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Compositional patterning in coherent and dislocated alloy nanocrystals

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ABSTRACT

Variations in the distribution of the alloy components can significantly influence the electronic properties of self-organized alloy nanocrystals. Using a combination of finite element and quadratic programming optimization methods, we have developed an efficient numerical technique to compute the equilibrium composition profiles in coherent and dislocated nanocrystals. We show that the variations in composition profiles arise due to the competition between chemical mixing effects and the relaxation of composition-dependent mismatch strain as well as strain due to dislocations. We find that the composition profiles in these crystals depend strongly on morphological features such as the slopes and curvatures of their surfaces and the presence of corners, edges and dislocations at the nanocrystal–substrate interface. This approach provides the means for a quantitative description of the factors controlling equilibrium composition profiles in various coherent and dislocated self-organized alloy systems.

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1. Introduction

A particularly appealing approach to manufacturing nanoscale devices is to exploit the natural tendency of small material clusters to self-organize. While it is well known that strain-driven self-assembly can give rise to nanoscale pattern formation of two-dimensional (2D) domains and patterns [1], it also provides a versatile means to fabricate nanoscale islands in lattice-mismatched semiconductor *alloy* systems which can serve as functional elements in optical, electronic and photovoltaic devices [2,3]. The electronic structure of these nanoscale islands or nanocrystals is strongly influenced by their shape, elastic deformation and most importantly by their composition, thereby enabling the device properties to be controlled. A tighter control of these characteristics significantly reduces power consumption and heat generation, while the small dimensions of the devices allow order of magnitude advances in miniaturization. Self-assembled SiGe [4–6] and InGaAs [7] quantum dots have received particular attention as the former material system can be readily integrated with the well-developed Si integrated circuit technology while the latter has been successfully applied in photovoltaic and photonic bandgap applications.

The past few years have seen tremendous advances in the development of processing and patterning techniques that have led to a uniform array of nanocrystals of nearly identical shapes and sizes [8,9]. However, the key factors that play a role in controlling the variations in composition within the nanocrystals remain poorly understood. A quantitative determination of the composition profiles is critical in device applications as variations in composition at the nanoscale can substantially influence the electronic properties (for example, excitonic transitions [10], electron–hole band alignment and band gaps [11]) and therefore directly influence the performance of devices. While there is a large body of theoretical work on the formation and growth of nanocrystals, almost all of it neglects alloying effects by assuming a uniform composition distribution within the crystals.

In recent years, considerable progress has been made in measuring the composition profiles within individual quantum dot nanocrystals with nanoscale resolution [12–18]. These experimental studies show two distinct types of scenarios. The work of Stanley Williams and coworkers using X-ray scattering and independent selective etching techniques [13,16,18] shows a Si-rich core covered by a Ge-rich shell for dome shaped SiGe quantum dots at 600 °C. In distinct contrast, the work of Schmidt and coworkers using a combination of selective wet chemical etching and atomic force microscopy [14,15] shows that for pyramid and dome shaped islands, the corners are highly intermixed, whereas the edges, apexes and the centers of the pyramids remain Ge rich at 550 °C. Given the sensitivity of the composition profiles in the nanocrystals to growth conditions and the differences between the experimental measurements from different groups, information from these experiments can only be properly interpreted with models that

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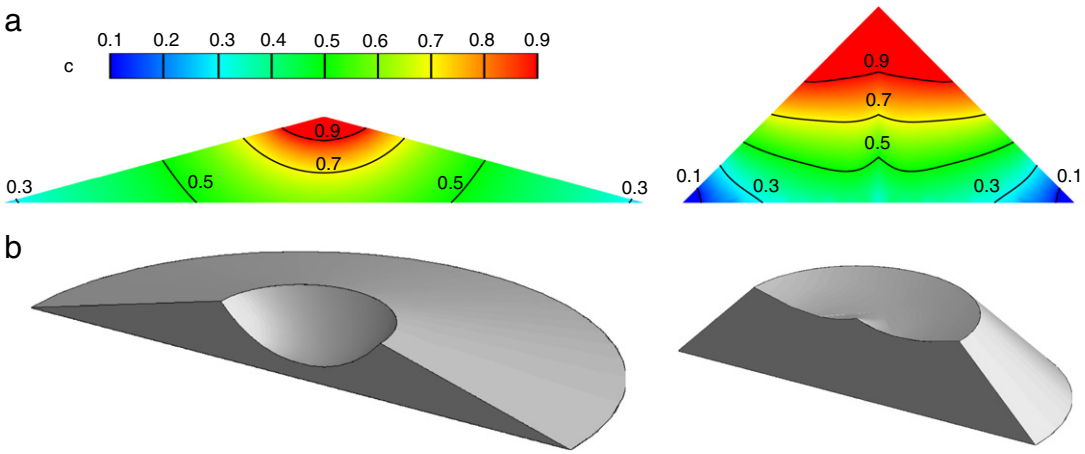

Fig. 1. Influence of morphology on the equilibrium composition profiles in alloy nanocrystals [28]. (a) Composition profiles in axially symmetric quantum dots of identical size, but with shallow (left) and steep sidewalls (right). The steeper sidewalls allow for larger strain relaxation resulting in a greater degree of segregation of alloy components at the apex and in the periphery of the nanocrystal. The composition profiles are obtained for $F_0 = -0.2$ and with average composition $\bar{c} = 0.5$. (b) The 3D rendering of the shapes of the quantum dots in (a) upon etching with a selective chemical agent that dissolves regions of the dot whose composition, c, exceeds 65%. The segregation indices Eq. (4) for the steep and shallow dots are 0.177 and 0.051, respectively.

can distinguish the differences between composition profiles under different growth conditions. To that end, a key question that one is generally faced with in these experiments is whether or not a measured profile is close to equilibrium.

As alloy nanocrystals continue to grow, dislocations can nucleate to relax the elastic strain energy in the crystal and the substrate [19]. It is known that, depending on the average composition in the nanocrystal and its size, there can be one or more loops of dislocations at the interface with the substrate [20,21]. Such tree-ring interface dislocation structures and the critical crystal size for their nucleation [22] have been well studied for SiGe quantum dots. Since dislocations give rise to their own characteristic strain fields, the nucleation of a dislocation during growth can significantly alter the strain and therefore the composition distribution in an alloy nanocrystal. Most of the work concerning dislocations in alloy nanocrystals typically assumes a uniform composition throughout the crystal; experimental studies measuring the composition profiles in individual dislocated nanocrystals have been far fewer compared to those in coherent crystals. For example, it has recently been shown that for both coherent and dislocated SiGe nanocrystals, the Ge mole-fraction decreases while moving from the apex towards the substrate; however, coherent crystals are characterized by a sublinear variation, while dislocated crystals show a plateau in the composition in the near-apex region [23]. In order to understand such nanoscale variations in composition in dislocated crystals and the factors controlling them, one needs to carefully analyze the coupling between the elastic fields due to the dislocations and due to the composition variations in equilibrium.

In equilibrium, for a given size and shape of the crystal, the composition profile is obtained by minimizing the total free energy, which consists of the elastic energy and entropic and chemical mixing energies. The primary difficulty in obtaining composition profiles is that the shape, strain and composition are all coupled to each other. Furthermore, in equilibrium, the total free energy has to be minimized by holding the overall ratio of the alloy components in the dot at a fixed level, making the optimization problem even more difficult. In addition, the coupling between the strain fields arising due to dislocations and due to composition variations in dislocated nanocrystals adds to the complexity of the optimization problem. Consequently, only calculations that adopt a number of simplifying assumptions are available. For the case of coherent crystals, these approximations include small slopes of the sidewalls of the quantum dots [24] and linear extrapolation of the composition profiles from the surface to the bulk [25]. The approximations made in the calculations allow only for the analysis of pre-pyramid clusters with very shallow sidewalls. In the case of dislocated crystals, approximate strain fields obtained by assuming that a dislocation lies at the center of solids with simple shapes such as a cylinder have been employed to compute their contribution to the total elastic energy of the system. Monte Carlo methods have also been employed to analyze quasi-equilibrium composition profiles [26,27], but the long-range nature of the elastic interactions makes statistical sampling of the large configuration space (required to obtain properly averaged composition maps in realistic structures) a very demanding and tedious task.

Here we study equilibrium composition maps in alloy nanocrystals by employing the finite element method for rigorous treatment of elastic fields without any restrictions on their shape and an optimization scheme based on quadratic programming methods. A brief account of the key results for composition maps in coherent alloy quantum dots is given in our earlier work [28]. We find that the shapes of the crystals play a very important role in determining the degree of alloy decomposition that can be achieved at a given temperature. The composition profiles in faceted quantum dot crystals with steep sidewalls are found to be characteristically different from the corresponding case of shallow dots. In the former case, segregation of the larger alloy component in the tensile regions of the quantum dot leads to the formation of 'cusped' composition profiles which manifest in the form of dimpled surface profiles upon selective etching of one of the alloy components (Fig. 1). Shallower crystals, on the other hand, are less decomposed and yield surface profiles with large etch pits. Both of these features have been observed during wet chemical etching of SiGe quantum dots [13,14,16].

In order to guide the interpretation of composition maps measured in experiments, the degree of alloy decomposition in faceted nanocrystals is presented in a phase diagram plotted in the space spanned by the orientation of their sidewalls and temperature. Based on this phase diagram, the effect of decomposition on the shape transition between quantum dots with different facet orientations is computed—the alloy decomposition is found to significantly decrease the transition volumes for shape transformation. To further demonstrate the role of shape and strain on alloy decomposition at the nanoscale, we have considered the composition profiles of dome, truncated pyramid and unfaceted pre-pyramid or Gaussian shaped quantum

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