Compatible composition profiles and critical sizes of alloyed quantum dots

H. L. Duan,[1] B. L. Karihaloo,[1,*] J. Wang,[2] and X. Yi[2]

[1]*School of Engineering, Cardiff University, Queen's Buildings, The Parade, Cardiff CF24 3AA, United Kingdom*
[2]*LTCS and College of Engineering, Peking University, Beijing 100871, People's Republic of China*

We present first a compatibility equation for the misfit strains induced in alloyed quantum dots (QDs) by the mismatch in the lattice constants or the thermal-expansion coefficients of their alloying elements and show that it imposes some restrictions on the alloy composition profiles from a theoretical point of view. We then solve the strain field in embedded alloyed QDs induced by the nonuniform misfit strains. It is found that the induced field is uniform if the misfit strains satisfy the compatibility equation, but not otherwise. Finally, we consider the energy of nucleation of a circular prismatic dislocation loop to relieve the misfit strain and calculate the critical size of a dislocation-free alloyed QD. We show that this size is much larger when the alloy composition meets the restrictions imposed by the strain compatibility equation than when it does not.

I. INTRODUCTION

The behavior of the electronic devices made of alloyed quantum dots (QDs) (e.g., $In_xGa_{1-x}As$, $CdTe_xSe_{1-x}$) is strongly affected by their enriched but nonuniform composition.[1–4] The possibility of tuning a particular composition profile via alloying is of great importance as it represents another degree of freedom in the design of self-assembled heteroepitaxial structures.[5] Many theoretical and experimental investigations have been conducted to understand how different growth parameters influence the size, shape, and composition of alloyed QDs, in the hope that such understanding will allow better control of their electronic properties.[5–16] A recent literature review[17] suggests that no existing theory can predict the complicated interdependence of QD shape, strain, and composition. Moreover, if a QD island grows sufficiently large, it will eventually induce strain-relieving misfit dislocations.[4] Hence the assessment of the composition profiles and strains is important to both the identification of the dominant growth mechanisms and the modeling of the confining potential of quantum dots.[5,18,19]

There is much experimental evidence in support of position-dependent compositions in various QDs.[7,15,16,18] Rosenauer *et al.*[7] evaluated the composition of $In_xGa_{1-x}As/GaAs$ QD structure by measuring local lattice parameters and displacements assuming a linear dependence of the lattice parameter on the In content (Vegard's law). Chu and Wang[20] and Duan *et al.*[21] analyzed the strain fields for QD structures with a nonuniform composition, and showed that the strain fields are not uniform in the QD. In this paper, by assuming that the lattice constants or the thermal-expansion coefficients of alloyed QDs obey Vegard's law, we present first a compatibility equation for the misfit strains induced in alloyed quantum dots (QDs) by the mismatch in the lattice constants or the thermal-expansion coefficients of their alloying elements and show that it imposes some restrictions on the alloy composition profiles in a theoretical sense. Then, we reveal the profound effect that the compatibility of the misfit strains induced by the nonuniform composition has on the strain fields and the critical sizes of dislocation-free QDs.

II. MISFIT STRAINS

To reveal the profound effect of a nonuniform composition on the stress state of a QD, consider, for simplicity, a spherical alloyed QD embedded in an infinite matrix (relative to the size of the dot, Fig. 1). The analytical method is equally applicable to QDs of other shapes, sizes, and composition profiles. We assume that the nonuniform composition of the QD is spherically symmetric, i.e., it is a function of the radial coordinate r only. Therefore the misfit eigenstrains $\boldsymbol{\varepsilon}^*(r)$ induced by the mismatch of the lattice constants or thermal-expansion coefficients can be expressed as

$$\boldsymbol{\varepsilon}^*(r) = \varepsilon_{rr}^*(r)\mathbf{e}_r \otimes \mathbf{e}_r + \varepsilon_{\theta\theta}^*(r)(\mathbf{e}_\theta \otimes \mathbf{e}_\theta + \mathbf{e}_\varphi \otimes \mathbf{e}_\varphi), \quad (1)$$

where $\mathbf{e}_r$, $\mathbf{e}_\theta$ and $\mathbf{e}_\varphi$ are the *local* unit base vectors in the spherical coordinate system, and $\varepsilon_{rr}^*(r)$ and $\varepsilon_{\theta\theta}^*(r)$ are the misfit strains in the radial and tangential directions, respectively. The misfit strains induced by the mismatch in the lattice constants and those by the mismatch in the thermal-expansion coefficients are[20,22,23]

$$\varepsilon_{rr}^*(r) = c_r(r)\varepsilon_{m0}^*, \quad \varepsilon_{\theta\theta}^*(r) = c_\theta(r)\varepsilon_{m0}^* \quad (2)$$
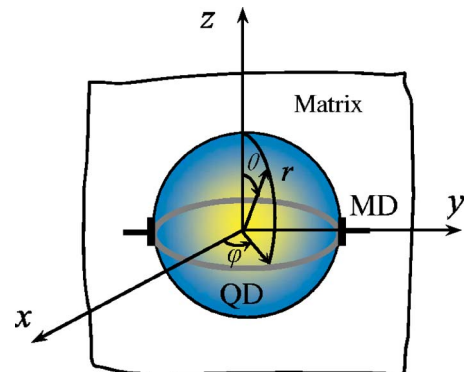
and

FIG. 1. (Color online) A spherical QD and a circular prismatic misfit dislocation loop nucleating in the QD cross section.

$$\varepsilon_{rr}^*(r) = c_r(r)\varepsilon_{tm0}^*, \quad \varepsilon_{\theta\theta}^*(r) = c_\theta(r)\varepsilon_{tm0}^*, \tag{3}$$

where $\varepsilon_{m0}^*[=(a_{in}-a_{ex})/a_{ex}]$ and $\varepsilon_{tm0}^*[=(\alpha_{in}-\alpha_{ex})\Delta T]$ are the misfit strains arising from the different lattice constants and the thermal-expansion coefficients between different uniform phases, respectively, a_{in}, a_{ex} and α_{in}, α_{ex}, are the lattice constants and the thermal-expansion coefficients of the interior and exterior phases, respectively, and ΔT is the temperature difference. c_r and c_θ are the fractions of the ingredient at the location r in the radial and tangential directions, respectively. If $c_r \equiv 1$ and $c_\theta \equiv 1$, Eq. (1) reduces to that for a uniform composition. As ε_{m0}^* and ε_{tm0}^* are constants, we will often make no distinction between $\varepsilon_{rr}^*(r)$ and $c_r(r)$ and between $\varepsilon_{\theta\theta}^*(r)$ and $c_\theta(r)$. In fact, the linear expressions in Eqs. (2) and (3) are the so-called Vegard's law[22] which states that for an alloyed material $E_{alloy}=xE_A+(1-x)E_B$, where E_A, E_B, and E_{alloy} are the respective properties of pure A, pure B and the alloy A_xB_{1-x}, and x is the fraction of one ingredient in a material point.[3] For example, experiments have shown that the lattice constant of the nonuniform nano-onion ($Zn_xCd_{1-x}S$) exhibits a nearly linear relation with the Zn content x, which is consistent with Vegard's law.[24,25]

III. ELASTIC FIELDS

The nonuniform distribution of the eigenstrains will result in an elastic field in a QD, even when its surface is not constrained, i.e., in a free-standing QD. To obtain simple analytical solutions in a free-standing QD induced by the nonuniform eigenstrains in Eq. (1), we assume that the elastic constants of the alloyed QD are uniform, and have the same values as the surrounding isotropic matrix (Fig. 1). This is a reasonable assumption because the alloyed semiconductor QDs usually contain compounds (e.g., InAs/GaAs, CdTe/CdSe) with nearly identical elastic constants, and it has been validated by comparing isotropic and anisotropic solutions for semiconductor materials.[26]

Let the eigendisplacement vector in the free-standing QD be **u***. Then, according to the theory of infinitesimal elasticity, the governing equation to obtain **u*** is

$$C_{ijkl}(u_{k,lj}^* - \varepsilon_{kl,j}^*) = 0, \tag{4}$$

where the eigenstrains $\varepsilon_{ij}^*(\mathbf{x})$ are given in Eq. (1), and C_{ijkl} is the elastic modulus tensor of QD. Substituting Eq. (1) into Eq. (4), it follows that the only nonvanishing component of the displacement vector **u***, viz. $u_r^*(r)$, must satisfy the equation

$$r^2\frac{\partial^2 u_r^*}{\partial r^2} + 2r\frac{\partial u_r^*}{\partial r} - 2u_r^* - \varepsilon_{m0}^* r^2$$
$$\times\left[\frac{\partial c_r}{\partial r} + \frac{2\nu}{(1-\nu)}\frac{\partial c_\theta}{\partial r} + \frac{2(1-2\nu)}{(1-\nu)}\frac{(c_r-c_\theta)}{r}\right] = 0, \tag{5}$$

where ν is the Poisson ratio of the QD. Equation (5) and the corresponding boundary conditions constitute the basic equations to find $u_r^*(r)$. When the variations of $c_\theta(r)$ and $c_r(r)$ are known, $u_r^*(r)$ can be easily determined.

For the considered alloyed spherical QD, the only nonvanishing equation of compatibility of misfit eigenstrains ε_{rr}^*

and $\varepsilon_{\theta\theta}^*$ represented in Eq. (1) reduces to an equation relating the radial and tangential alloy composition profiles,

$$r\frac{\partial c_\theta(r)}{\partial r} + c_\theta(r) = c_r(r). \tag{6}$$

Equation (6) is identically satisfied when the composition is uniform, but it imposes restrictions on c_r and c_θ when the composition is nonuniform. This fundamental relation is not met in the literature on QDs of nonuniform composition. As will be shown below, the strain fields induced by nonuniform composition profiles that meet Eq. (6) are vastly different from those induced by profiles that violate this condition, however slightly. Thus the compatibility condition [Eq. (6)] provides a theoretical basis for designing the composition profile of an alloyed QD and for estimating its lattice deformation. We do not, however, underestimate the difficulty that the practical realization of such a composition profile may present.

The composition profile of an alloyed QD is usually given in terms of the spatial coordinates of the alloying elements with reference to the QD center.[5,7,18] Without loss of generality, here $c_\theta(r)$ in Eq. (6) is chosen as $c_\theta(r)=k_0+k_1 r/r_{co}$. Then it follows from Eq. (6) that the compatible c_r is $c_r(r)=k_0+2k_1 r/r_{co}$, where k_0 and k_1 are two constants and r_{co} is the radius of the QD. The corresponding unique $u_r^*(r)$ is given by Eq. (5),

$$u_r^*(r) = k_0\varepsilon_{m0}^* r + \frac{r^2 k_1 \varepsilon_{m0}^*}{r_{co}}. \tag{7}$$

When the alloyed QD is embedded in an infinite medium (relative to its size), the constraint imposed by the exterior medium will induce an additional displacement field, identified by superscript 1 in the QD and superscript 2 in the matrix: $u_r^1=F_1 r$, $u_r^2=G_2/r^2$. The constants F_1 and G_2 are determined from the interface condition $u_r^2 = u_r^1 + u_r^*|_{r=r_{co}}$ and continuity condition of tractions across the interface. The components of the elastic strain $\boldsymbol{\varepsilon}^1$ and $\boldsymbol{\varepsilon}^2$ in the alloyed QD and the uniform matrix due to the linear radial and tangential misfit eigenstrains that satisfy the compatibility equation (6) are, in the spherical coordinates,

$$\varepsilon_{rr}^1 = \varepsilon_{\theta\theta}^1 = \varepsilon_{\varphi\varphi}^1 = -\frac{2(k_0+k_1)(1-2\nu)\varepsilon_{m0}^*}{3(1-\nu)},$$

$$\varepsilon_{rr}^2 = -2\varepsilon_{\theta\theta}^2 = -2\varepsilon_{\varphi\varphi}^2 = -\frac{2(k_0+k_1)(1+\nu)\varepsilon_{m0}^* r_{co}^3}{3(1-\nu)r^3}. \tag{8}$$

It follows from Eq. (6) that the elastic strain in the alloyed QD is uniform when the nonuniform misfit eigenstrains satisfy the compatibility equation. We have previously shown that the strain field is nonuniform when the compatibility of strains is violated, for example, when $c_\theta(r)=c_r(r)=k_0+k_1 r/r_{co}$.[21] For other variations of $c_\theta(r)$, e.g., it could vary in a logarithmic or exponential manner with r, $u_r^*(r)$ can be determined from Eqs. (5) and (6), whereafter the strain fields can be calculated in the same manner as for the linear profile above. It can be shown that (we do not present the details here) the strain field in the alloyed QD is uniform
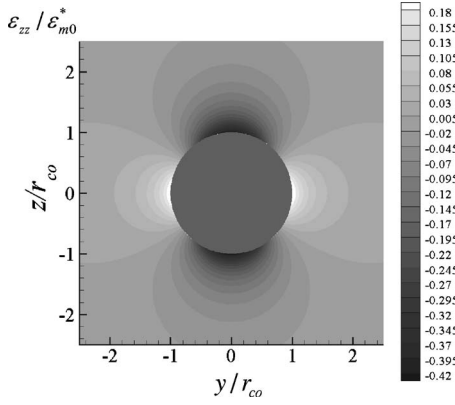
FIG. 2. Distribution of normalized elastic strain $\varepsilon_{zz}/\varepsilon_{m0}^*$ in the embedded QD (In$_x$Ga$_{1-x}$As/GaAs) subjected to nonuniform eigenstrains $\boldsymbol{\varepsilon}^*$ satisfying the compatibility equation ($k_0=0.8$; $k_1=-0.4$).

irrespective of the composition profile provided the nonuniform misfit eigenstrains satisfy the compatibility equation, but not otherwise.

To illustrate the above finding, let us calculate the elastic strain field in the embedded alloyed QD In$_x$Ga$_{1-x}$As (core)/GaAs(matrix) induced by the misfit eigenstrains. The radius of the core In$_x$Ga$_{1-x}$As is $r_{co}=9$ nm, and the lattice constants of InAs and GaAs are $a_{in}=6.0584$ Å, $a_{ex}=5.6532$ Å, respectively. The elastic constants of GaAs are bulk modulus 92.8 GPa, Poisson's ratio 0.236. We consider both situations: when the nonuniform eigenstrains satisfy the compatibility equation [$c_\theta(r)=k_0+k_1 r/r_{co}$ and $c_r(r)=k_0+2k_1 r/r_{co}$], and when they do not [$c_\theta(r)=c_r(r)=k_0+k_1 r/r_{co}$]. The numerical results are shown in Figs. 2–4. It can be seen that the strain distributions in and around QDs are very different in the two situations; the strain in the alloyed QD is uniform when the compatibility is satisfied but nonuniform otherwise. Moreover, it can be inferred from Figs. 2–4 that if there were two neighboring alloyed QDs in close proximity, there would be a strong interaction in their elastic strain fields.

IV. CRITICAL SIZES OF DISLOCATION FREE QDS

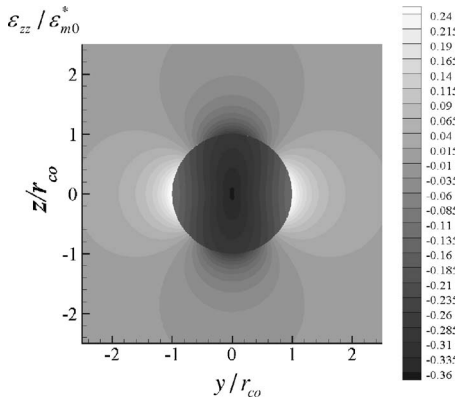Strains play a very important role in the nanofabrication technology, and strain relaxation through the formation of

FIG. 3. Distribution of normalized elastic strain $\varepsilon_{zz}/\varepsilon_{m0}^*$ in the embedded QD (In$_x$Ga$_{1-x}$As/GaAs) subjected to nonuniform eigenstrains $\boldsymbol{\varepsilon}^*$ not satisfying the compatibility equation ($k_0=0.8$; $k_1=-0.4$).
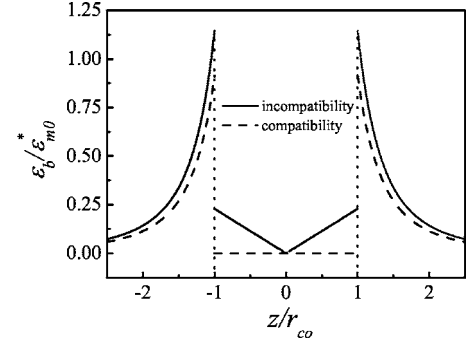

FIG. 4. Normalized biaxial strain $\varepsilon_b/\varepsilon_{m0}^*$ ($\varepsilon_b=[(\varepsilon_{xx}-\varepsilon_{yy})^2+(\varepsilon_{yy}-\varepsilon_{zz})^2+(\varepsilon_{zz}-\varepsilon_{xx})^2]^{1/2}$) in the embedded QD In$_xGa_{1-x}$As/GaAs structure subjected to nonuniform eigenstrains $\boldsymbol{\varepsilon}^*$ that either satisfy the compatibility equation or not ($k_0=0.8$; $k_1=-0.4$).

dislocations is highly undesirable for the performance of the semiconductor devices.[4,27–29] Kolesnikova and Romanov[29] obtained the critical radii of spherical QDs and cylindrical quantum wire (QW) with uniform composition by considering the energy of nucleation of circular prismatic dislocation loops from a spherical QD and a cylindrical QW.

We calculate the critical radii of the spherical alloyed QD at which the nucleation of a misfit prismatic dislocation (MD) loop shown in Fig. 1 becomes energetically favorable. We will again study the effect of the compatibility of misfit strains. The condition for the nucleation of an MD loop is[29] $E_L+W_{IL}\leqslant 0$, where E_L is the elastic energy of the prismatic dislocation loop and W_{IL} is the interaction energy between it and the QD. E_L of a dislocation loop of radius r_L and Burgers vector of magnitude b is[30]

$$E_L \approx \frac{\mu b^2 r_L}{2(1-\nu)}\left(\ln\frac{8\alpha r_L}{b}-2\right), \quad (9)$$

where α is a parameter that takes into account the energy of the dislocation core. W_{IL} is

$$W_{IL} = -\int_{V_L}\varepsilon_{ij}^{*L}\sigma_{ij}^1 dV = -\int_{S_L}(-b)\sigma_{zz}^1 dS, \quad (10)$$

where V_L and S_L are the volume and area of the dislocation loop, respectively. Plastic distortion ε_{ij}^{*L} of a prismatic dislocation loop located in the xoy plane in the xyz coordinate system with the origin at the loop center (Fig. 1) is $\varepsilon_{zz}^{*L}=\pm bH(1-r/r_L)\delta(z)$, $H(1-r/r_L)$ is the Heaviside function and $\delta(z)$ is the Dirac delta function. σ_{ij}^1 are the stresses in the QD, with σ_{zz}^1 the normal stress in the z direction.

For the spherical QD under nonuniform eigenstrains $\boldsymbol{\varepsilon}^*$ satisfying the compatibility equation of strains, the critical radius R_{cI} works out to be

$$R_{cI} = \frac{R_{c0}}{(k_0+k_1)}, \quad (11)$$

where R_{c0} is the critical radius of a spherical QD under uniform hydrostatic eigenstrain ε_{m0}^*,[29]

$$R_{c0} = \frac{3b}{8\pi(1+\nu)\varepsilon_{m0}^*}\left(\ln\frac{1.083\alpha R_{c0}}{b}\right). \quad (12)$$
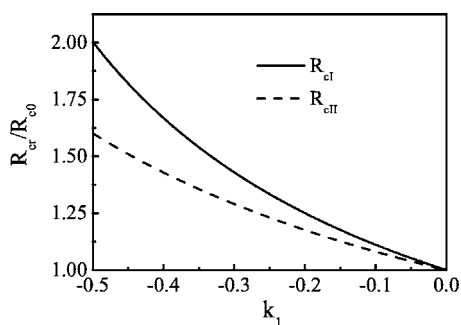
FIG. 5. Variation of critical radii of quantum dots with the composition parameter k_1 ($k_0=1$).

For the spherical QD under the nonuniform eigenstrains $\boldsymbol{\varepsilon}^*$, not satisfying the compatibility equation, the critical radius R_{cII} is

$$R_{cII} = \frac{R_{c0}}{(k_0 + 0.75k_1)}. \tag{13}$$

It can be seen from Eqs. (11) and (13) that R_{cI}/R_{cII} $=1-0.25k_1/(k_0+k_1)$. It is evident that, $k_0>0$, $k_0+k_1>0$. Generally, for the "self-capping" alloyed QD (e.g., $In_xGa_{1-x}As$ on GaAs substrate), the core is enriched in In whereas the outermost layer becomes progressively depleted in In.[4] Therefore in the composition profile chosen here, $k_1<0$. Figure 5 shows the variation of the normalized critical radii R_{cr}/R_{c0} with k_1 [$k_1<0$, where R_{cr} stands for R_{cI} and R_{cII}. The results show that dislocation nucleation is more difficult in a compositionally nonuniform QD than in a uniform one (cf. $R_{cr}/R_{c0}>1$) in both situations]. However, it is even more difficult when the compatibility equation is satisfied than when it is not ($R_{cI}/R_{c0}>R_{cII}/R_{c0}$ for $k_1<0$).

V. CONCLUSIONS

We have studied the implications of the satisfaction of the compatibility equation for the nonuniform misfit strains in alloyed QDs and shown that if the composition profiles are such that the misfit strains satisfy this equation then the strain field inside a buried alloyed QD is uniform notwithstanding the nonuniformity of the misfit strains. Such an alloyed QD will be defect-free and likely to remain so until its size reaches a critical value. Moreover, this critical size is much larger than that of an alloyed QD whose misfit strains and hence the alloy composition profiles do not satisfy the compatibility equation. This theoretical study gives the ideal composition profiles of alloyed QDs with a uniform strain, but it cannot throw any light on how difficult it would be to achieve such ideal compositions in practice.

*Author to whom correspondence should be addressed. Electronic address: karihaloob@cardiff.ac.uk

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