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Role of dimensionality and quantum confinement in *p*-type semiconductor indium phosphide quantum dots

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We characterize the impurity state responsible for current flow in zinc-doped indium phosphide nanocrystals through first-principles calculations based on a real-space implementation of density-functional theory and pseudopotentials. We found the activation energy of the acceptor state to range from the value of the acceptor state in the bulk (0.03 eV) to up to values of ~ 2.5 eV in the smaller nanocrystals as a result of the three-dimensional quantum confinement. This maximum value for the nanocrystals is an order of magnitude bigger than the maximum value found for one-dimensional nanomaterials (nanowires) within the same theoretical approach (~ 0.2 eV). Our results show that the progressive reduced dimensionality in *p*-type indium phosphide materials strongly reduces the capability of the materials to generate free carriers.

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Semiconductor nanowires (NWs) and quantum dots (QDs) are nanomaterials that have attracted enormous attention. Besides their reduced dimension, NWs and QDs offer the possibility to tune the electronic and optical characteristics of their macroscopic counterparts following the effects that the quantum confinement has on the electronic states. As such, semiconductor NWs and QDs represent ideal building blocks for highly integrated electronic and optoelectronics, and are now seen as materials to play a prominent role in the semiconductor industry of the near future.

Indium phosphide nanowires (InP-NWs) and quantum dots (InP-QDs) are among the semiconductor nanomaterials for which very promising advances have been made. Doped InP-NWs grown as *p*-type NWs are known to function as light emitting diodes and field effect transistors when assembled with *n*-type NWs;[1,2] InP-QDs, also doped as *p* type, were shown to transport electrical carriers (holes) in photoelectrochemical cells.[3] Therefore, a complete understanding of the effects that quantum confinement has on the properties of interest of these nanomaterials is important. For example, in a previous first-principles study on *p*-type InP-NWs we have predicted that the activation energy of the acceptor state in thinner NWs can be an order of magnitude bigger than in the bulk as a result of the two-dimensional quantum confinement.[4] As such, in these NWs only a small fraction of the impurities will ionize and contribute to free carriers. Following our previous work, here we characterize *p*-type InP-QDs from first principles. With it, we intend not only to provide information that could be useful for designing devices and applications based on InP-QDs. From a fundamental point of view, we are interested in determining how the different dimensionality of quantum confinement (two dimensional in NWs, and three dimensional in QDs) would affect the characteristic properties of InP by establishing a direct comparison with our previous work.[4,5]

We have studied *p*-type doped InP-QDs obtained through the introduction of Zn impurities in the host QDs, following experimental techniques for *p*-type doping these nanomaterials.[3] Our calculations are based on pseudopotentials constructed within density-functional theory as implemented in the PARSEC code.[6] In this implementation, the Kohn-Sham equations are solved self-consistently on a three-dimensional real-space grid. Only one parameter, the grid spacing, is necessary to control numerical convergence. The core electrons are represented by norm-conserving *ab initio* pseudopotentials.[7] The local-density approximation is used for the exchange and correlation potential.[8]

Spherical clusters of InP-QDs were constructed with the zinc-blende structure using the bulk lattice constant. In and P dangling bonds at the surface of the quantum dot were passivated using fictitious, hydrogenlike atoms with fractional charge[9] in order to remove states related to dangling bonds from the gap. The passivation is performed in such a way that no In or P atom is bonded to more than two fictitious atoms. The Kohn-Sham equations were solved for a domain that was chosen to be a sphere of about 6 a.u. (1 a.u. $=0.529$ Å) larger than the distance of the outermost hydrogenlike atom to the center of the nanocrystal (the Kohn-Sham wave functions were required to vanish at the boundary of the domain). Within this domain, the real-space grid was generated for a spacing of 0.60 a.u. (convergence tests were made for grid spacings down to 0.40 a.u.). All the studied nanocrystals were centered on an In atom, and this is the atom that was replaced by the impurity in the doped QDs. The sizes of the nanocrystals studied range from the deep nanometer regime (~ 1 nm) to up to diameters of ~ 6 nm (nanocrystals constituted by up to 4000 atoms of crystalline core were considered in this work; see Table I). The ionic positions of the atoms were allowed to relax for nanocrystals with diameters up to 2.4 nm. We found structural relaxation to be relevant only for the two smaller nanocrystals studied in this work. The main structural effect of the relaxation is to

TABLE I. Indium phosphide nanocrystals studied in this work. The number of InP atoms constituting the crystalline core of the nanocrystals (N_{InP}) as well as the number of hydrogenlike atoms used to passivate the surface dangling bonds (N_{H}) are listed for each of the dots. I_p and A_d are the ionization energy and electron affinity calculated for the pure and p-type doped nanocrystals, respectively. The difference between these two quantities gives the activation energy of the acceptor state (E_{act}). The doped nanocrystals were created by replacing the In atom placed at the center of the nanocrystals by a Zn atom (see the text).

Diameter (nm)	N_{InP}	N_{H}	I_p (eV)	A_d (eV)	E_{act} (eV)
1.16	35	36	7.64	5.12	2.53
1.51	87	76	6.82	4.89	1.93
1.85	147	100	6.79	5.13	1.66
2.39	293	172	6.27	4.89	1.38
3.19	705	300	5.95	4.99	0.96
4.38	1863	604	5.79	5.03	0.76
4.96	2593	780	5.69	5.01	0.69
5.16	2989	823	5.68	5.02	0.66
5.72	4001	1012	5.61	5.01	0.60

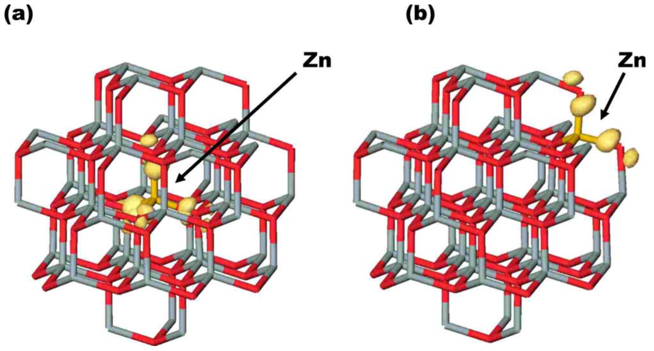

FIG. 1. (Color online) Charge density associated to the acceptor state introduced in InP-QDs by Zn doping as obtained from our real-space first-principles approach: (a) Triply degenerate acceptor state introduced in InP-QDs when the Zn impurity is placed at the center of the dot. (b) Singly degenerate acceptor state introduced in InP-QDs when the Zn impurity is placed at an In crystal site just below the surface of the dot. The charge density is plotted at the 30% of its maximum value for both panels (a) and (b). Gray (red) symbols stand for In (P) atoms. (Hydrogenlike atoms used to saturate dangling bonds in the QDs are not shown.) The nanocrystal models in the figure correspond to the dot with diameter 1.51 nm.

shorten the Zn–P bonds between the impurity atom and its four first neighbors by ~0.1 Å.

The replacement of an In atom by a Zn introduces in the host nanocrystal a triply degenerate state with t_2 symmetry having anion p character. This state is located at the impurity, as it can be shown in the left panel of Fig. 1. In this figure, the impurity charge density is computed as the square of the impurity wave function, and the isosurface of the impurity charge density corresponding to the 30% of its maximum value is represented. The T_d crystal symmetry in the vicinity of the impurity is preserved, that is, we found no significant Jahn-Teller distortion associated to the fractional occupation of degenerate states. The activation of the impurity state to give an electrical carrier entails two separate processes. First, an electron is physically removed from a pure (undoped) quantum dot; and second, the electron is transferred to the quantum dot containing the acceptor state. Thus, the activation energy of the impurity state, E_{act}, is defined as the difference between the ionization energy of a pure quantum dot, I_p, and the electron affinity of the dot containing the impurity, A_d. These two latter quantities are calculated as $I_p = E_p(n-1) - E_p(n)$ and $A_d = E_d(n) - E_d(n+1)$, where $E(n)$ represents the total energy of a quantum dot with n electrons, and the subscripts p and d stand for the pure and doped systems, respectively. It is worth noting that this definition contrasts with that of a system containing any "periodicity" such a crystal or nanowire. In these systems, the valence-band states form a continuum, so the activation energy of the impurity state equals its binding energy, which is defined as the difference between the dopant energy level and the valence-band edge of the host material.[4,5] In nanocrystals or QDs this situation is no longer true. The eigenvalues form a discrete spectrum, so the ionization occurs via the continuum of states above the potential barrier at the surface.

In the left panel of Fig. 2 we represent the activation energy obtained for the different InP-QDs studied in this work (circles). In the same figure we represent the results obtained for the activation energy of an isolated $\mathrm{Zn_{In}}$ impurity in two InP-NWs (triangles; 0.20 and 0.12 eV for NWs with diameters of 0.96 and 1.91 nm, respectively),[4] along with the value obtained for an isolated $\mathrm{Zn_{In}}$ impurity in the bulk, 0.034 eV (dashed line).[5] All the results represented in Fig. 2 were obtained using the same theoretical approach, e.g., the local-density approximation to the density-functional theory and real-space pseudopotentials as implemented in the PARSEC code.[6] In the study of the doped crystal and nanowires we have followed a periodic representation of theory that is consistent with the periodic nature of these systems.[10] In the case of QDs, this periodicity is switched off, the study being restricted to a spherical domain that contains the nanocrystal.[11] No artificial periodicity is imposed in the study of the nanocrystals, as it occurs, for example, in plane-wave approaches.

Figure 2 clearly shows the effects that the different dimensionality of quantum confinement has on the activation energy of the acceptor state. As reported previously, the two-dimensional radial quantum confinement increases an order of magnitude the energy cost needed to ionize the impurity in the thinner NWs with respect to the bulk. As we see in Fig. 2, this energy cost is increased an order of magnitude further in the nanocrystals, where the electronic states are confined in a three-dimensional physical domain.

In the right panel of Fig. 2 we represent the variation in E_{act}, I_p, and A_d with respect to the diameter of the nanocrystal (numerical values are listed in Table I). As we see in the figure, the size-dependence of E_{act} is determined by the size dependence of the ionization energy of the pure quantum dot, I_p. The electron affinity A_d of the doped nanocrystal shows to be almost invariant with the size of the system. This can be explained by the localized nature of the acceptor state (Fig. 1). The electron captured by the p-type nanocrystal in the

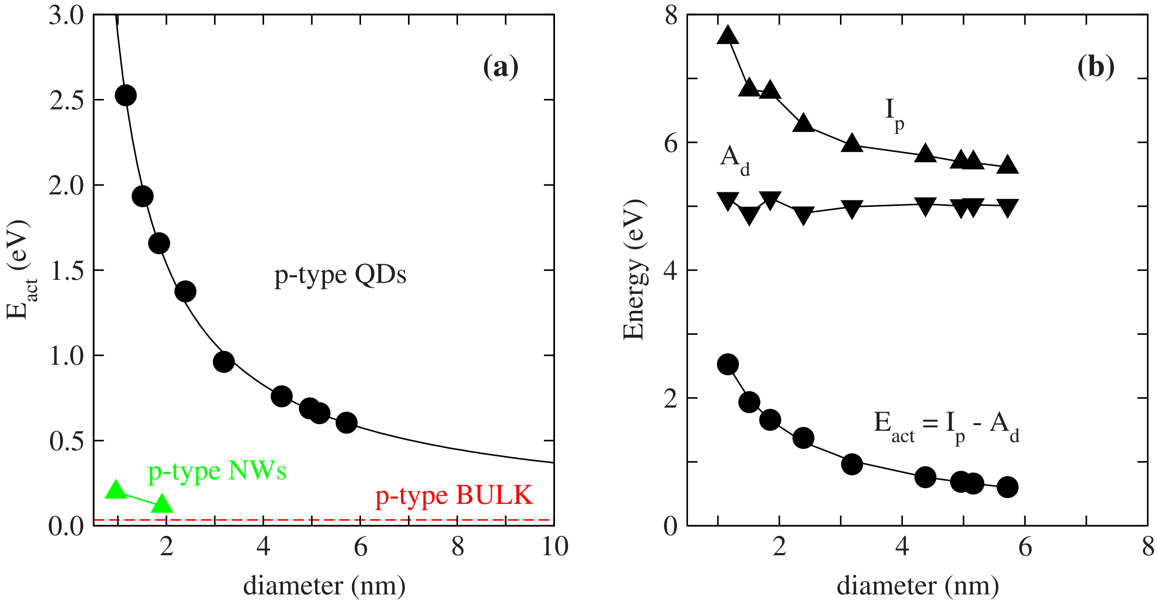

FIG. 2. (Color online) (a) Activation energy of the acceptor state introduced in InP-QDs by Zn doping as obtained from our real-space first-principles approach (circles). The activation energies obtained for Zn-doped InP nanowires (triangles) and bulk (dashed line) obtained in our previous work using the same theoretical approach are also shown (Refs. 4 and 5). The solid line corresponds to an analytical fit to the data (see the text). (b) Activation energy of the acceptor state introduced in InP-QDs by Zn doping (E_{act}; circles), as long as the ionization energy (I_p; up triangles) and electron affinity (A_d; down triangles) calculated for the pure and *p*-type doped nanocrystals, respectively. The values for the three quantities represented in this panel are listed in Table I.

ionization process occupies this state, whose characteristics are not significantly affected by quantum confinement (the more localized a level is, the less it is affected by confinement). This result is consistent with a previous study on *n*-type silicon nanocrystals, in which a virtually no dependence of the ionization energy of the doped nanocrystal with size was found.[12]

In the bulk limit, one expects the results obtained for the activation energy of *p*-type InP-QDs to give a value consistent with that of the *p*-type crystal obtained from theory and experiment, 0.03 eV.[5] Even though within our theoretical approach we are able to study systems with diameters up to ~6 nm from first principles (Table I), our results for this quantity still variate for the larger dots. This can be explained by the large exciton Bohr radius of InP (~22 nm), when compared, for example, to that of other semiconductor materials of use such as silicon (~5 nm). As such, in InP the effects of quantum confinement are expected to be present at relatively large crystal sizes. This makes the study of InP nanocrystals from first principles very challenging.

In order to extrapolate our results to the bulk limit, we fit our results to a power law of the form $E_{act}(d)=E_{act}^{bulk}+a_0/(d)^{a_1}$, where E_{act}^{bulk}, a_0, and a_1 are fitting parameters, and d is the diameter of the dot. As we see in Fig. 1, we found this fit to work well for our data. We found a value for the activation energy in the bulk limit (E_{act}^{bulk}) of 0.02 eV. For the parameter a_1 we found a best value of 0.91. A linear scaling of E_{act} with the inverse of the diameter d of the dot ($a_1=1$ in the expression above) is indicative of the activation energy being driven by an almost unscreened electron-hole Coulomb interaction, as it was found in previous work on silicon nanocrystals.[13,14] Our results are consistent with this view.

We have examined the effect of changing the location of the Zn impurity within the nanocrystal. We found no significant change in the total energy of the dot when the impurity atom is displaced from its center. Also, we found no significant change in the activation energy of the acceptor state. For example, if we displace the Zn impurity located at the center of the $In_{87}H_{76}$ QD to an In crystal site just below the surface we find the activation energy to change 4%. The only significant difference we found is in the breaking of the T_d crystal symmetry around the impurity and the subsequent splitting of the triply degenerate acceptor state to give a single degenerate acceptor state (see the right panel of Fig. 1).

In summary, we studied Zn-doped InP-QDs using first-principles calculations based on a real-space pseudopotential approach. We found the energy needed to activate the acceptor state to increase monotonically with decreasing diameter of the nanocrystal as a result of the three-dimensional quantum confinement. A maximum value of ~2.5 eV is predicted to be reached in the smaller QDs. This value is one order of magnitude bigger than the maximum value found in Zn-doped InP-NWs and two orders of magnitude bigger than the energy needed to ionize the acceptor state in Zn-doped bulk. Globally, our studies on *p*-type InP materials (bulk InP, InP-NWs, and InP-QDs) determine how a reduction in the dimensionality of these materials (that is maximum in InP-QDs) is against the capability of the materials to generate free carriers, which constitutes a limitation to their use in functional devices within semiconductor industry, specially if those devices are fabricated in the deep nanometer regime. We find this as a consequence of the intrinsic nature of the materials, that is, as a result of quantum confinement.

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