Factors influencing the distribution of charge in polar nanocrystals

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We perform first-principles calculations of wurtzite GaAs nanorods to explore the factors determining charge distributions in polar nanostructures. We show that both the direction and magnitude of the dipole moment **d** of a nanorod, and its electric field, depend sensitively on how its surfaces are terminated and do not depend strongly on the spontaneous polarization of the underlying lattice. We identify two physical mechanisms by which **d** is controlled by the surface termination, and we show that the excess charge on the nanorod ends is not strongly localized. We discuss the implications of these results for tuning nanocrystal properties, and for their growth and assembly.

Nanocrystals and nanorods are valued for their unique electronic and optical properties, which differ substantially from bulk materials of the same composition.[1] They are being exploited in a host of applications (including imaging in biology,[2] light-emitting diodes,[3] lasing devices,[4] and solar cells[5]) that continue to grow in number and diversity as we gain finer control over their properties.[6] This requires greater understanding of how those properties depend upon size, shape, internal structure, and chemical environment. The distribution of charge within and on a nanorod plays an important role in determining its physical properties: Nanostructures with large dipole moments (**d**) are sources of large electric fields which, internally, affect their optical properties and, externally, affect their interactions with their surroundings, thereby influencing both their growth and assembly into superstructures.[7] The charge distribution is related to the chemical environment and to the conditions of synthesis; however, this relationship is not well understood. In this Rapid Communication, we present first-principles calculations that provide substantial insight into how charge is distributed within a nanocrystal and we identify the most important factors determining this distribution. Our findings can be used to inform the choice of synthesis conditions appropriate for the design of nanorods with specific physical properties.

Much theoretical and experimental work on nanorods has focused on the magnitude and origin of their dipole moments, with somewhat contradictory results. Some studies attribute large dipole moments to the noncentrosymmetric nature of the wurtzite structure,[8] which is associated with an intrinsic spontaneous polarization, an interpretation that is widely accepted.[9] However, a theoretical study has revealed a strong enhancement of the polarity of nanorods compared with thin films of the same length along the [0001] direction,[10] and experimental observations by Shim and Guyot-Sionnest[11] show that ZnSe nanocrystals with the cubic zincblende structure can exhibit moments of similar magnitude to wurtzite CdSe. Both studies cast doubt on the relevance of crystal symmetry. Other studies have attributed importance to different factors, including nanocrystal shape,[12] molecular passivation of surfaces,[12,13] surface reconstruction,[13,14] and a piezoelectric effect caused by strain at the nanocrystal surfaces.[15] Finally, an electrostatic force microscopy study of CdSe nanorods observed no dipole moment in the samples studied.[16]

Computational modeling of nanorods gives us the control necessary to disaggregate the factors contributing to the dipole moment in a way not possible experimentally. Until recently, nanostructures of realistic sizes have been beyond the reach of accurate quantum-mechanical methods. However, developments in linear-scaling density functional theory (DFT) methods have now made possible the simulation of nanostructures comprising thousands of atoms with high accuracy. We take advantage of these methods, as implemented in our ONETEP code,[18,19] to accurately simulate polar semiconductor nanorods of realistic sizes. For our investigation, we choose nanorods of wurtzite GaAs because GaAs has a relatively low computational cost while having the essential features that bestow all polar nanorods (e.g., CdSe, ZnO) with an asymmetric distribution of charge, namely, there is a degree of ionicity to the bonding and the crystal structure lacks inversion symmetry. This allows us to access the extensive size regime in which a nanorod's dipole moment increases linearly with its length and width.

Our results highlight the importance of surface chemistry to the distribution of charge in polar semiconductor nanorods and show that the symmetry of the corresponding bulk crystal structure can play a much less important role than has often been assumed. Indeed, for some surface terminations, **d** can be in the opposite direction to that suggested by the spontaneous polarization of the bulk crystal. We show that excess charge on the ends of a nanorod can be highly delocalized, meaning that internal electric fields are nonuniform and that some simple models of electrostatic interactions between nanoparticles may be overly simplistic. We explain the relationships that we find between the surface terminations of a nanorod and its dipole moment in terms of the electronic structure. Finally, we show that our findings are robust when the atomic structure is allowed to relax.

The ONETEP code uses DFT in a formulation equivalent to the plane-wave pseudopotential method.[17] Initially, we model unrelaxed, stoichiometric nanorods of wurtzite (w-) GaAs. Our nanorods are "grown" parallel to the wurtzite c axis with a length ~ 12 nm and hexagonal cross sections of width ~ 2 nm: an example is shown in Fig. 1. Six different nanorods consisting of 2106–2862 atoms were created to represent a variety of lateral ($\parallel c$) and polar ($\perp c$) surface terminations, either bare or saturated by chemisorption. They are labeled H/H, H/B, H/P, B/H, B/B, and B/P to indicate how the lateral
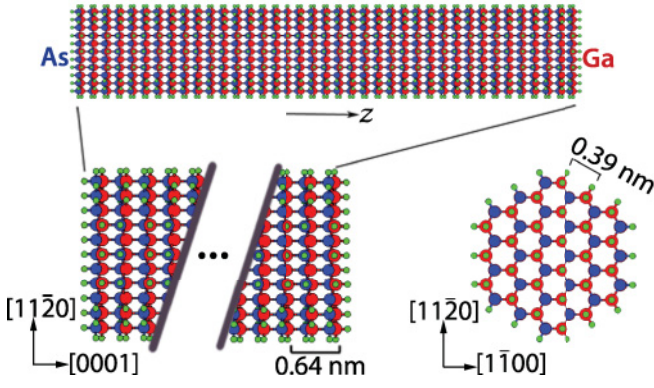
FIG. 1. (Color online) An unrelaxed GaAs nanorod with Ga, As, and H atoms colored red (medium gray), blue (dark gray), and green (light gray), respectively. The Ga and As terminated ends are indicated.

and polar surfaces are terminated, respectively. H signifies termination by hydrogen atoms and B signifies a bare surface. P denotes termination by pseudoatoms,[20] each with one electron and fractional nuclear charges of $+\frac{5}{4}$ and $+\frac{3}{4}$ for passivating surface Ga and As atoms, respectively. By approximating the electronegativities of As and Ga, one might expect them to form bonds with the surface atoms of similar character to those found in the bulk and render the III-V semiconductor surfaces electronically inert[20] without contributing any net charge to them. A H atom, on the other hand, passivates a surface dangling bond but also contributes a net negative (positive) charge of magnitude $\frac{1}{4}$ to the surface when it binds to a Ga (As) atom. In all of these models, symmetry dictates that only the longitudinal component of **d**, i.e., d_z, is nonzero.

A plane-wave energy cutoff of 450 eV, with a local orbital radius[21] of 0.53 nm for each atomic species, is found to be sufficient to converge all properties of interest. The density kernel is not truncated so that metallic and insulating structures are treated on an equal footing. We use norm-conserving pseudopotentials with nonlinear core corrections, and $3d$ electrons frozen into the core. Exchange and correlation are treated within the local density approximation. To eliminate interaction between a nanorod and its periodic images, we have used a cylindrically truncated Coulomb interaction.[22]

Table I shows that both the magnitude and direction of **d** depend critically on the chemistry of both the lateral and polar surfaces and, therefore, can not be dominated by the spontaneous polarization of the wurtzite lattice. We have calculated this quantity for bulk w-GaAs to be 0.005 C/m^2, implying a contribution to d_z for nanorods of our size of $+62$ D, if the polarizations are similar.[14] H/B and B/B both show positive d_z, meaning that the Ga-terminated end carries a net positive charge, while B/P has a very small d_z and the other rods exhibit negative d_z. These observations suggest that the synthesis conditions of nanorods and their chemical environments must play crucial roles in determining **d**, insofar as they affect the coverage of the surfaces with adsorbates.

Figure 2 shows the calculated d_z of nanorods with fully H-terminated lateral surfaces, but with a varying coverage of H atoms on the polar surfaces. Each point represents a single sample chosen at random from the ensemble of nanorods

TABLE I. Dipole moment d_z, net charge of the left-hand half Q_L, and electric field at the mid-point E_m of the nanorods.

Nanorod	H/H	H/B	H/P	B/H	B/B	B/P
d_z (D)	−614	+330	−531	−235	+125	+41
Q_L (e)	+1.00	−0.56	+0.95	+0.39	−0.18	−0.08
E_m (V/nm)	−0.100	+0.050	−0.105	−0.030	+0.013	+0.005

with a given coverage. It is clear that d_z tends to decrease significantly as the hydrogen coverage increases and that **d** changes direction around 56% coverage. This means that, if one could control the degree of coverage of the polar surface (e.g., by varying the temperature, pressure, or the chemical potentials of the various species during synthesis), one could vary d_z over a wide range of values. At $T = 0$ K, we have calculated that over the range of realistic hydrogen chemical potentials μ_H for which water molecules are stable, the thermodynamically stable hydrogen coverage, namely, that which minimizes $E - \mu_H n_H$, goes from 0 to around 70%. In principle, this therefore allows access to values of d_z of between -200 D and $+330$ D. Even at full coverage, if there were competing adsorbing species, we suggest that d_z could be tuned by varying their proportions. Indeed, terminating each of the polar surfaces with 13 H and 14 pseudoatoms yields $d_z = -552$ D, between H/H and H/P.

In Fig. 3(a), we plot the function

$$\tilde{\rho}(z) = \frac{1}{L\sqrt{2\pi}} \iiint \rho(x',y',z') e^{-\frac{(z-z')^2}{2L^2}} \, dx' \, dy' \, dz',$$

which is the laterally averaged charge density profile along the length of the nanorod (the z direction in this work, $\parallel c$), convolved with a Gaussian of standard deviation $L = 0.32$ nm in the z direction. This smooths out the large variations in the density on the length scale of a unit cell, revealing how excess charge is distributed along the length of the nanorod; clearly, it is spread over several nanometers from the ends of the nanorods. The amount of excess charge on the left-hand (As-terminated) end Q_L is shown in Table I. This has been calculated by integrating the quantity $\tilde{\rho}(z)$ up to the middle of the nanorod.

The observed spread of the excess charge could be important for models of nanoparticle self-assembly that usually treat nanocrystals as point dipoles or assume that excess charge is perfectly localized on the polar surfaces.[7,9] These assumptions would lead to quantitatively, or even qualitatively, incorrect results at short distances. Furthermore, the delocalization of
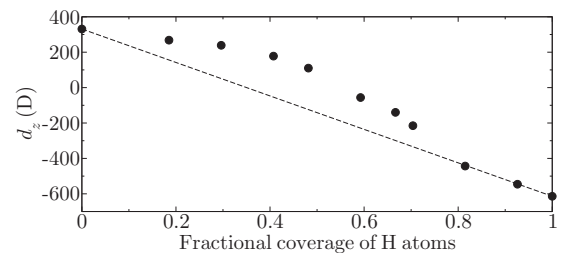

FIG. 2. Dipole moment d_z as a function of H atom coverage of the polar surfaces for a nanorod with fully H-terminated lateral surfaces.
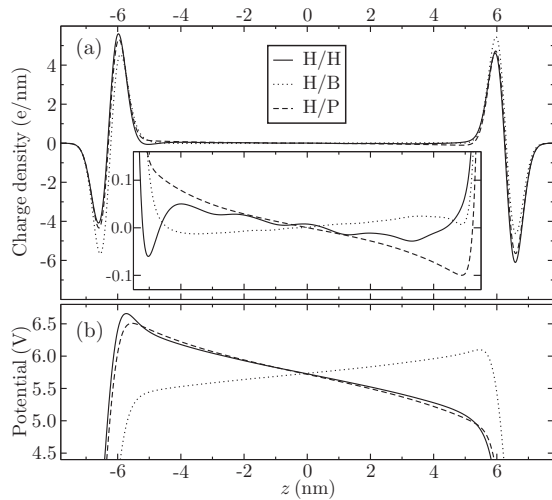
FIG. 3. (a) Charge density and (b) electrostatic potential as a function of position z along the long axes of the H/H, H/B, and H/P nanorods. Both quantities are integrated over the plane perpendicular to the long axis and smoothed on the length scale of a wurtzite unit cell.

charge suggests that nanorods may be highly polarizable, which could significantly affect the interactions between nanorods.

Figure 3(b) shows the smoothed potential as a function of position along three different nanorods, and Table I gives the values of the electric field at the center of each nanorod E_m. It is clear that the internal electric fields are not uniform but stronger near the polar surfaces than in the middle. The voltage drops we have observed are of order 0.1 V/nm, reaching as high as 0.6 V/nm near the polar surfaces of H/H. These fields are of similar magnitude to those observed in strained quantum wells and are expected to significantly affect optical absorption frequencies, selection rules, and carrier recombination rates.

Figure 4 shows the calculated slabwise local densities of states (LDOS) for nanorods H/H, H/B, and B/H. We define a slab LDOS as follows. Each nanorod is nominally divided into 20 slabs in the z direction, each consisting of four planes of atoms: two each of Ga and As. The slab LDOS is the sum of the contributions to the total DOS from the local orbitals centered on those atoms. Superposing these slab LDOS, as in Fig. 4, shows that the electric field shifts the spectrum from

slab to slab. This shift has the effect of smearing out the total DOS so that none of the nanorods studied has an electronic energy gap despite individual slabs having well-defined gaps.

Closer examination of Table I reveals two distinct trends. First, that all other things being equal, terminated polar surfaces result in the most negative d_z, and bare polar surfaces result in the most positive. Second, terminated lateral surfaces result in **d** of larger magnitude than bare lateral surfaces.

Figure 4 helps us to understand these trends: Polar surface dangling bond states on H/B can clearly be identified in Fig. 4(b) on the data sets associated with the first and last slabs of the nanorod. The Ga (As) dangling bond states lie mostly above (below) the Fermi level E_F, resulting in an excess of electrons on the As-terminated end and a more positive d_z. In contrast, Fig. 4(a) reveals that both the Ga–H and As–H bonding states on the polar surfaces of H/H lie below E_F, resulting in an excess of electrons on the Ga–H terminated end and a depletion on the As–H end. This is because the $\frac{3}{4}$ of an electron nominally available from the Ga atom and the one electron available from H are insufficient to fully populate the Ga–H bond. Conversely, the $\frac{5}{4}$ electrons from As provide a surplus for the As–H bond. Hence, the formation of these bonds redistributes charge between the two polar surfaces to produce a negative d_z. In real systems, a mechanism is required to redistribute charge between two distant end surfaces, such as the presence of a solvent capable of mediating the transfer.

Regarding the second trend, comparison of Figs. 4(a) and 4(c) shows that the nanorod with bare lateral surfaces (B/H) does not exhibit a large local energy gap as H/H does due to the presence of lateral surface dangling bond states. A large **d** is associated with a large internal electric field and a slab-by-slab energy shift. However, for nanorods with lateral surface states close to E_F, the electric field pushes these states above E_F at one end and below at the other, thereby reversing the charge buildup on the ends and reducing the field. We conclude from these observations that a large local energy gap clear of surface states is a necessary condition for a large **d**, and the quenching of surface states on unstable lateral surfaces by the introduction of adsorbates can be an important polarity enhancement mechanism in nanorods.

So far, we have considered pristine nanorods. However, structural relaxations might be expected to play a large role for two reasons: some of the surfaces studied above may be unstable and, given our arguments above, reconstructions are likely
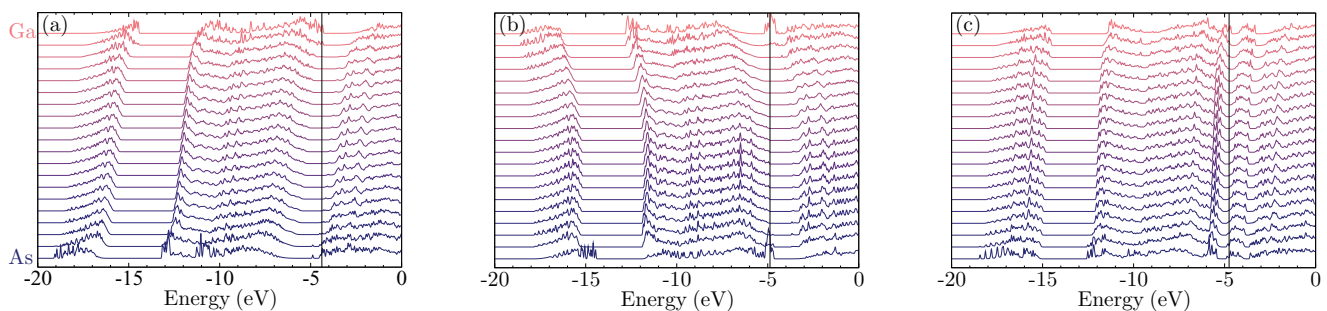

FIG. 4. (Color online) Local densities of states for three nanorods: (a) H/H, (b) H/B, and (c) B/H. The global Fermi level is plotted in each case. Red (light gray) curves correspond to slabs close to the polar surfaces terminated by Ga and the blue (dark gray) curves correspond to slabs close to the polar surfaces terminated by As.

TABLE II. Configurations and dipole moments d_z before and after structural relaxation of the four nanorods.

Nanorod		h/h	h/b	b/h	b/b
$d_z \begin{Bmatrix} \text{Before} \\ \text{After} \end{Bmatrix}$	Relaxation	−131.64	+55.20	−22.81	+15.38
	(D)	−103.03	+67.99	−89.23	+21.52

to have a large effect; strain caused by the surface may also induce significant charge separation. Regarding the first concern, it has not been our intention here to determine the stability of a particular surface, but rather to investigate the link between termination and **d**, regardless of stability. Second, to assess the effects of surface-induced strain, we performed structural relaxations on four nanorods of length ~ 3.5 nm, width ~ 1.2 nm, and with different surface terminations (b/b, h/b, h/h, and b/h, following the same convention as before). Table II shows d_z before and after structural relaxation: there is no qualitative change in any of the values except b/h. No dipole moments changed direction, and the ordering of the magnitudes stayed the same. The increase in $|\mathbf{d}|$ on b/h is attributable to the shifting of the lateral surface dangling bond states away from E_F on relaxation, opening up the energy gap and, consistent with the argument above, allowing the rod to support a larger **d**.

In summary, we find that, for polar nanorods, both the orientation and magnitude of the dipole moment depend sensitively on the chemical terminations of both the polar end surfaces and the nonpolar lateral surfaces. This sensitivity can overwhelm any contribution that may arise from the noncentrosymmetric crystal structure. The sensitivity to adsorbates arises in two main ways: adsorbates may be charged and therefore contribute directly to **d**; they also determine the stability of surface electronic states, which, in turn, determines the magnitude of the internal electric field that a rod can sustain. When the electric field becomes large enough to shift the energy of an occupied state on one end above an unoccupied state on the other, a transfer of electrons between the ends occurs that lowers **d**, as long as such a transfer can be facilitated by the environment. The synthesis conditions and environment of a nanorod therefore play crucial roles in determining both the ground-state charge distribution of a nanorod and whether or not it can reach this ground state. We also find that surface charge is not localized at the ends of the nanorod but delocalized over several nanometers, also implying a nonuniform internal field. This has implications when considering the energetics of self-assembly of polar nanostructures.

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