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A simple thermodynamic model for the doping and alloying of nanoparticles

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Abstract
Impurity incorporation into nanoparticles is modeled using thermodynamics. For small particles, entropically driven impurity incorporation is reduced, rendering doping difficult. We show that the free energy of surface impurities in small nanoparticles is lower than core impurities, surface doping therefore occurs preferentially. A critical size for core doping is identified, below which it is energetically unfavorable. In all cases, core impurity concentration is reduced as particle size decreases. We show larger than bulk impurity concentrations are possible, corresponding to increased alloying.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Doping of semiconductors is a well-established technique used to tailor the electrical and optical properties of devices [1]. In recent years, considerable work on the doping of nanoparticles and nanostructures has been carried out, with varying levels of success [2–6]. While it is possible to dope nanoparticles, as their size decreases, the ability to incorporate impurities into the core of the structure becomes increasingly difficult [5, 7, 8]. The two governing forces, kinetics and thermodynamics, have both been studied extensively [7–10]. The binding of impurity atoms to the surface of nanoparticles—which is the assumed mechanism driving nanoparticle doping in the kinetics model [9]—requires many assumptions and complex calculations. Treating doping as a purely thermodynamic process involves only a few minor assumptions (particle shape, structure, etc), which leads to a more well-defined model that can be trivially extended to various semiconductor systems. We employ a simple thermodynamic model, considering Gibbs free energy, enthalpy, and entropy as they relate to doping. This simple model provides physical insight and understanding into an otherwise complicated phenomenon. We propose that thermodynamics on its own is sufficient to explain the doping properties of nanoparticles.

Doping models based solely on kinetics make two major assumptions: (1) that thermodynamic equilibrium is not realized and (2) that diffusion within the nanoparticle is virtually non-existent. Erwin *et al* [9] cite kinetics as the limiting mechanism to nanoparticle doping, and propose that surface binding energies, as well as impurity adsorption times, are the primary factors to be considered. Their model requires impurities to be able to bind to the nanoparticle surface and then reside there long enough for subsequent layers to be overgrown, essentially trapping the impurity within the particle core [11]. Recently, progress has been made in synthesizing doped nanoparticles, and focus has since shifted to thermodynamics in order to further understand the physics of doping on the nanoscale [7, 8, 12]. An energetic model should generally be valid for all nanoparticle synthesis techniques, as all techniques require materials to be, at the very least, in local thermodynamic equilibrium with their surroundings during growth. While Erwin's model assumes a lack of diffusion, a thermodynamic model inherently assumes diffusion occurs to bring the system into equilibrium. This assumption seems justified for particles where diffusion

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lengths are only a few nanometers. Stegner *et al* [13] synthesized P-doped Si nanoparticles of varying size (3–50 nm). They reported that for particles with diameters smaller than 12 nm, 80–95% of the P atoms segregated to the surface as growth continued. This is in direct contrast to the model originally proposed by Erwin *et al* [9], in which impurities become trapped inside a nanoparticle [11]. Therefore, even though kinetics is sometimes invoked to explain nanoparticle doping, thermodynamics need at least be considered, regardless of the growth mechanism and conditions involved, as systems will not be pinned in high energy configurations. Impurities in small particles will tend to be driven to the surface as growth progresses [13], moving the system towards a lower energy state, predicted by thermodynamics.

Recent energetics modeling has focused on impurity enthalpies and largely neglected entropy, studying formation energies as a function of nanoparticle size ranging from 1.4 to 20 nm [2, 3, 6, 15, 16]. Dalpian and Chelikowsky [8] found the impurity formation energy—the extra energy required to form a substitutional defect—to increase as nanoparticle size decreases, rendering doping more difficult. This trend has been verified in multiple papers [2, 4, 15]. Other work has involved investigating impurity formation energies at various locations in/on the nanoparticles [4, 5, 14] as well as showing the possibility to achieve dopant concentrations greater than that of the bulk [5]. Cantele *et al* [4] show that impurity formation energy decreases as the dopant is located closer to the surface. As a result, it is energetically favorable for dopants to be found on the surface, rather than in the core, as nanoparticle size decreases.

In this work, we consider the effects of entropy. We assume all nanoparticle surfaces are completely passivated. The distinction between core and surface impurities is therefore an important point; impurities which settle on the surfaces of nanoparticles, rather than in the core, are not electrically active dopants as the extra carriers they provide will tend to fill or empty dangling bonds. Impurities are therefore only dopants if they can be incorporated within the particle core and contribute to the free carrier concentration. To model this, configurational entropy, which is strongly dependent on particle size, must be taken into account in addition to enthalpy. For simplicity, we neglect second-order effects, both in enthalpy (strain, non-nearest-neighbor bonds, etc) and in entropy (vibrational contributions, etc). Despite these assumptions, we will show we are able to capture the underlying physics of impurity incorporation, but producing quantitative agreement with experimental data is likely to require consideration of some of these effects. The aim of this paper is to model the interplay of the competing mechanisms of enthalpy and entropy to determine plausibility of core (versus surface) doping and to determine maximum achievable doping concentrations for any given system. Both are considered as a function of nanoparticle size.

2. Methods

To model the potential for impurity incorporation in nanoparticles we minimize the Gibbs free energy of the system. We therefore consider the differential form of Gibbs free energy (normalized to $k_{\mathrm{B}}T$)

$$\Delta G = \Delta H - T\Delta S \tag{1}$$

which refers to the difference in the free energy of a system between different states or configurations. Processes are thermodynamically driven when $\Delta G < 0$, and a stable configuration occurs when ΔG is minimized. The change in enthalpy, ΔH, is given by

$$\Delta H = \Delta U + p\Delta V \tag{2}$$

where ΔU is the difference in internal energy of a system, p is the pressure, and V is the volume. Since we are dealing with nanocrystalline solids, the change in volume is negligible and we neglect its contribution to the enthalpy. We therefore treat enthalpy as a direct measure of the change in internal energy of a system with two different bonding configurations. In our model this depends on the energy difference between an A–A bond and an A–B bond, where species B is an impurity in species A. Therefore, ΔU should not be confused with the A–A bond energy, U. The last term in (1) includes the change in entropy, ΔS, of the system, which is a measure of the disorder, or the number of possible configurations of a system, $\Delta S = k_{\mathrm{B}} \ln \Omega$. In this expression, Ω refers to the total number of configurations of the system: $\frac{m!}{(m-d)!d!}$, with m being the total number of atoms or atomic sites in the nanoparticle and d being the total number of impurities introduced into the structure. The Gibbs free energy is normalized to $k_{\mathrm{B}}T$, making all results unitless. We assume for simplicity that an impurity can occupy any one of the m atomic sites. While this is true for single component nanoparticles, in more ionic systems, a dopant will generally occupy only one type of site (cation or anion), changing by m some factor, but preserving all underlying physics. We also assume a simple cubic crystal structure for our model nanoparticle, with n atoms on a side ($m = n^3$) and octahedral coordination. Although we make these assumptions for simplicity, this model can be trivially extended to fit more complex systems.

Previous work has discussed the location of impurities in nanostructures [4, 5, 14]; since we are concerned with electrically active dopants (i.e. impurities found in the core) we differentiate between core atoms and surface (face) atoms for the enthalpy term in (2). A core atom in an octahedral structure has six bonds or nearest neighbors ($\Delta H = 6 \times \frac{\Delta U}{k_{\mathrm{B}}T}$), while there are only five bonds for a face atom (see figure 1, inset). The term $\frac{\Delta U}{k_{\mathrm{B}}T}$ refers to the normalized difference in bond energy between a host–host bond and a host–dopant bond. Gibbs free energy is minimized when impurities are incorporated into bulk materials because this leads to more possible configurations, increasing the entropy of the system. However, there is often (but not always) an enthalpic penalty, resulting from the difference in bond energies between the host and the impurity. This penalty is not enough to overcome the increase in entropy of bulk systems, but it starts to dominate as size decreases. It is this relationship between the enthalpic penalty of the impurity and the entropic gain of the system that determines if, and where, impurities can incorporate [16].

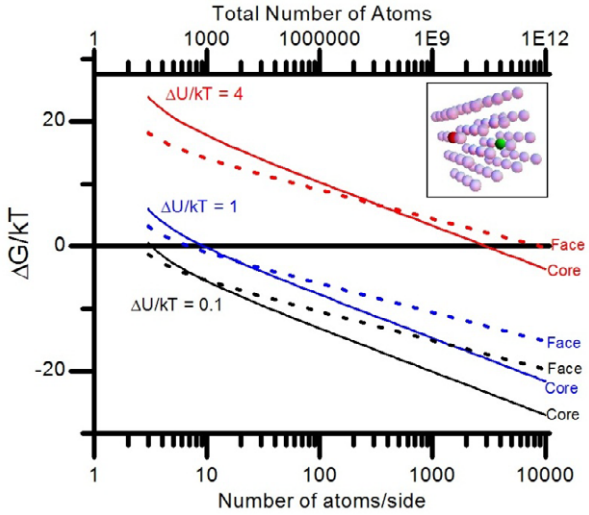

Figure 1. Gibbs free energy (normalized to $\frac{1}{k_B T}$) versus n of nanoparticles for different bond energies ($\Delta U/kT$), as indicated. Core and face incorporation are indicated by solid and dashed lines, respectively. Inset: depiction of a cubic nanoparticle as described in this paper: facial position is indicated in red, while core position is indicated in green.

To begin, we assume there is only one dopant ($d = 1$) located either on the surface or in the core. This is a logical partition because it takes into account first-order bonding configuration, or number of bonds per atom; as previously stated, for an octahedral coordination there are six bonds for a core atom and only five for a surface atom. Therefore, to first order, all core atoms are interchangeable. To treat both locations (core and surface) independently we use different values of m (total number of atoms). Recall a cubic particle with n atoms per side ($m = n^3$), the total number of core atoms is $(n-2)^3$, while the rest, $n^3 - (n-2)^3$, are surface atoms. For large particles, the core will contain more atoms than the surface, and the introduction of one dopant will result in a larger increase in entropy compared to the surface. However, as the size decreases, the surface area to volume ratio of the nanoparticle increases [5, 7], leading to more available states located on the surface than in the core. Therefore it is more energetically favorable for an impurity to reside on the surface rather than in the core of smaller particles due to the larger entropies associated with these locations. These results are in qualitative agreement with previous work [4, 8, 14, 15], which showed that doping becomes increasingly difficult as we move toward smaller nanostructures. This model likely becomes invalid for clusters containing fewer than 100 atoms (between $n = 4$ and 5) due to the increasing importance of particle shape at these small sizes.

3. Results and discussion

3.1. Doping of nanoparticles

Impurity incorporation will only occur if there is a net reduction in the Gibbs free energy of the system. To model this we combine the entropy and enthalpy terms to arrive at our normalized Gibbs free energy,

$$\frac{\Delta G}{k_B T} = \beta d \frac{\Delta U}{k_B T} - \ln \Omega \tag{3}$$

where β is the number of bonds per impurity substituted, d is the number of impurities, and $\frac{\Delta U}{k_B T}$ is the normalized energy difference per bond. Figure 1 is a plot which illustrates how the addition of a single impurity ($d = 1$) affects the change in Gibbs free energy, as a function of nanoparticle size (n). Values of β correspond to the number of substituted bonds, five for a surface impurity and six for a core impurity. The change in Gibbs free energy is also given for different values of $\frac{\Delta U}{k_B T}$, the solid and dashed lines represent the core and surface, respectively. Figure 1 shows that for increasing values of $\frac{\Delta U}{k_B T}$, there is an increase in the free energy of the nanoparticle, meaning that it is more difficult to dope these systems. Also evident in figure 1 is a crossover or critical point, where the dashed and solid lines intersect each other. For different values of $\frac{\Delta U}{k_B T}$, the curve which is lower (dashed or solid) will be the location (surface or core) that is most energetically favorable to dope. In some instances, the core curve is always lower than the surface curve when $\frac{\Delta G}{k_B T} < 0$, therefore any doping in these systems will be core doping. For curves with smaller values of $\frac{\Delta U}{k_B T}$, there are values of n for which both core and face curves are below zero, but doping the surface is more energetically favorable than doping the core. Core doping will only occur for particles larger than the critical point. This is significant because it allows for the possibility of impurity incorporation in small nanoparticles [2, 3, 13], but not electrically active doping (i.e. surface doping). It is therefore important to carefully distinguish concentrations of dopants from the resulting—and possibly different—carrier concentration. The results of our model, as well as the idea of a critical size for doping, are in good qualitative agreement with experimental results [13, 17–19]. Quantitative agreement can be achieved for phosphorus doped silicon nanoparticles [13] and nanowires [19] by increasing the entropy contribution by a factor of 1.8–2. This suggests the importance of additional sources of entropy, such as vibrational modes, which are neglected in the first-order model. To the best of our knowledge, quantitative comparisons of predicted impurity location to experimental data have not been reported using competing models.

Figure 2 is a plot of the normalized Gibbs free energy per atom, Δg, where $\Delta g = \frac{\Delta G}{m}$. It is given as a function of both d and n (number of impurities and number of atoms per side, respectively) with a constant $\frac{\Delta U}{k_B T}$ of 0.5. Once again, values of β are 5 and 6 for surface and core impurities, respectively. Previously we accounted for how a single dopant affected the Gibbs free energy; however, as more dopants are added, the number of possible configurations increases, increasing the entropy of the particle. Since entropy is also dependent on particle size, figure 2 shows how d and n affect the Gibbs free energy. The colored contours in figure 2 represent decreases in Gibbs free energy of core impurities, while the grayscale contours represent increases. The hatched region represents the area where the Gibbs free energy of the surface is both negative and lower than that of the core. For these values of

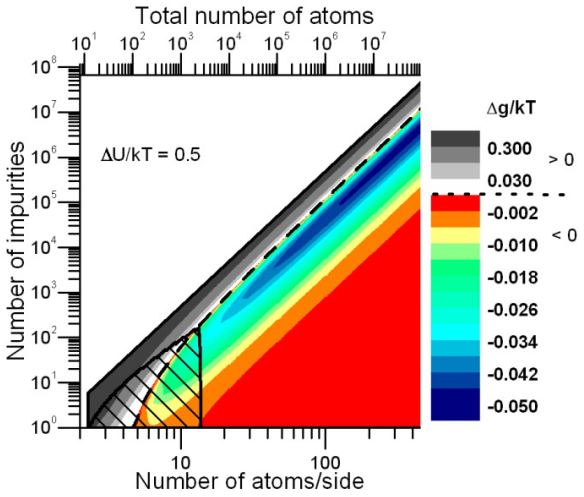

Figure 2. Gibbs free energy per atom versus d and n. Similar patterns are observed for different values of $\Delta U/kT$. The hatched region indicates where the Gibbs free energy for a surface impurity is both negative and less than the Gibbs free energy of a core impurity at the same (n, d) coordinate. The dashed line corresponds to $\Delta g = 0$.

d and n, it is more energetically favorable for impurities to incorporate on the surface of the particle. The dashed line is where $\Delta g = 0$; above this, no core doping will occur. To the left of this $\Delta g = 0$ line within the hatched region, we obtain only surface incorporation. Figure 2 also implies a critical size for nanoparticle doping, as suggested above and in previous research [14, 15]. This is represented by the vertical line on the right-hand side of the hatched region.

3.2. Alloying of nanoparticles

From this model, it is possible to predict impurity concentrations in nanoparticles. Some reports have indicated that it is possible to achieve higher impurity concentrations when alloying nanoparticles as compared to the concentrations found in the bulk material [6]. In figure 3, overall impurity concentrations are plotted as a function of nanoparticle size (given by the length of a side, n atoms). Each point corresponds to the optimal impurity concentration for each value of n, which we define as the number of impurities that minimizes the Gibbs free energy for a nanoparticle of that size. For the sake of physicality, we restrict our concentrations to integer numbers of dopants, which can be seen for the smallest nanoparticles in figure 3(c) as periodically decreasing concentrations for small numbers of dopants; each line corresponds to the incorporation of a single additional impurity. According to figure 3, regardless of the value of $\frac{\Delta U}{k_B T}$, the overall impurity concentration in the nanoparticles will increase relative to its bulk counterpart as particle size decreases. It is interesting to note, however, the location of the impurity atoms. Figure 3 shows that the concentration of impurities in the core of the particle is monotonically decreasing as particle size decreases. Although concentration enhancements have been reported in alloyed nanoparticles [2, 5, 6], the location of the alloying atoms has not been specified. This model shows that this increase is due entirely to surface concentration, with no increase in core concentration. It is worth noting that the mechanism causing an increase in concentration was not previously explained.

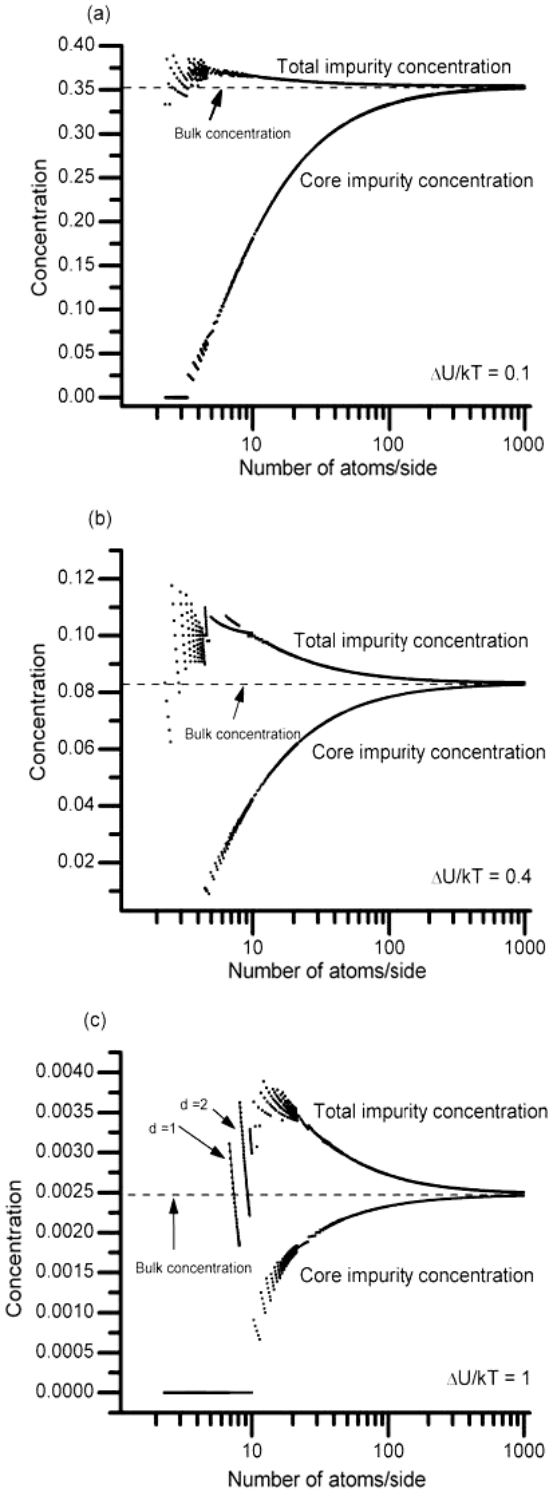

Figure 3. Overall and core impurity concentrations versus side length (in number of atoms) for small nanoparticles. Both concentrations are relative to the total number of atoms. Bulk impurity concentration is indicated by a dashed line. (a) $\Delta U/kT = 0.1$ (typical enthalpy for alloying), (b) $\Delta U/kT = 0.4$, (c) $\Delta U/kT = 1$.

3.3. III–V and other material systems

Values of $\frac{\Delta U}{k_B T}$ for some common III–V alloys range from 0.3 (In:AlAs) to about 2 (In:GaP). Because these materials exhibit tetrahedral coordination, as opposed to octahedral coordination, the values should be compared to the somewhat lower values in figure 1 (approximately 0.2–1.3). For II–VI alloys and dopants and group IV materials, values of $\frac{\Delta U}{k_B T}$ are similar but slightly higher, typically ranging from 0.7 to ∼4. Again, as with the III–V alloys, critical sizes for materials exhibiting zincblende structures will be slightly lower on figure 1, corresponding to values of $\frac{\Delta U}{k_B T}$ that are approximately 2/3 the above-listed values. Bond enthalpies were calculated using the *CRC Handbook of Chemistry and Physics* [20].

As an example of this model, we have investigated the preferred position of Mn impurities in InAs quantum dots within a GaAs matrix. These materials are interesting for their magnetic properties [5, 21, 22]. This work is reported in detail elsewhere [21]. Briefly, we treat the InAs quantum dot as a spherical nanoparticle with zincblende structure and calculate the Gibbs free energy for a single Mn dopant. We replace the assumption of perfectly passivated surfaces with the GaAs matrix. We calculate a critical diameter of 26 nm; for nanoparticles below this size, Mn is expected to incorporate on the surface, while above this size, it is expected to incorporate in the core. This finding is consistent with reports in the literature; Holub *et al* [22] produced quantum dots with diameters of 35–37 nm and reported that most Mn atoms are found within the core of the particle, while Dasika *et al* [21] produced 12 nm quantum dots and found most Mn atoms are located near the surface.

4. Conclusions

Using basic thermodynamics, we have explained the difficulty with doping very small nanoparticles. As particle size decreases, competition between enthalpy and entropy becomes more pronounced, and the concentration of dopants in the core will decrease. We have developed the idea of a critical nanoparticle size, for varying values of $\frac{\Delta U}{k_B T}$, below which core doping is energetically unfavorable. The preferred location of an impurity depends on the particle size and will move from the core to the surface for very small nanoparticles. This can lead to an increase in the alloying of the nanoparticle to values greater than that of the corresponding bulk material, but not increased doping. We note that interactions between charged dopants are neglected in this model. This is irrelevant for systems with only one dopant (as in figure 1), but could become a source of error when multiple dopants are present (figures 2 and 3). In most cases, however, we posit that charged impurities must be present in large concentrations in order to be in close enough proximity to each other to cause significant effects. This simple model can also be extended to one- and two-dimensional structures, such as nanowires and quantum wells, and can be applied to material systems with different particle shapes and coordinations, including doping of polymers. Although this model neglects kinetics and therefore the possibility of nanoparticles being pinned into metastable states, kinetics arguments suggest there is a reduced possibility of metastable states as particle size decreases [8]. A model based on thermodynamic equilibrium is therefore, at the least, a good predictor for the plausibility of doping nanoparticles.

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