

Strain and Structure in Nanocrystals

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ABSTRACT

Layered nanocrystals consist of a core of one material surrounded by a shell of a second material. We present computation of the atomistic strain energy density in a layered nanocrystal, using an idealized model with a simple cubic lattice and harmonic interatomic potentials. These computations show that there is a critical size r_s^* for the shell thickness r_s at which the energy density has a maximum. This critical size is roughly independent of the geometry and material parameters of the system. Moreover it agrees with the shell thickness at which the quantum yield has a maximum, as observed in several systems.

Keywords: nanocrystals, strain energy, quantum yield.

1 Introduction

The size dependence of electric, optical, and structural properties of nanocrystals has been important issues in nanosciences. The synthesis of an epitaxial core/shell system allows the research on size and shape control. The photostability (hole confinement in the core), electronic accessibility (electron spreading into the shell), and high quantum yield makes these core/shell nanocrystals very attractive for use in optoelectronic devices in [1]. A stringent requirement for the epitaxial growth of several monolayers of one material on the top of another is a low lattice mismatch between the two materials. If this requirement is not met, strain accumulates in the growing layer, and eventually may be released through the formation of misfit dislocations, degrading the optical properties of the system. Moreover, if the strain of shell becomes too great, then it is relieved by irregular growth of shell in [2].

In core/shell epitaxial growth, strain is induced by mismatch between the lattice constants in the core and those in the shell. We use the equilibrium lattice of core as a reference lattice in shell. At the atomistic level, this means that zero displacement corresponds to a homogeneous strain such that the lattice constant has been changed from lattice constant of core to that of shell throughout the material. The derived elastic equation have external force at core/shell and its strength is lattice mismatch.

We examine qualitatively and quantitatively the elastic energy density that arises from the nanocrystal model. We propose that the elastic energy density of nanocrystal is concentrated near interfaces between core/shell and their maximal value as a function of shell thickness has a peak with small shell thickness. We define this shell thickness as critical shell thickness and compare and contrast these results to known photoluminescence quantum yield results from experiments in [1]. Furthermore, we examine the sensitivity of the critical shell thickness to material parameters and the size of core.

2 Atomistic Strain Model

The elastic energy density of the strained substrate is given by the tensor contraction of strain and stress, so that the total elastic energy is the integration of elastic energy density on the whole material. The force balance equations are obtained by setting the variation of the elastic energy with each of the displacements equal to zero. The general approach is not to discretize the force balance equations directly. Instead, we construct a discrete version of the elastic energy density corresponding to finite difference method for continuum elasticity in a cubic lattice. At each point of the grid, the energy contribution only involves terms from the 27 point stencil (nearest and next-nearest neighbors) centered at point itself. If the computational grid is the same as the underlying atomistic lattice, then the discrete version of the energy may be considered purely atomistic.

Here is the discrete elastic energy density

$$E = \sum_{k,p} \alpha_k^p (S_{kk}^p)^2 + \sum_{k \neq l, p, q} \{ 2\beta_{kl}^{pq} (S_{kl}^{pq})^2 + \gamma_{kl}^{pq} S_{kk}^p S_{ll}^q \}. \quad (1)$$

where p, q is + or - and k, l is 1, 2. To make discrete energy density and continuum energy density to be consistent, we can get elastic coefficients from Voight constants

$$(\alpha, \beta, \gamma) = (C_{11}, C_{44}, C_{12})/4. \quad (2)$$

The significant geometric parameters are the core radius r_c and the shell thickness r_s and the lattice mismatch

$$\epsilon = \frac{l_c - l_s}{l_c} \quad (3)$$

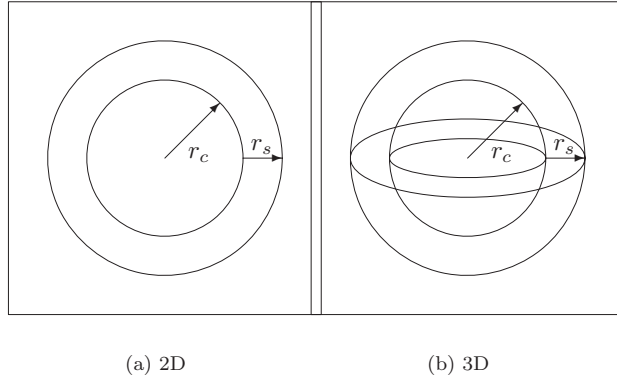


Figure 1: Basic geometry of core/shell nanocrystal model

for elastic strain energy parameter where l_c and l_s are the lattice constants of core and shell, respectively. The core consists of atoms whose lattice position x (before displacement) satisfies $|x| \leq r_c$, and the shell consists of atoms with $r_c < |x| \leq r_c + r_s$.

We now turn our attention to elastic energy density of core/shell nanocrystal produced by our model. The model in [5] with infinite step train shows the clearly distinct strain fields produced by the surface step and the buried interface step. Our model with consecutive steps on the vicinal and top surfaces gives the possibility of concentration of elastic energy near buried interface steps or surface steps. The experimental results on the irregular growth on shell with large lattice mismatch for thicker nanorods [2] imply that interfacial strain plays a more important role than surface strain. We will verify the significance of interfacial strain by calculating the elastic energy density and showing the concentration of elastic energy fields.

3 Simulation Results

Computational results are presented here from minimization of the total elastic energy (after removing degenerate modes corresponding to translation and rotation), corresponding to balance of all of the forces in the system, for 2D (circular, or equivalently rods of infinite length) and 3D (spherical) nanocrystals. For the harmonic potentials used here, this amounts solving a linear system of equations, in which the forcing terms come from the lattice mismatch ϵ . The simulation results include values of the displacements, the forces and energy density. Graphical results will be presented for the last of these. As a figure of merit for the atomistic strain field in a nanocrystal, we shall use the maximum value E_m of the discrete energy density. The energy at each atom consists of elastic energy and bond energy. The atomic bond can be broken when the elastic energy is larger than bond energy. Therefore, the maximum energy density can be one of the indicators to explain

instability with thicker shell.

3.1 Elastic energy density

Figures 2 show the elastic energy density of 3D layered nanocrystals of fixed core size r_c for various values of shell thickness r_s . In the 3D nanocrystal simulation (Figure 2), the shell has thickness values $r_s = 1, 2$ and 7 monolayers, on a core of radius $r_c = 8$ monolayers with the elastic constants $\alpha = 5, \beta = 1$ and $\gamma = 3$ and lattice mismatch $\epsilon = 0.04$.

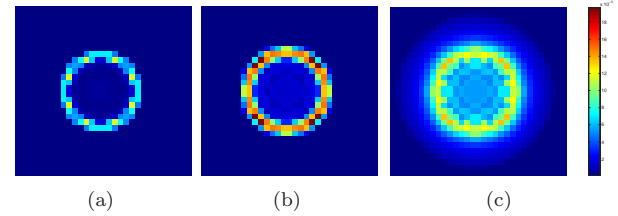


Figure 2: Elastic energy density on a cross section with maximum energy density for a 3D layered nanocrystals with core size $r_c = 8$ monolayers and with shell thickness r_s of size (a) 1 monolayers, (b) 2 monolayers and (c) 7 monolayers.

Figure 2 show that the energy is concentrated in the region of the shell, along the interface with the core. Moreover, the energy density is more concentrated for thicker shells. In addition the largest values of the energy density are close to the diagonal.

3.2 Critical Thickness

Figure 3 shows the maximum energy density for a layered nanocrystal, as a function of shell thickness r_s , for a fixed value of the core size r_c . Figure 3 shows that the maximum energy density increases with increasing shell thickness r_s up to a critical shell thickness r_s^* . For $r_s > r_s^*$, the maximum energy density is decreasing as a function of r_s . The general similarity between the critical shell thickness in 2D and 3D is indicative of the robustness of this result. The physical core diameter of CdSe/CdS core/shell nanocrystal is ranging from 23Å to 39Å which is equivalent to core radius of 3 monolayers to 6 monolayers, since one full monolayer is approximately 3.5Å [1].

Next we examine the critical shell thickness r_s^* and its dependence on the material and geometric parameters of the nanocrystal, in particular the dependence of r_s^* on the core size r_c , lattice mismatch ϵ and elastic parameters α, β and γ . We find that the critical shell thickness r_s^* does not depend on the lattice mismatch ϵ and has weak sensitivity of critical shell thickness r_s^* on the core radius r_c for 2D and 3D nanocrystals. Additional computations show that the critical shell thickness r_s^* does not depend sensitively on the elastic parameters α, β and γ . All the computational results are shown in [7].

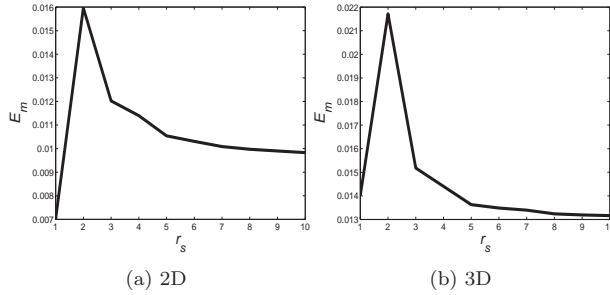


Figure 3: (a) Maximum energy density E_m vs. shell thickness r_s for (a) 2D and (b) 3D nanocrystal of core radius $r_c = 8$ monolayers.

4 Discussion

4.1 Step Interactions

Some insight into the existence of a critical shell thickness r_s^* comes from consideration of step interactions. On the outer edge of the shell, the shell atoms will relax towards their equilibrium lattice constant, lowering the strain energy density. This relaxation will be greatest along the diagonal, where the atoms have the smallest number of neighbors. On the other hand, along the core/shell interface, shell atoms near the diagonal have the largest number of core atom neighbors and so they have the largest strain. This maximum is increased by their interaction with the atoms along the diagonal on the outer edge, but that interaction decreases as the shell thickness increases. This indicates a critical thickness.

This is analogous to the strain field produced by a surface step, on an epitaxial surface, interacting with a buried step, on the interface between an epitaxial thin film and the substrate, as studied in [5].

Simplified single step simulations show that the maximum energy E_m peaks when one step on the surface and one on the buried interface are close. This supports the above arguments. More details are in [7].

4.2 Comparison to Quantum Yield

The critical shell thickness, observed in the simulations presented above, correlates closely to the maximum value of the quantum yield from experiments. Photoluminescence quantum yield data come from both CdSe/CdS [1] and InAs/CdSe [3] layered nanocrystals. We compare their quantum yields results with our simulation results and found that both have the peak at the small shell thickness. More computations of the material properties are studied from the simulations in [7].

5 Conclusion

The simulation results presented above are for a highly idealized model of a layered nanocrystal. The robust-

ness of these results with respect to variation of dimension, geometry and material parameters suggests that these results are qualitative and generally applicable. In addition, there is some evidence that the critical shell thickness found in these simulations is related to the maximal values of quantum yield, as found experimentally.

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