Excitons in alloyed nanowire quantum dots have unique spectra as shown here using atomistic calculations. The bright exciton splitting is triggered solely by alloying and despite cylindrical quantum dot shape reaches over 15 µeV, contrary to previous theoretical predictions, however, in line with experimental data. This splitting can however be tuned by electric field to go below 1 µeV threshold. The dark exciton optical activity is also strongly affected by alloying reaching notable 1/3500 fraction of the bright exciton and having large out-of-plane polarized component.

Quantum dots (QDs) main spectral properties are governed by size, shape and average chemical composition. However the detailed, fine structure of their optical spectra that plays an essential role for applications in quantum optics and information is determined by atomic scale details related to microscopic symmetry of underlying lattice, presence of facets and alloying randomness. Potential applications, the bright exciton (BE) recombination in QDs is considered as a tool for entanglement of entangled photons through biexciton-exciton cascade, whereas the dark exciton (DE) gained attention as a candidate for long-lived, though optically addressable quantum bit.

The calculations are performed in a series of computational steps beginning with valence force field approach for strain, empirical tight-binding (ETB) for the single particle spectra, and configuration interaction (CI) for many-body excitonic properties. Figure I shows results obtained for an alloyed NWQD as a function of phosphorus (P) content. The QD is disk-shaped with 30 nm diameter and 4.2 nm height and is embedded in [111] oriented InP host zinc-blend nanowire with diameter of 72 nm. To account for alloying a uniform composition profile is used mimicking migration of P anions into the QD during the VLS growth. The overall nanostructure’s symmetry is $C_{3v}$ for pure InAs system.
FIG. 1. Exciton ground state energy (a), dark-bright exciton splitting (b), dark (c) and bright (d) exciton splitting as function of phosphorous (P) content in the alloyed NWQD.

and is reduced by alloying to $C_1$. For each P content there are 6 randomly generated samples corresponding to the same average composition. P content is varied from 10 to 80% with a 5% step, and from 0% to 10% with a 1% step for greater accuracy. There are thus 29 various average compositions times 6 random samples per composition, total of 174 different nanostructures presenting a challenging computational problem.

On Fig. 1 (a) the ground excitonic energy increases with P content, from 768 meV for pure InAs to about 1305 meV for InAs$_{0.80}$P$_{0.20}$ QD. The growth of the excitonic energy originates from the introduction of the higher band gap energy barrier material into the QD, and to a very good approximation is linear with a 6.7 meV/% slope. The spread of excitonic energies due to alloy randomness reaches at most 8 meV, and is practically non-apparent on Fig. 1 (a). On the other hand the dark-bright splitting [Fig. 1 (b)], i.e. the energetic difference between the lowest bright and the higher energy dark exciton is reduced with the increasing P content since P add-mixture effectively decreases depth of confinement, and thus so-called isotropic electron-hole exchange, controlling the dark-bright splitting. The spread of calculated values is notable and has maximum of about 20 meV for P content equal to 30%, then it drops with P. Intuitively this could be understood in terms of a number of different possible phosphorous atomic arrangements (combinations), growing with P, reaching maximum for P = 50% and then reducing again. Speculatively this effect combined with the overall decrease of dark-bright splitting due to P content give maximal spread for P ≈ 30% rather then P = 50%.

The impact of alloy randomness on excitonic fine structure [Fig. 1 (c) and (d)] is fundamentally stronger. Both the DES and the BES are exactly zero by symmetry for pure InAs NWQDs, yet already a few percent P add-mixture introduces non-negligible splittings. For the BES [Fig. 1 (d)], these splittings reach maximal values of about 15 µeV for P content between 10% and 30% and curiously these maxima are quenched again with further alloying, speculatively due to the same mechanism as for the dark-bright splitting. For P content in between 20% and 60% minimal values do not drop below about 3 µeV, only for lowest P concentration, and for P content over 70% the BES can drop below 1 µeV. Not only these values are typically much larger than EPM’s predictions, but also show pronounced dot-to-dot fluctuations as seen in the experiment. Similarly the DES ([Fig. 1 (c)]) is also triggered by alloying, however this splitting is very small, often below 0.11 µeV. Maximal values of the DES increase with P up to about 20%, then the trend saturates with only some spikes (of about 0.15 µeV) for largest considered P of 75 − 80%. The DES distribution is more uniform with no apparent lower bound.

Alloying has a strong impact on oscillator strengths of excitons, specially on the DE which gains which a substantial optical activity as shown on Fig. 2 (a), where the ratio of DE to BE oscillator strengths is used as a measure of relative DE optical activity. For non-alloyed QD the DE oscillator strengths are about 160,000 weaker than the BE. However for alloyed NWQDs this activity is increased by nearly an order of magnitude, up to about 1/15,000 fraction of the BE, with further significant increase for taller quantum dots, as discussed later in the text. Alloying also affects NWQDs polarization properties. For the BE, the emitted light is to a very good approximation in QD plane polarized, yet with linear polarization directions randomized from dot-to-dot. The BE
FIG. 3. The dark exciton polarization properties as function of height for alloyed NWQD and two average compositions (a) InAs$_{0.5}$P$_{0.5}$ and (b) InAs$_{0.2}$P$_{0.8}$. Diamonds (blue)/triangles (green) denote in-plane and out-of-plane polarizations correspondingly.

emission is thus in-plane polarized with a much weaker (6 orders of magnitude) out-of-plane (growth direction, "z") component. For the disk-shaped NWQD there is only little BE's polarization anisotropy, growing with alloying, yet reaching at most about 1% for $P = 0.8$. The DE exciton spectra of alloyed systems is more curious [Fig. 2 (b)]. For the pure InAs NWQD the DE is still fully in-plane polarized, having exactly the same polarization properties as the BE. However with the increasing $P$ content the DE gains large out-of-plane component of the emission. For the highest considered $P$ content, the out-of-plane oscillator strengths are comparable and can even exceed the in-plane ones. This is thus very different from low-symmetry SADs or non-alloyed $C_{3v}$ QDs.

It is also curious to check how spectra of excitons in alloyed NWQDs depend on the growth direction confinement. This is shown on Fig. 3 and Fig. 4 where the height of NWQDs varies from 1.4 nm to 8.4 nm (11 different cases). All other QD and nanowire dimensions are the same as above. Four different $P$ concentrations were considered ($P = 50\%$ and $80\%$, as well as $60\%, 70\%$ for comparison). There were 8 random samples generated for each average composition, leading to a formidable problem of $(11 \times 8 \times 8) = 352$ separate atomistic computations.

For InAs$_{0.5}$P$_{0.5}$ NWQDs and heights lower than 3 nm, the DE is mostly out-of-plane polarized with a weak in-plane components [Fig. 3(a)]. This is quite curious and it seems that due to randomness the DE polarization properties in flat alloyed NWQDs resemble more $C_{2v}$ SADs spectra [23] with DE "z" polarized emission, rather than $C_{3v}$ pure InAs NWQDs with "x/y" polarization. However with the increase of QD height, the in-plane component grows faster then the out-of-plane one, and the in-plane polarization dominates the tall QD DE spectra of the $P = 0.5$ case. For heavily alloyed $P = 0.8$ systems and small QD heights, the DE emission is mostly out-of-plane polarized [Fig. 3(a)]. For taller QDs and high $P = 0.8$ content both components are comparable.

However there are several notable cases where the out-of-plane polarization becomes dominant for $h > 7$ nm, again very distinct from non-alloyed $C_{3v}$ systems.

Further studies of QDs height dependence are shown on Figure 4. Here for completeness Figure 4 (a) presents the ground excitonic state energy evolution as a function of both height and $P$ content. The increased QD height reduces confinement and decreases excitonic energy, whereas the $P$ content shifts up excitonic energy and flattens the trends. The spread of calculated values due to alloy randomness is again relatively small ($\approx 10$ meV). Figure 4 (b) shows the DE activity with respect to BE, similar to Fig. 2 (a), yet this time as a function of QD height. For $P = 0.5$ there is about five-fold increase of the DE optical activity as a result of reduced confinement. Similarly for $P = 0.8$ the DE/BE oscillator strengths ratio is much larger for taller QDs than for flat ones, with an exception of really flat, several monolayer ($< 2$ nm) thick QDs, where DE/BE ratio is also increasing. Notably for the highly alloyed and high aspect ratio, tall QDs the DE can reach significant optical activity being $1/3500$ fraction of the BE. Further, Figure 4 (c) and (d) present DES and BES correspondingly as a function of QD height. The DES spread increases with QD height, reaching about $0.15 \mu$eV for $h < 5$ nm and about $0.3 \mu$eV for taller systems. The lower bound of the DE spin’s coherent precession time [25] (Planck’s constant divided by eigenstates’ energy difference) will thus
the NWQDs, three different InP$_{0.2}$ monolayer thick (0.5 nm) SADs are embedded in GaAs barrier and are placed on substrates of 25 nm and heights equal to 3 nm. This reduces the BES at zero field BES [Figure 5 (a)] is large and equal to 56.4 µeV. Field affect this splitting and actually even reverse the order of BE lines. The splitting can be controlled by vertical electric field, F, and for NWQDs as well as SADs for comparison. Two lens-shaped SADs are considered: a non-alloyed InAs of C$_{2v}$ symmetry and alloyed InGa$_{0.5}$As$_{0.5}$ of C$_1$ symmetry. SADs dimensions are identical with diameters of 25 nm and heights equal to 3.5 nm. Both SADs are embedded in GaAs barrier and are placed on 2 monolayer thick (0.6 nm) InAs wetting layer. As for the NWQDs, three different InP$_{0.8}$As$_{0.2}$ alloyed dots are shown on Figure 5 (c). These NWQDs have identical dimensions (h=4.2 nm, d=30 nm) and average composition, the only difference between them being random alignment of P atoms. Separate ETB and CI calculations were performed for total of 215 different cases.

In conclusion, it has been shown shown that alloying in nanowire quantum dots is responsible for a non-vanishing bright exciton splitting occurring merely due to alloy randomness without any shape deformation, off-center quantum dot position, nor non-uniform composition. The BEs depend highly on the composition intermixing and varies considerably between individual dots. The splitting can be controlled by vertical electric field, with a field dependence very different from SADs. Dark exciton properties in nanowire quantum dots are sensitive to the alloying as well. The DE gains notable optical activity that grows with alloying and quantum dot height. Heavily alloyed nanowire quantum dots can have strongly out-of-plane polarized dark exciton emission, whereas in weakly alloyed NWQDs the DE will be in-plane polarized.

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