Size dependence of lattice constants of semiconductor nanocrystals

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Abstract

We have theoretically examined the size dependence of the equilibrium lattice constant of nanocrystals of Si, GaAs and CdSe. While deviations from the bulk lattice constant are as large as 1-2% for unpassivated nanocrystals of Si, the deviations drop to \( \sim 0.3\%-0.4\% \) once the surfaces are passivated. Inspite of the fact that the average equilibrium bond-lengths are bulk-like, we find that the nearest-neighbor bond-length exhibits an unusual strain profile with bulk like bond-lengths in the core and shorter (\(~ 1\%\) ) bonds at the surface.

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The properties of semiconductor nanocrystals have received a lot of attention in the past two decades as a result of strong size dependence of various physical properties. The underlying crystal structure plays an important role in determining the electronic structure and the ensuing physical properties. However the basic issue of structure determination is difficult in the context of materials at the nanoscale. Even the most powerful techniques that one is familiar with for the characterization of bulk crystals are found to fail in the case of nanocrystals [1]. The difficulties arise because in the present case one does not have a homogeneous distribution of particles. Not only do the sizes vary over several percent depending on the synthesis procedure, one also finds different shaped particles as a result of the growth techniques. Further most of the commonly used techniques provide an averaged lattice constant / bond-length. Hence several of the basic questions in the context of nanoparticles remain unanswered. It is here that theoretical calculations play an important role. They can simulate the ideal situation and hence can be used to provide insight into the modifications in the lattice constant that take place as a function of nanoparticle size.

Nanocrystals consist of a sizeable number of atoms on the surface. In an ideal situation, all atoms at the surface would have broken coordination, while the rest would have bulk-like coordination. To make up for the lost coordination, stress develops at the surface and decays into the bulk. Naively as a result of this one would have longer / bulk-like bonds in the interior and shorter bonds at the surface. The naive picture would be modified as the surface atoms are usually passivated by ligands and so the strain effects are not as strong as one would expect in the unpassivated case.

The experimental literature has conflicting reports of bulk-like nearest-neighbor bond-lengths [2], small-intermediate strains resulting in modified lattice constants for the nanocrystals [3] as compared with the bulk. However, the issue of the development and variation of strain is difficult to obtain experimentally. In this context theoretical models will be able to address the issue, as well as ascertain the role of the passivants.

We construct nanocrystals by cutting a spherical fragment of a bulk crystal, which has the underlying geometry of the zinc-blende lattice (Si, GaAs and CdSe) / wurtzite lattice (CdSe) [4]. Now to define a spherical nanocrystal in this way we need to specify the center of the sphere and the radius. In all our studies the nanocrystal is centered on one atom and then the remaining atoms are generated by adding all atoms within the sphere of pre-defined radius and maintaining bulk-like geometry. Consequently the generated zinc-blende nanocrystals
will have a $T_d$ point group symmetry. This prescription for constructing nanocrystals is similar to what has been used earlier in the literature \[5\]. It is believed to be valid for large cluster sizes as various experiments have found bulk-like coordination \[6\]. Table I provides the cluster sizes, defined in terms of the number of layers around the central atom, as well as the number of atoms of types A and B in the cluster with atom A at the center. As we use a plane wave implementation of density functional theory and are constrained to work with periodic systems, the electronic properties of the clusters are calculated by considering periodic clusters separated by $\sim 10 \text{ \AA}$ so that the interaction between the clusters is very small.

The electronic structure of the clusters was calculated within plane wave pseudopotential calculations using the implementation in VASP \[7\]. The semi core 3$d$ states on the Ga for the GaAs cluster calculations were treated as a part of the core. For silicon we used the LDA approximation for the exchange while the GGA PW91 approximation \[8\] to the exchange has been used for CdSe and GaAs and the calculations were performed at Gamma point alone. A cut off energy of 250.0 eV was used for the plane wave basis for Si and GaAs calculations while we used 274.3 eV for CdSe.

Initially the equilibrium bond-length is determined by minimizing the energy with respect to the lattice constant allowing for a uniform expansion or contraction of the volume. The equilibrium lattice constant was determined by fitting the energy as a function of volume to the Murnaghan equation of state \[9\]. Then the nanocrystals were passivated with hydrogen atoms in the case of silicon and with pseudo-hydrogens \[10\] in the case of binary nanocrystals. All atoms of the nanocrystals were relaxed to attain the minimum energy configuration. An average bond-length was determined by averaging over all the nearest-neighbor bond-lengths. This was then used to determine an average equilibrium lattice constant. While generating the nanocrystals we can start with either an anion or a cation at the center. In the present case we have considered both schemes of generation of the binary nanocrystals. As the conclusions arrived at were similar in both cases we present the results for only one case.

We find it useful to use the definition of Masadeh et. al \[3\] to define the surface stress. The surface stress generated in the nanocrystals is defined as

$$\text{Bondstrain} (\%) = \frac{(r_0 - r)}{r_0}$$

(1)

where '$r_0$', is the nearest neighbor bond-length between the atoms, is calculated using the
theoretical equilibrium lattice constant for the bulk. ‘r’ is the nearest neighbor bond-length that one obtains after the optimization of the structure described earlier. It should be noted that ”r” varies from shell to shell of the cluster, and could be different even for atoms of the same type in a given shell. This arises because of the differences in surface coordination that one can have because of the truncation scheme considered. Inspite of these variations, the qualitative aspects are similar.

We consider the case of an elemental semiconductor, Si. The calculated equilibrium lattice constants are shown in Table II as a function of cluster size. One finds that the equilibrium lattice constant is 5.407 Å for the bulk. The lattice constant computed for the nanocrystals is smaller than the bulk in all the cases, as expected from the naive considerations presented earlier. A strong size dependence of the lattice constant is found in the unpassivated case which shows deviations ranging from 2.27 % to 1.02 % when we go from smaller clusters with 3 layers around the central layer to larger clusters with 6 layers around the central layer. However the size dependence of the lattice constant is much smaller for the passivated nanocrystals, with deviations ∼ 0.3% - 0.4% and approaches bulk-like values for very small cluster sizes. Similar conclusions are arrived at for nanocrystals of CdSe and GaAs.

Inspite of the fact that the bulk lattice constant is reached quickly in the present case, we do find deviation in the bond-lengths as a function of depth from the surface, being maximum at the surface. Quantifying this in terms of the bond strain (Fig 1(a)) we find that in the core of the nanocrystal, for the size considered we find ∼ 0 % bond strain. Beyond the second layer, the strain exhibits a linear variation. Since we have a single parameter that changes i.e. depth, we would expect a linear variation with depth. This is however not the case, and we find that the strain is invariant between the third and the sixth layers. However between the first and third layers one has a linear variation with depth, with the core showing almost bulk-like lattice constants. The unusual strain profile that we find here is probably a result of a competition between the microscopic considerations determining the strain profile in the interior being different from those determining it at the surface. Hence the bond strain profile depends on the strength of the surface passivant. Consequently, the strain profile is different in the case of GaAs (Fig.1(b)) and CdSe (Fig.1(c)).

In the case of CdSe we considered both the zinc blende as well as the wurtzite polymorphs. As in the zinc blende case, the average lattice constant is almost bulk-like for clusters larger than 15 Å diameter. The bondlength profile as a function depth (Fig.1(d)) is however
very different. The equatorial and the axial bonds show very different depth dependences, showing stronger anisotropies in the core region than in the bulk, in addition to an oscillatory dependence with depth. The latter could arise because the wurtzite structure has a finite dipole moment. Interestingly the averaged bond length for each layer follows a depth profile very close to one’s naive expectations being constant upto the third monolayer and then showing a linear variation with depth.

We have examined the deviation from bulk-like lattice constants considering nanocrystals of Si, GaAs and CdSe. Naive arguments based on broken coordination at the surface lead us to expect shorter bonds at the surface of the nanocrystal. Indeed this is found to be the case, though the surface stress generated is found to be typically ~ 1% or less when we consider nanocrystals passivated by hydrogen or pseudo-hydrogens, with almost bulk-like bond-lengths obtained 5-6 layers below the surface. Averaging over all the bond-lengths of the cluster we find that bulk-like bond-lengths are obtained for small cluster sizes.

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TABLE I: Atom 'A' centered spherical binary nanocrystals (AB) considered with an underlined zinc-blende and wurtzite geometry. $N_A$ and $N_B$ are the number of 'A' and 'B' type of atoms in each nanocrystal.

| nanocluster | cluster size (n) | $N_A$ | $N_B$ |
|-------------|-----------------|-------|-------|
| Zinc-blende | 6               | 79    | 68    |
|             | 5               | 43    | 44    |
|             | 4               | 19    | 16    |
|             | 3               | 13    | 16    |
| Wurtzite    | 5               | 51    | 41    |
|             | 4               | 19    | 20    |
|             | 3               | 13    | 14    |

TABLE II: Comparision of the equilibrium lattice constant and average bond strain for the unpas-sivated Si nanocrystals with the average equilibrium lattice constant and average bond strain for the passivated Si nanocrystals as a function of cluster size.

| cluster size (n) | diameter (Å) | lattice constant (Å) | average bond strain (%) |
|------------------|--------------|----------------------|-------------------------|
|                  |              | unpassivated         | passivated              | unpassivated | passivated |
| ∞                | ∞            | 5.407                | -                       | 0.00         | -          |
| 6                | 17.10        | 5.352                | 5.392                   | 1.02         | 0.28       |
| 5                | 14.05        | 5.345                | 5.384                   | 1.15         | 0.43       |
| 4                | 10.81        | 5.323                | 5.379                   | 1.55         | 0.52       |
| 3                | 8.97         | 5.284                | 5.384                   | 2.27         | 0.43       |

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FIG. 1: Calculated bond strain variation between indicated layers (x-axis) for a) Si (n=6), b) Ga-centered GaAs (n=6), (c) Cd-centered zinc blende CdSe (n =6) and d) Cd-centered wurtzite CdSe (n=5) nanocrystals. The corresponding nearest neighbor bond-length between the atoms at the theoretically obtained equilibrium bulk lattice constant for each case is given by $r_0$. In the case of wurtzite nanocrystals the axial (red dashed line), equatorial (green dotted line) as well as the average bond strain (black solid line) for each layer have been shown as a function of depth. The values of the bond length for some layers have been indicated. A positive strain corresponds to compression of bonds by definition.