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We compute by envelope function calculations the binding energy E_B of donor atoms in thin slabs of semiconductor bounded by air, accounting for the dielectric mismatch between air and the semiconductor. We detail how E_B depends on the donor-site and on the thickness of the slab. We show that due to the competition between surface and dielectric mismatch effects, E_B does not monotonically decrease from the center to the surface of the nanostructures. Finally, we discuss our results in regard to recent photoluminescence experiments performed on ensemble and single GaN nanowires. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4765031]

Contrary to their bulk counterpart, GaN nanowires are strain- and defect-free UV light emitters[1,2] that can be grown on Si substrates,[3,4] making them suitable for integration into optoelectronic devices. Although no quantum confinement is expected due to the usual diameters encountered for GaN or ZnO nanowires (typically a few tens of nanometers), the nanometric sizes appeared to alter the optical properties of excitonic complexes in these nanowires.[5,6] Those results suggest an enhanced contribution of surface effects, for instance by modification of intrinsic properties of shallow donors. Following previous theoretical works that treated the case of donors or excitons close to flat semiconductor surfaces,[7,8] the binding energy of donor atoms (E_B) in nanowires with large surface-to-volume ratio is expected to be reduced compared to the bulk situation.[5,6] Such a decrease results from the distortion of the electron wavefunction when the donor nucleus is located close to the surface. However, in systems with a dimension of a few nanometers, recent measurements and simulations have revealed an increase in E_B with respect to the bulk case.[9–11] This increase has been ascribed to the combined effect of the confinement of charge carriers and of the dielectric mismatch between the semiconductor nanostructure and its surrounding medium. Nevertheless, the effect of image charge potential has to our knowledge only been considered for treating excitons in semi-infinite layers[12] or in specific interface-related configurations.[13,14] As far as donors are concerned, the dielectric confinement has only been envisaged in nanostructures with a dimension of a few nanometers.[9] It is therefore not clear how the dielectric mismatch affects the properties of donor atoms in systems with sizes in the 10 to 100 nm range.

Here, we study the influence of the surface and of the dielectric mismatch on E_B in GaN, ZnO, and GaAs nanostructures. We compute using an envelope function approach the site-dependence of E_B for slabs of thickness $6 < L < 150$ nm. We show how the combination of the confinement and the dielectric mismatch affects E_B and we demonstrate that con-

trary to the usual assumptions, E_B does not monotonically decrease when the donor nucleus is moved from the core of the material to the surface. Finally, we discuss the consequences of our results to the understanding of the emission properties of donor-bound excitons in GaN nanowires.

We consider the interaction between a donor nucleus and an electron in a slab of thickness L bounded by air. We work in cylindrical coordinates with the z-axis perpendicular to the air/semiconductor interfaces. The (ρ,θ,z) coordinates of the donor nucleus and of the electron are $(0,0,d_0)$ and (ρ_e,θ,z_e), respectively, and the Hamiltonian H for the electron bound to the donor nucleus is[12,15]

$$H = -\frac{\hbar^2}{2m_e}\nabla^2 + V_e(z_e)$$
$$- \frac{e^2}{4\pi\varepsilon_1\varepsilon_0}\left\{ \sum_{n=-\infty}^{+\infty}\left(\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^{|n|}\frac{1}{\sqrt{(z_e-d_n)^2+\rho^2}} \right.$$
$$\left. - \sum_{n=-\infty,n\neq 0}^{+\infty}\frac{1}{2}\left(\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2}\right)^{|n|}\frac{1}{|z_e-z_n|} \right\}. \quad (1)$$

ε_1 and $\varepsilon_2 = 1$ are the relative dielectric constants of the semiconductor medium and air, respectively, m_e is the electron effective mass and $V_e(z_e)$ is the crystal potential. The discontinuity of the dielectric constant causes at the air/semiconductor interfaces charge accumulation induced by the donor nucleus and the electron. The redistribution of the polarization field inside the semiconductor layer is treated by the image charge method and z_n and d_n are the positions of the nth image charges of the electron and of the donor nucleus, respectively.[15] The interaction between the electron and the images of the donor and the electron self-energy are taken into account in the last two terms of the right-hand side of Eq. (1). We choose for the electron envelope function $\Psi(\rho_e,z_e) = Nf_e(z_e)\exp(-\rho_e/\lambda)$, where N is a normalization coefficient and λ is the in-plane extension of the electron wave function. Following the method described in Ref. 16, we average $H\Psi = E\Psi$ over the ρ_e dependent part of Ψ and

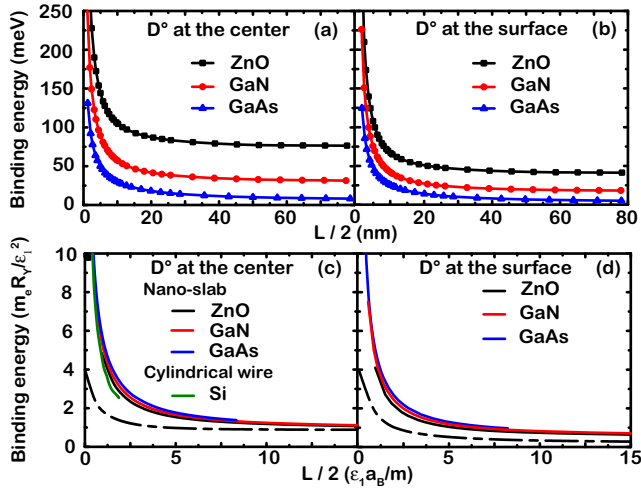a)Corresponding author: pmc53@cam.ac.uk.

FIG. 1. (a,b) Binding energy E_B for a donor located at the center (a) or at the surface (b) of a ZnO (squares), GaN (circles) and GaAs (triangles) nanostructure bounded by air with respect to the half of the thickness of the nanostructure ($L/2$). (c,d) E_B in reduced units of energy and length for a donor located at the center (c) or at the surface (d) of a ZnO (black), GaN (red) and GaAs (blue) nanoslab. The result of tight-binding calculations (Ref. 9) for a donor atom located on the axis of a Si cylindrical wire with radius $L/2$ is also shown (green solid line). The dashed-dotted lines show E_B in absence of dielectric mismatch for a semi-infinite slab.

we obtain a one-dimensional second order differential equation for f_e

$$-\frac{\hbar^2}{2m_e}\frac{d^2 f_e(z_e)}{dz_e^2} + \tilde{V}_e(z_e)f_e(z_e) = Ef_e(z_e), \quad (2)$$

where $\tilde{V}_e(z_e)$ is the effective potential felt by the electron. We solve Eq. (2) and we minimize E against λ to obtain E_B. We apply our calculations to the case of GaN, ZnO, and GaAs using $m_e = 0.2$, 0.24, and 0.067 and $\varepsilon_1 = 9.5$, 6.5, and 13.1, respectively.[17]

We plot in Figure 1 E_B for a donor located at the center of a nano-slab with respect to $L/2$. For large values of L, we compute $E_B = 28$, 72, and 6 meV when the donor is located at the center of a GaN, ZnO, and GaAs layer, respectively. The discrepancy between these values and the effective mass donor binding energy $R_Y^* = m_e R_Y/\varepsilon_1^2$, ($R_Y = 13.6$ eV is the hydrogen atom Rydberg) comes from the chosen Ψ. When reducing L, E_B increases due to the combined action of the confinement and of the dielectric mismatch. Now, while in absence of dielectric mismatch E_B tends to $4R_Y^*$ when $L \to 0$

[Figure 1(c)], the combination of confinement and Coulomb attraction between the electron and the image of the donor nucleus results in E_B larger than $5R_Y^*$ already for $L < \varepsilon_1 a_B/m_e$ (a_B is the hydrogen atom Bohr radius). Figure 1(c,d) show a general pattern that is nearly material-independent. For $L < 2\varepsilon_1 a_B/m_e$, our results agree with *ab initio* calculations for donor atoms located at the center of Si nanowires.[9] Consequently, the E_B calculated here for donors in thin slabs will be used to discuss qualitatively E_B in nanowires.

We show in Figure 2 the site-dependence of E_B across the slab. In a 155 nm thick GaN layer, E_B increases from 31 to 34 meV, when the donor is moved from the center of the layer to 7 nm away from the surface. This increase arises from the enhanced interaction between the electron and the images of the donor nucleus and was not considered in previous works.[5,6] For smaller distances between the donor atom and the surface, the barrier potential at the air/semiconductor interface distorts Ψ (Figure 3). The evolution of the shape of Ψ from $1s$ to $2p$-like, when going from the bulk to the surface case, is accompanied by a decrease in E_B. While in earlier works, this reduction was found to attain $R_Y^*/4$, for the surface donor atom,[7,8,18] our calculations give a final reduction from 34 to 18 meV, for a 155 nm-thick-thick GaN nano-slab. Similarly, the donor at the surface of thick GaAs and ZnO layers exhibit $E_B \sim 0.6R_Y^*$ [Figure 1(d)]. For thinner slabs the carrier confinement increases E_B for both core and surface donors (Figure 1). In the case of GaN, the surface (*core*) E_B increases from 18 to 100 meV (32 to 122 meV), when L is reduced from 155 to 7 nm [Figure 2(a)].

From these results, we first find that contrary to the usual assumptions,[5,6] E_B does not monotonically decrease when going from the center to the surface of a nanostructure. This is due to the competition between the effect of the dielectric mismatch and of the surface: While the former affects the donor binding energy even when the donor nucleus is located typically $10\varepsilon_1 a_B/m_e$ away from the surface, the latter is short-range and is important only when the donor nucleus lies in a surface layer of thickness of the order of $2\varepsilon_1 a_B/m_e$ (Figure 2). Consequently, we expect nanowires to present three regions where donor atoms show a distinct behavior: (i) a core region where E_B is similar to that of bulk material, (ii) a shell region where E_B is increased due to the effect of the dielectric mismatch, and (iii) a surface region where Ψ is distorted and E_B reduced compared to the bulk situation. We remark that the critical sizes that we just discussed are strongly material-dependent. For instance, while one cannot obtain a bulk-like
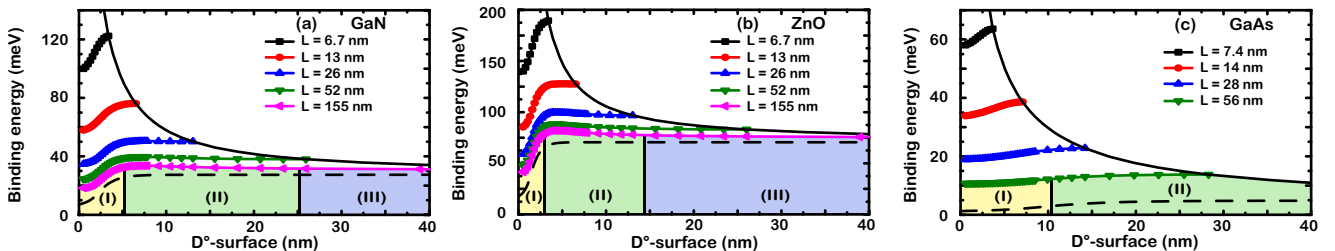

FIG. 2. Donor binding energy E_B in a GaN (a), ZnO (b) and GaAs (c) nano-slab of thickness L, with respect to the distance d_0 between the donor nucleus and the closest surface. Dashed lines show E_B in absence of dielectric mismatch for a semi-infinite slab. The black solid line shows E_B for a donor located at the center of a nanoslab of thickness $2d_0$. (I), (II) and (III) show the extension of the surface, intermediate and bulk regions of the nanoslab, respectively.
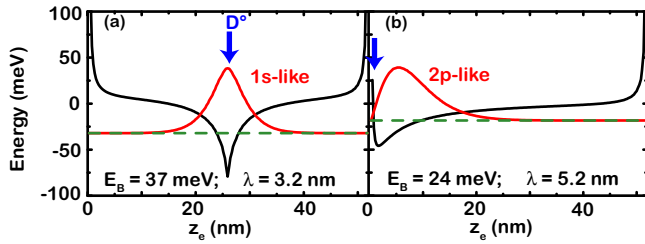
FIG. 3. Effective potential (black) and envelope function f_e (red) for an electron bound to donor nucleus in a 52 nm-thick GaN nanoslab. The distance between the donor nucleus and the surface is 26 (a) and 0.5 nm (b), as pointed out by the arrow. Dashed lines show the energy of the electron lowest-energy level. When going from the core to the surface of the structure, f_e changes from a 1s to a 2p-like symmetry.

donor in a 40 nm-thick GaAs nano-slab, all donor types will be encountered in GaN or ZnO slabs of the same size (Figure 2).

We now discuss our results in the light of some features regularly observed in the emission properties of GaN nanowires. At low temperature, the emission from GaN is dominated by the recombination from donor-bound excitons (D°X), whose recombination energy is given by the energy difference between the D°X and the D° states. Despite being structurally perfect nanocrystals, ensembles of GaN nanowires exhibit a D°X emission with linewidth at 10 K of 1-5 meV.[2,5,6,19] To explain this seemingly self-contradictory behavior, we proposed that the random distribution of donor atoms in nanowires leads to a distribution of E_B and therefore to a distribution of D°X emission energy.[5] Our calculations verify this proposal, as we find E_B ranging between 18 and 34 meV in 155 nm-thick GaN nanostructures. Accordingly, low-temperature micro-photoluminescence experiments showed that while the emission from D°X in single GaN nanowires is narrow (linewidth below 300 μeV), several D°X emission peaks can be observed, with energy varying over a few meV.[6] When averaged over an ensemble of nanowires, the surface-induced dispersion of D°X and D° energies then results in a broad emission. It would be of interest to compute the site-dependence of D°X binding energy in nanostructures. Such a model would indeed allow to conclude whether surface and dielectric mismatch effects result in D°X emission energy distributed over few meV,[6] or over few tens of meV.[5] In particular, this would indicate if the emission at 3.45 eV observed in thin GaN nanowires is related to D°X and to D° excited states for donors located close to the surface, or to another surface defect.[20] This is however a complicated problem, as any model of the D°X binding energy requires treating the interaction between the donor nucleus, the two electrons, the hole

and their images. Moreover, to get a complete picture of all possible transitions, including their site-dependent energies and relative probabilities, a thorough calculation of all excited states of both D°X and D° is required, which is beyond the scope of this paper. Nevertheless, this preliminary investigation of the site dependence of the D° ground state, including dielectric mismatch effects, qualitatively justifies the intuitive interpretation of previous experimental data.[5,6]

In conclusion, we have computed by envelope function calculations the binding energy E_B for donors in semiconductor nano-slabs surrounded by air. The dielectric mismatch between the semiconductor layer and air leads to an increase in E_B. When the donor is at the surface, E_B is reduced down to ∼0.6 times the bulk value, while a factor of four is obtained when the dielectric mismatch is neglected. We then show that due to the competition between surface and dielectric mismatch effects, nanowires exhibit two distinct shell layers where E_B is either increased or decreased with respect to the bulk case. The site-dependence of E_B is consistent with the broadening of the donor bound exciton luminescence reported for ensemble of GaN nanowires at 10 K. Our study therefore highlights the role played by image charge effects on the emission properties of semiconductor nanowires with diameter of typically 10 to 50 nm.

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