

Ab initio thermodynamic model to assess stability of heterostructure nanocrystals

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(Received 13 January 2010; accepted 3 February 2010; published online 10 March 2010)

The tendency for homogenization of CdSe-CdTe heterostructure semiconductor nanocrystals (NCs) with an abrupt interface has been studied using a phenomenological model with parameters determined by *ab initio* density functional theory. Results indicate that wurtzite-based CdSe-CdTe heterostructure NCs with sizes greater than ~ 1000 Å are the most stable, preferring an abrupt interface below 500 K. © 2010 American Institute of Physics. [doi:10.1063/1.3330924]

Recently, semiconductor heterojunction nanocrystals (NCs) have drawn considerable interest for use in electroluminescence and photovoltaic devices.^{1,2} The classification of such heterostructures falls into two categories, depending upon the relative alignment of the valence and conduction band edges across the interface. In Type I heterostructures, the nested band alignment is favorable for the localization and recombination of photoexcited electrons and holes. Conversely, the staggered band alignment in Type II heterostructures provides a natural mechanism for the dissociation of excitons. In either case, the abruptness of the interface is crucial, as alloying/mixing at the interface can significantly affect the positions of the energy levels, reducing the interfacial band offset and consequently, the tendency for recombination or dissociation of charge carriers. Through modern colloidal chemistry techniques, NCs with such well defined interfaces can be synthesized,³ and have been observed to be highly stable under ambient conditions for a variety of materials.⁴ However, the structural quality of these interfaces is expected to decrease at elevated temperatures, as the interdiffusion of constituent atoms across the heterojunctions may result in NC alloying.⁵

In view of these expectations, the purpose of this study is the development of a thermodynamical model to account for the effect of temperature on the stability of heterostructure NCs composed of two components *A* and *B*. In particular, the critical temperature for mixing above which an alloyed A_xB_{1-x} NC (where *x* is the mole fraction of component *A*) is preferred over *A* and *B* separated by an abrupt interface ($A_x|B_{1-x}$) is determined for the heterostructure geometries shown in Fig. 1. This model is subsequently applied to wurtzite and zincblende CdSe-CdTe heterostructure NCs.

To determine the temperature above which the NC prefers to be in a completely mixed state, we define the free energy of mixing (ΔG_{mix}) per unit A_xB_{1-x} for a heterostructure initially in the unmixed state as follows:

$$\Delta G_{\text{mix}} = \Delta H_{\text{mix}} + E_{\text{strain}} + k_B T \Omega - T(\Delta S_{\text{vib}} + \Delta S_{\text{el}}) - \frac{A_i \sigma}{N} + \frac{A_s \Delta \gamma}{N}, \quad (1)$$

where $\Delta H_{\text{mix}} = E_{A_xB_{1-x}} - [xE_A + (1-x)E_B]$ is the enthalpy of

mixing per unit A_xB_{1-x} with $E_{A_xB_{1-x}}$, E_A , and E_B the respective energies of the alloyed and pure components at equilibrium. E_{strain} represents the strain energy due to lattice mismatch at the interface, assuming coherency is preserved. The configurational entropic contribution to ΔG_{mix} is captured in the third term, where k_B is the Boltzmann constant, T the temperature, and $\Omega = [x \ln(x) + (1-x) \ln(1-x)]$. The number of A_xB_{1-x} units in the NC is $N = V/v$, where V is the total volume of the NC and v the volume per A_xB_{1-x} unit. The change in the vibrational and electronic entropy (per unit A_xB_{1-x}) between the mixed and the unmixed state is represented by ΔS_{vib} and ΔS_{el} , respectively. The final two terms account for the energy associated with the interface as well as the NC surface, with σ denoting the interfacial energy and $\Delta \gamma$ the difference in surface energy between the mixed and unmixed state, all per unit area. A_i and A_s represent the area of the interface and outer surface, respectively.

As formulated, Eq. (1) is completely general, and applicable to any material system. For the basis of this study, a number of assumptions are made to simplify this expression and facilitate determination of the mixing temperature. First, E_{strain} is neglected. Indeed, strain can significantly affect the properties of NCs (Ref. 6) however, for this analysis, the strain energy can be captured in the determination of σ , as described below. Second, ΔS_{el} is ignored since *A* and *B* are semiconductors and few electrons populate excited states at nominal temperatures. Third, the change in vibrational en-

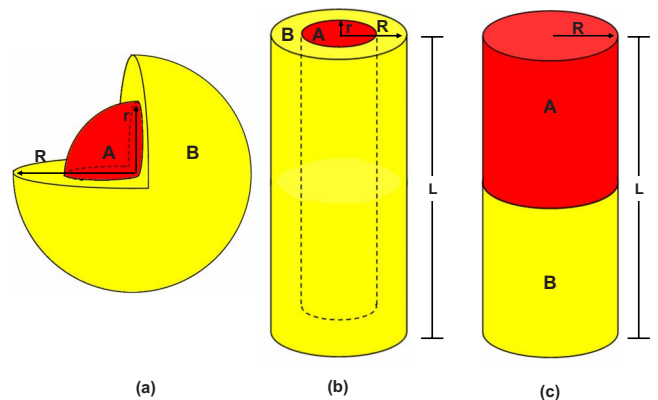


FIG. 1. (Color online) Schematic of $A_x|B_{1-x}$ heterostructure NCs considered in this study: (a) core-shell nanoparticle, (b) core-shell nanowire, and (c) nanowire with an axial heterojunction.

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trophy between the A_xB_{1-x} and $A_x|B_{1-x}$ states is assumed to be small compared to the corresponding configurational entropy difference, allowing for the neglect of ΔS_{vib} . Finally, $\Delta\gamma$ is taken to be zero under the assumption that A and B are chemically similar.

Making these approximations and setting Eq. (1) to zero, the critical temperature above which it is no longer favorable for A and B to remain separated by an abrupt interface is as follows:

$$T_{\text{mix}} = \frac{1}{k_B\Omega} \left(\frac{A_i v \sigma}{V} - \Delta H_{\text{mix}} \right). \quad (2)$$

In this expression, the effect of NC geometry is contained in the first term, and is specified by A_i and V . For the NCs depicted in Fig. 1, A_i and V have the following definitions: $4\pi r^2$ and $4/3\pi R^3$ for core-shell nanoparticles, $2\pi rL$ and πR^2L for core-shell nanowires, and πR^2 and πR^2L for nanowires with an axial heterojunction (with r , R , and L defined in Fig. 1). In the limit of infinite radius or length, the first term drops out and the critical mixing temperature $T_{\text{mix}}^{\text{bulk}} = -\Delta H_{\text{mix}}/k_B\Omega$, represents the temperature above which the mixed state is preferred in the bulk. We therefore have

$$T_{\text{mix}} = T_{\text{mix}}^{\text{bulk}} + \frac{A_i v \sigma}{k_B\Omega V}, \quad (3)$$

with the second term always being negative, implying that finite sizes will decrease T_{mix} relative to the corresponding bulk value.

In addition to A_i and V , three other quantities, namely, ΔH_{mix} , v , and σ are needed to determine the mixing temperature according to Eq. (2). These quantities are not analytic and represent material properties of A and B , taken here to be CdSe and CdTe. In the bulk, CdSe and CdTe form a pseudobinary solid solution over the entire composition range, adopting the zincblende or wurtzite structure depending on the amount of CdSe present in the alloy.⁷ Here, we assume that CdSe, CdTe, and the mixed phase are either all in the wurtzite phase or all in the zinc blende phase. We believe that this is more appropriate for the process modeled here. To determine ΔH_{mix} , v , and σ , *ab initio* density functional theory (DFT) calculations were carried out within the local density approximation (LDA) using SIESTA,⁸ a local orbital code. Core electrons were described by norm-conserving pseudopotentials, constructed according to the Troullier–Martins scheme⁹ with atomic configurations of [Kr]5s²4d¹⁰, [Ar 3d¹⁰]4s²4p⁴, and [Kr 4d¹⁰]5s²5p⁴ for Cd, Se, and Te, respectively. A double- ζ plus polarization basis set with an orbital confining cutoff radius specified by an energy shift parameter of 0.002 Ry was used for all calculations. Sampling the Brillouin zone using a $(4 \times 4 \times 4)$ Monkhorst–Pack k -point mesh¹⁰ yielded well converged results. The equilibrium positions of all atoms were determined by requiring the force upon each atom to be no greater than 0.04 eV/Å.

The predicted wurtzite (CdSe: $a=4.28$ Å, $c=7.02$ Å, CdTe: $a=4.62$ Å, $c=7.55$ Å) and zincblende (CdSe: $a=6.08$ Å, CdTe: $a=6.52$ Å) lattice constants are in good agreement with available theoretical work at the same level of theory^{11–13} and with the corresponding experimental values.¹⁴ Ordered CdSe _{x} Te _{$1-x$} alloys were then simulated using 32 and 64 atom supercells for the wurtzite and zincblende phases, respectively. Within the supercell, the composition of the alloy was varied using the procedure of

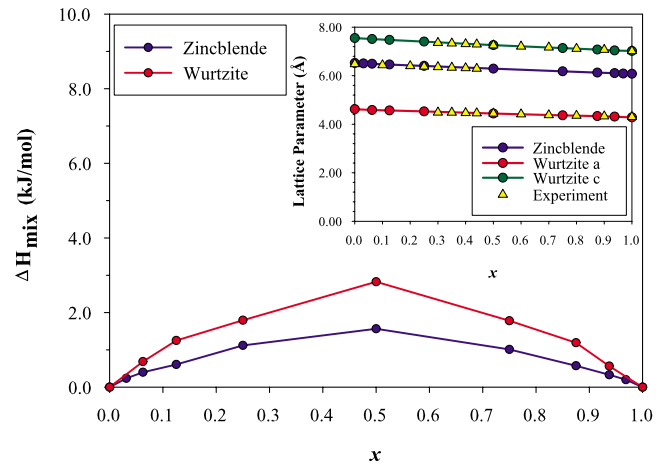


FIG. 2. (Color online) Calculated enthalpy of mixing and lattice parameter (inset) of a homogeneous CdSe _{x} Te _{$1-x$} alloy as a function of CdSe composition for the wurtzite and zincblende phases. Also shown are the experimental values of the lattice parameter, taken from Ref. 7.

Pelucchi *et al.*,¹⁵ systematically replacing Se atoms with Te atoms to create a homogeneously mixed system. The total energy at each chosen composition was then obtained by allowing the atomic positions and the lattice constants to relax to their most stable configuration.

Figure 2 shows the dependence of the ΔH_{mix} and lattice constants on the alloy composition. The predicted lattice constants are in excellent agreement with available experimental data.⁷ Moreover, ΔH_{mix} is greater than zero for both the wurtzite and zincblende phases, indicating that at $T=0$ it is thermodynamically favorable for CdSe and CdTe to remain separated regardless of composition.

To determine σ , a series of heterostructure superlattices were constructed with interfaces oriented along crystal planes most commonly observed in zincblende and wurtzite NCs.^{5,16} These interfaces as well as their corresponding energies are presented in Table I. Although standard supercell techniques are capable of determining the σ of the nonpolar interfaces, the lack of inversion symmetry in wurtzite and zincblende crystals makes the isolation of polar interface energies nontrivial.^{17,18} In these instances, the σ is taken as the average between the polar interface plane and its complement [i.e., the (111) and $(\bar{1}\bar{1}\bar{1})$ interfaces for zincblende, and the (0001) and $(000\bar{1})$ in the case of wurtzite]. To incorporate the strain energy [E_{strain} in Eq. (1)] into σ , the total energy of the heterostructure with optimized lattice parameters and atomic positions was determined and referenced to the bulk energies of CdSe and CdTe at their equilibrium (strain-free) lattice

TABLE I. Energy (in meV/Å²) of various types of zincblende and wurtzite interfaces.

System	Interface	σ
Zincblende	(110)	16.8
	(001)	17.1
	(111)	17.5
Wurtzite	(10 $\bar{1}$ 0)	15.6
	(01 $\bar{1}$ 0)	15.9
	(11 $\bar{2}$ 0)	15.7
	(0001)	16.4

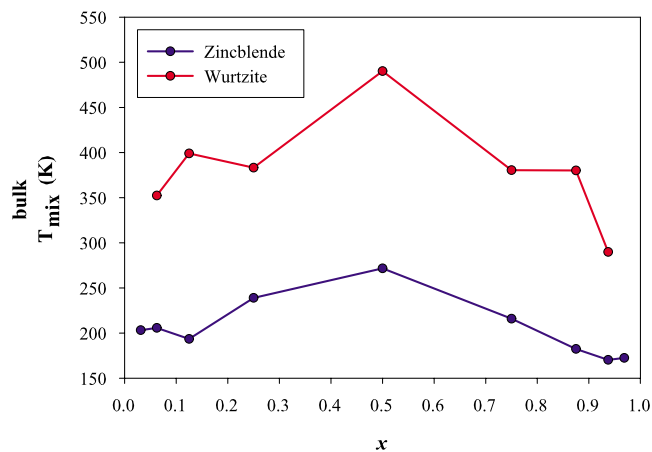


FIG. 3. (Color online) Critical bulk mixing temperature above which the mixing reaction $x\text{CdSe} + (1-x)\text{CdTe} \rightarrow \text{CdSe}_x\text{Te}_{1-x}$ is expected to occur with all systems involved being either in the wurtzite or zinblende bulk phases.

constants. As the interface energies were roughly the same for all cases considered, the average of these energies, $16.4 \text{ meV}/\text{\AA}^2$ was taken as σ to be used in Eq. (2).

Having determined ΔH_{mix} , v (in terms of the lattice constants) and σ , we now proceed to address the stability of CdSe-CdTe NCs with the geometries shown in Fig. 1. In Fig. 3, the critical mixing temperature in the bulk $T_{\text{mix}}^{\text{bulk}}$ is shown as a function of CdSe mole fraction. From this, it is evident that heterostructures involving equal amounts of CdSe and CdTe (i.e., $x=0.5$) have the highest $T_{\text{mix}}^{\text{bulk}}$ and hence are most resistant to component mixing. In particular, for the wurtzite 50–50 composition, the critical temperature for mixing is $\sim 500 \text{ K}$. This estimate is consistent with recent experimental findings in which CdSe-CdTe nanowires exposed to a 600 K environment for an extended period ripen into spherical CdSe_xTe_{1-x} alloyed NCs.⁵ In comparison, the much lower $T_{\text{mix}}^{\text{bulk}}$ of the zinblende heterostructures relative to wurtzite indicates that mixing is favored at room temperature, regardless of composition or size.

Figure 4 shows a plot of T_{mix} [Eq. (3)] for a 50–50 mixture of the three types of CdSe-CdTe heterostructure NCs considered. NCs with other compositions as well as zinblende-based NCs exhibit a qualitatively similar behavior. In particular, core-shell nanoparticles and nanowires with diameters below 1000 \AA and nanowires with axial heterojunctions that are smaller than 1000 \AA show substantial reductions in mixing temperatures relative to their respective $T_{\text{mix}}^{\text{bulk}}$ values. We expect these predictions to be semiquantitative, in view of the errors due to LDA and the approximations made in this treatment. Nevertheless, these results place a thermodynamic limit on the length scale to which heterostructure NCs may be scaled down while still preserving the stability of the abrupt interface.

In summary, a thermodynamic model, with parameters determined through DFT calculations has been applied to account for the effects of temperature on the stability of CdSe-CdTe heterostructure NCs with respect to alloying or homogenizing. Results indicate that regardless of composi-

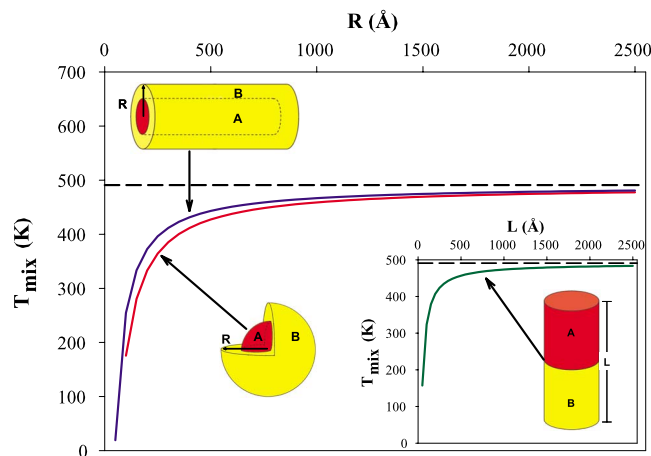


FIG. 4. (Color online) Mixing temperature [Eq. (3)] as a function of size for wurtzite heterostructure NCs containing equal mole fractions of CdSe and CdTe. The dashed line indicates the limiting mixing temperature ($T_{\text{mix}}^{\text{bulk}}$) for this composition.

tion, zinblende-based heterostructures are thermodynamically unstable to alloying at room temperature. Nevertheless, wurtzite-based NCs with equal amounts of CdSe and CdTe and sizes larger than $\sim 1000 \text{ \AA}$ are the most resistant to alloying, showing a thermodynamic preference to maintain an abrupt interface at temperatures below $\sim 500 \text{ K}$.

The authors would like to acknowledge financial support of this work through a grant from the National Science Foundation (NSF) as well as computational support through an NSF Teragrid Resource Allocation.

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