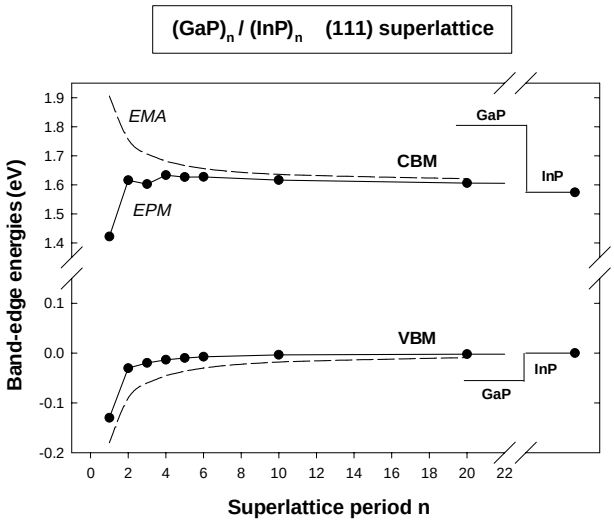

FIG. 2. The EPM calculated band edge energies in $(GaP)_n/(InP)_n$ [111]-superlattices as a function of period n. Also shown as the asymptotic $n \to \infty$ limit are the valence and conduction band offsets in coherently [111]-strained, lattice-matched GaP/InP interface. The dashed lines illustrate schematically the band edge energies based on the effective-mass approximation (EMA).

$\bar{\Gamma}_{1c}(\Gamma_{1c})$ state is very strong, thus the $\bar{\Gamma}_{1c}(\Gamma_{1c})$ energy of $n = 1$ is pushed down [2]. The $\Gamma - L$ coupling is reduced for $n = 2$, thus the $\bar{\Gamma}_{1c}(\Gamma_{1c})$ energy of the $n = 2$ is higher than the $\bar{\Gamma}_{1c}(\Gamma_{1c})$ energy of the $n = 1$. On the other hand, we find that the energy of valence band maximum goes up in energy monotonically as the superlattice period n increases. Thus, both conduction and valence band-edge energies for $(GaP)_2/(InP)_2$ are *higher* in energy than for $(GaP)_1/(InP)_1$, resulting in a strong type-II band alignment. This band alignment (194 meV in conduction band minimum, 100 meV in valence band maximum) is shown via thick solid lines in the upper panel of Fig. 3. The thin horizontal lines depict the calculated confined levels of a single Ga-Ga-In-In ($V2$) layer sandwiched between $(CuPt)_N$ regions of thickness N. The crucial observation is that the $h1$ hole state, originating from the $V2$ layer, persists in the $(CuPt)_N$-$V2$-$(CuPt)_N$ structures, residing 79 meV ($N = 2, 5$) above the valence band maximum of CuPt. This state is strongly localized in the In-In part of the $V2$ region, as shown in the lower panel of Fig. 3, and thus its energetic position is insensitive to the thickness of the CuPt region surrounding it. In contrast, the second hole state $h2$ is localized in the CuPt region. As the CuPt layer thickness N increases, the $h2$ energy approaches the valence band maximum of CuPt. The energy separation Δ between $h1$ and $h2$ ranges from 104 to 84 meV as N increases from 2 to 5. To see if the presence of a Ga-Ga layer is crucial for the electronic structure created by Ga-Ga-In-In ($V2$), we have also calculated the structure $(CuPt)_N$-In-In-$(CuPt)_N$ in which the Ga-Ga layer of $V2$ is removed. We find the character and energetic position of the $h1$ and $h2$ hole states remains very much the same ($\Delta = 70$ meV) [19]. This

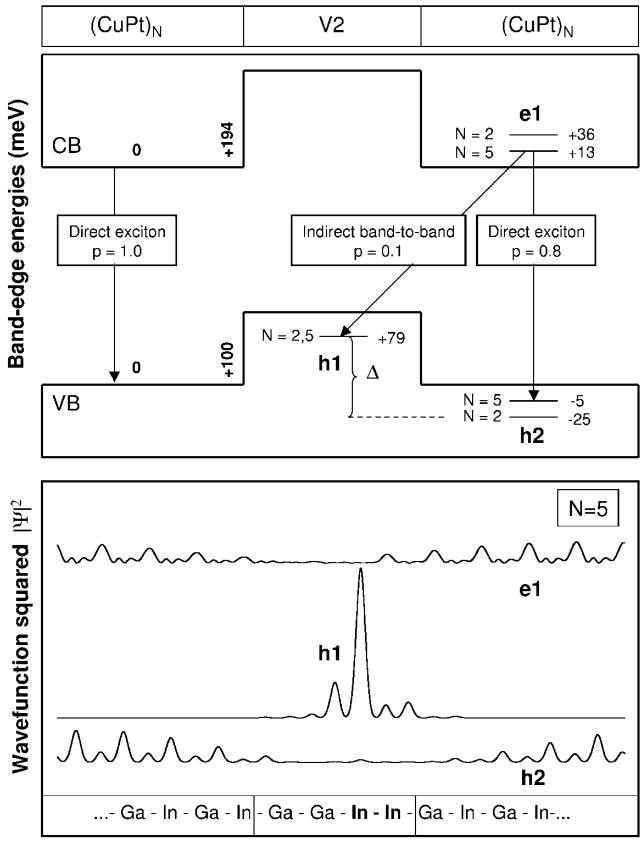

FIG. 3. The EPM calculated band edge energies for $(\mathrm{CuPt})_N$-$V2$-$(\mathrm{CuPt})_N$ structures (N is the thickness of CuPt region surrounding $V2$ region). The energies are in meV. The LDA-calculated band offset between CuPt and $V2$ for conduction band minimum (valence band maximum) is 150 (56) meV, confirming the type-II alignment predicted by EPM. For $N = 2$ the LDA-calculated value for $\Delta = h1 - h2$ is 80 meV, verifying the EPM predicted appearance of $h1$ level above $h2$. The lower panel shows the $e1$, $h1$, and $h2$ wave functions squared for the $N = 5$ system.

insensitivity to the presence of Ga-Ga segment is expected, since the Ga-Ga double layer acts as a barrier (Fig. 3), and thus does not play an important role for the band edge localization. The lowest conduction state $e1$ remains localized in the CuPt region as shown in the lower panel of Fig. 3, and its energetic position approaches the conduction band minimum of CuPt as the thickness N of the CuPt region surrounding $V2$ is increased. The important observation emerging from Fig. 3 is that the occurrence of a sequence mutation in the form of an In-In layer in the CuPt structure creates a spatially *indirect, low-energy* transition (from $e1$ to $h1$), in addition to the spatially direct, excitonic transition (from $e1$ to $h2$).

To see the strength of various transitions, Fig. 3 shows the calculated dipole matrix elements $p = \langle \psi_{e1} | \hat{p} | \psi_{h1,h2} \rangle^2$ between these states, normalized with respect to the $e1$-$h1$ (band gap) transition in pure CuPt. Since the $e1$-$h1$ transition is spatially indirect, we find that its transition probability is smaller than for the spatially direct transition $e1$-$h2$. However, the $e1$-$h1$ transition probability is still substantial when compared with the direct $e1$-$h2$ transition. Thus, the $e1$-$h1$ transition acts as the likely source for the observed E_{LE} transition, while $e1$-$h2$ corresponds to the excitonic transition E_X.

In order to explain the sharp spectral features in E_{LE} [7,8], we next explore the consequences of reducing the dimensionality of the mutated region from 2D to 0D [Fig. 1(b)]. To do this, we have constructed a large [111]-oriented supercell with $20 \times 20 \times 24$ zinc-blende unit cells (19 200 atoms) [20]. We then create a single Ga-Ga-In-In $V2$-like disk with radius r_0 surrounded by a CuPt region, shown in Fig. 1(b) [21]. Figure 4 shows the energetic position of $e1$, $h1$, and $h2$ band edge states as a function of the radius r_0 of the $V2$ quantum disk. The $r_0 \rightarrow \infty$ limit corresponds to 2D quantum well structure formed by the $V2$ layer (Fig. 3). We find that, as the quantum disk size is reduced, the conduction band energy $e1$ remains nearly constant. This is because the $e1$ state is confined to the CuPt region (Fig. 3), and is thus insensitive to the size of the $V2$ disk. This is also the case for the CuPt-confined $h2$ state. In contrast, the energy of the In-In-localized $h1$ state depends strongly on the quantum disk size (Fig. 4): As the disk radius is decreased, the energy separation $\Delta = h1 - h2$ decreases from 84 meV to $\sim$20 meV. The drop in $h1$ energy is due to the fact that the quantum confinement increases as the disk size decreases. The important observation is that qualitative behavior (localization) of $e1$, $h1$, and $h2$ states remains the same when moving from two-dimensional In-In-layer structures to zero-dimensional disks.

To establish a quantitative connection to the experimentally observed position of E_{LE} (20–50 meV below E_X), let us consider the effects due to the degree of long-range CuPt ordering. The structures in Fig. 4 represent the ideal case of perfect long-range order (ordering parameter $\eta = 1$). In actual samples the order parameter is usually

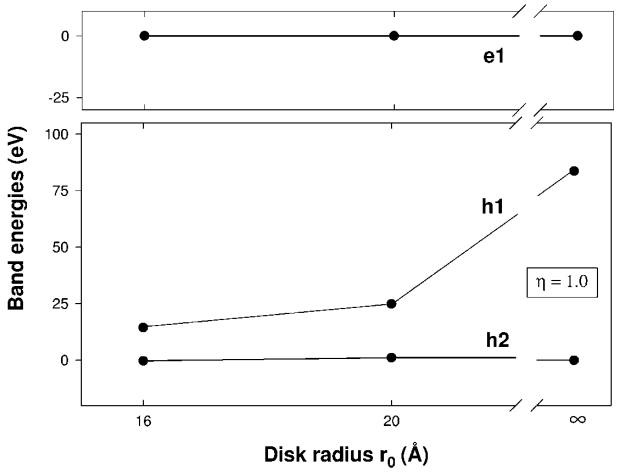

FIG. 4. The energetic position of $e1$, $h1$, and $h2$ band edge states in CuPt/$V2$/CuPt structure (Fig. 1) as the disk size (r_0) is reduced. $r_0 = \infty$ corresponds to the 2D $V2$ quantum well sandwiched between CuPt regions.

smaller $\eta \sim 0.5$ [7]. To mimic this situation, the In layers are replaced by random $In_{0.5+\eta/2}Ga_{0.5-\eta/2}$ layers and the Ga layers are replaced by random $In_{0.5-\eta/2}Ga_{0.5+\eta/2}$ layers. Our calculations show that when $\eta = 1$ is changed to $\eta = 0.5$ the $h2$ (CuPt-confined) state energy drops by 53 meV, while $h1$ ($V2$-confined) state energy decreases by 111 meV. The $h1$-$h2$ separation Δ thus decreases from 84 to 26 meV (roughly following the η^2 law [22]). Based on these results we see that the energy separation Δ between $h1$ and $h2$ depends on several factors: (1) the size of the quantum disk, (2) the order parameter of the CuPt region, and (3) the order parameter of the disk. Determined by these parameters, we see that Δ ranges from very small values $\sim$10 meV to large values $\sim$50 meV. This range is in excellent agreement with the experimental results for the energy difference between E_X and E_{LE}. In addition, the dependence of Δ on several parameters provides explanation for the observed broad line shape ($\sim$10$-$15 meV [7]) of the low-energy transition E_{LE}: In-In disks with varying size and shape inserted into the CuPt region account for the multitude of narrow dotlike emission lines. Finally, the existence of dotlike localized states offers a natural explanation for the observed blueshift of the PL energy as the excitation power increases [3–6], in terms of saturation of the lowest transition, and the emergence of the excited-state PL.

In summary, using plane-wave pseudopotential calculations we have demonstrated that (111) layer thickness fluctuations (sequence mutations) in the form of In-In double layers embedded in the CuPt-ordered $GaInP_2$ matrix induce localized hole states $h1$ above the CuPt-confined hole states $h2$. Since the lowest conduction band $e1$ is confined in the CuPt region, the transition from $e1$ to $h1$ is spatially indirect. This explains the experimentally observed type-II behavior for the below-band gap luminescence emission for CuPt-ordered $GaInP_2$ samples. The localization of the $h1$ state in the In-In layer persists even if the dimension of the In-In region is reduced from a 2D quantum well to 0D quantum disk. The calculated energies for the $e1$-$h1$ and $e1$-$h2$ transitions are in good agreement with experiment, and provide strong evidence that the experimentally seen peculiar luminescence properties of ordered $GaInP_2$ are a consequence of quantum-disk-like microstructures formed due to sequence mutations in [111]-superlattices.

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[19] We also find that the Ga_1In_2-ordered structure embedded in CuPt seen in recent STM studies [16] creates a $h1$ level with very similar energetic position and localization as $V2$.

[20] The third dimension of the supercell is along the [111] direction and is identical to the $N = 5$ structure in Fig. 3, but each (111) plane in the supercell now contains $20 \times 20 = 400$ cations. The resulting disk-disk separation in the (111) plane is 80 Å.

[21] We have used the $V2$-like structure inside the CuPt region instead of pure In-In disk in order to be commensurate with surrounding CuPt layers. However, as shown for the superlattices, the Ga-Ga double layer does not alter the physics involved since it acts as a barrier.

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