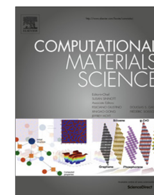
Computational Materials Science 130 (2017) 50–55

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci



# Control of surface induced phase separation in immiscible semiconductor alloy core-shell nanowires

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ARTICLE INFO

*Article history:*
Received 22 August 2016
Received in revised form 1 January 2017
Accepted 3 January 2017

*Keywords:*
Phase separation
Nanowire
Heterostructure
III-V semiconductors

ABSTRACT

Semiconductor nanowires have been shown to exhibit novel optoelectronic properties with respect to bulk specimens made of the same material. However, if a semiconductor alloy has a miscibility gap in its phase diagram, at equilibrium it will phase separate, leading to deterioration of the aforementioned properties. One way to prevent this separation is to grow the material at low temperatures and therefore to suppress kinetics. Such growth often needs to be followed by high-temperature annealing in order to rid the system of undesirable growth-induced defects. In this study, we propose a method to control phase separation in core-shell nanowires during high temperature annealing by tailoring geometry and strain. Using a phase field model we determined that phase separation in nanowires begins at the free surface and propagates into the bulk. We discovered that including a thin shell around the core delays the phase separation whereas a thick shell suppresses the separation almost entirely.
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## 1. Introduction

High surface to volume ratio and the possibility of a lateral strain relaxation make nanowires promising candidates for growth of semiconductor structures. Semiconductor nanowires have shown outstanding electronic and optical properties, and therefore are being considered for use as lasers [1], light emitting diodes [1,2], transistors [3] and sensors [4]. In particular, many studies have focused on nanowires made of III-V semiconductors because the band gap energy in these materials can be controlled by alloy composition [5,6]. One challenge in growing multi-component heterostructures, such as InGaAs, AlGaAs, and GaAsSb, is that these alloys have a miscibility gap in their phase diagrams and therefore at equilibrium these alloys phase separate [7]. During growth process, phase separation can be kinetically inhibited for most III-V semiconductors because of the relatively low growth temperatures. However, these materials often need to be subsequently annealed in order to remove defects introduced during growth and the high temperature annealing can lead to undesirable phase separation. For instance, Luna et al. [8] found spontaneous formation of a lateral composition modulation (LCM) in GaAsBi epilayers grown by Molecular Beam Epitaxy (MBE). Hsieh et al. [9] observed LCM in AlGaAs film upon annealing and found that the phase separation was more pronounced near the free surface. The authors proposed a stress-driven vacancy-assisted mechanism to be responsible for this phenomenon. Tang and Karma [10] used linear stability theory to study the role of free surfaces in spontaneous phase separation of alloys in thin films and found that stress relaxation begins at the surface. However, Tang and Karma did not study the effects of geometry and strain on formation of surface induced compositional modulations. Also they did not investigate potential pathways for controlling this phase separation.

As shown experimentally, the existence of a miscibility gap in phase diagrams of III-V semiconductors leads to compositional modulation during growth and annealing [8,9]. Here, we propose a method to control such phase separation under conditions where phase separation is thermodynamically favorable and kinetically allowed. This method takes advantage of the strain induced by a core-shell geometry of a nanowire. The effects of different factors, such as the miscibility gap, surface and bulk diffusion, and elastic strains, on the compositional modulation in the nanowire structure are investigated using the phase field model.

## 2. Model

We model the annealing process of the nanowires made of a generic immiscible alloy using phase field method combined with elasticity governing equations. We developed this continuum-

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http://dx.doi.org/10.1016/j.commatsci.2017.01.005
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based model earlier to study the growth of thin films on patterned substrates [11] and continuum approaches have been found to be applicable for strain and stress field calculations in core-shell nanowires [12]. In our model we do not account for possible faceting of the nanowires because our goal is to demonstrate the general effect of a shell on phase separation. For a given material pair, faceting may or may not play a role in phase separation and this effect should be further investigated. In this study, we do not include the effect of plastic deformations since they do not happen at the length scale of interest based on both theoretical predictions [13] and experimental observations [14–16].

The model assumes a rotational symmetry along the axis of the nanowire. The circumferential component ($u_\theta$) of the displacement field is zero while the radial ($u_r$) and the axial ($u_z$) components of the displacement field are treated as variables. Displacement and traction vector continuity is assumed at all internal boundaries. The substrate is fixed (no displacements along $r$ and $z$ directions) at the bottom while all the external boundaries are traction-free. Semiconductor nanowires have been grown experimentally with diameters as small as 3 nm [17]. However, the range of diameters of interest is usually between 15 and 100 nm [15,18,19] due to difficulties associated with the growth of very small nanowires (<10 nm in diameter) and no practical advantage of larger nanowires (>100 nm in diameter) [17]. Throughout this study, the height of the nanowire and the diameter of the core are kept constant and equal to 200 nm and 20 nm, respectively, while the shell material and thickness ($t_s$) vary. GaAsSb is chosen as an example of immiscible alloy for the core nanowire. GaAsSb is thermodynamically unstable at 650 °C and under equilibrium condition, it phase separates to GaAs-rich and GaSb-rich phases. Given that this phase separation process is effectively determined by interdiffusion of As and Sb on the same sublattice, diffusion of Ga does not play an important role and hence we have not included the diffusivity of Ga in this model. Hence we use a single concentration variable in our model. We use the effective diffusion coefficient with the value of $1 \times 10^{-18}$ cm$^2$ s$^{-1}$ [20], which was determined in experimental studies of Sb diffusion in GaAs. We define free energy density functional as

$$F = \int_\Omega \left( f(c) + W(c) + \frac{\varepsilon^2}{2} |\nabla c|^2 \right) d\Omega \tag{1}$$

where $\Omega$ represents the system volume, $W$ is the strain energy density, $\varepsilon^2$ is the gradient energy coefficient, $f$ is the free energy density, and $c$ is the concentration of Sb. For GaAsSb at 650 °C, the excess Gibbs free energy is taken from CALPHAD calculations [21] and it is given by

$$f_{core} = \frac{\left( G_{ideal} + L^0_{GaAsSb} c(1-c) + L^1_{GaAsSb} c(1-c)(1-2c) \right)}{V_m^{GaAs}} \tag{2}$$

where $V_m^{GaAs}$ is the molar volume of GaAs and $G_{ideal}$ the ideal Gibbs free energy. The interaction parameters $L^0_{GaAsSb}$ and $L^1_{GaAsSb}$ are defined as follows

$$G_{ideal} = \mathrm{RT}(c \ln(c) + (1-c)\ln(1-c)) \tag{3}$$

$$L^0_{GaAsSb} = 24824 - 7.74301 \times \mathrm{T} \tag{4}$$

$$L^1_{GaAsSb} = 4774 \tag{5}$$

where $R$ is the gas constant, and $T$ is the temperature in Kelvin. For numerical reasons, we fitted the Gibbs free energy with a ninth order polynomial (shown in Fig. 1) and we used this polynomial function in our model. The polynomial function is given by

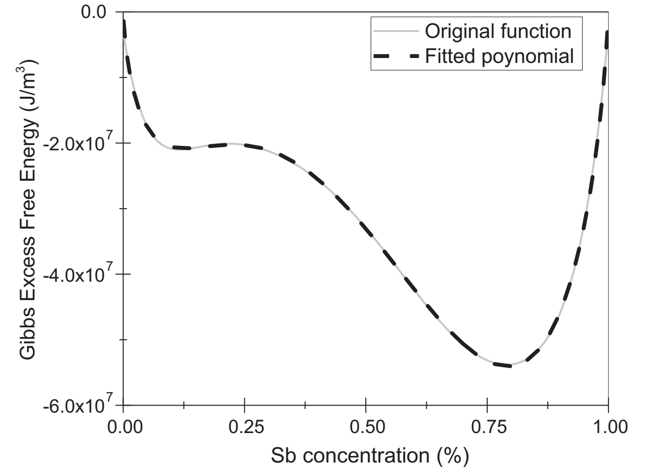


**Fig. 1.** Excess Gibbs free energy of GaAsSb at 650 °C (solid line). Ninth order polynomial has been used to fit the function (dashed line).

$$\begin{aligned} G_{ideal} = &-3.14808 \times 10^6 - 4.81905 \times 10^8 c + 5.02091 \times 10^9 c^2 \\ &- 2.64836 \times 10^{10} c^3 + 8.04754 \times 10^{10} c^4 - 1.4885 \\ &\times 10^{11} c^5 + 1.63584 \times 10^{11} c^6 - 9.76861 \times 10^{10} c^7 \\ &+ 2.44215 \times 10^{10} c^8 + 2.01987 c^9 \end{aligned} \tag{6}$$

For the shell, we have chosen a material (GaAs) that is thermodynamically stable material at the temperature of interest (650 °C) and hence in our formulation it is sufficient to use a single-welled free energy density [22] as follows

$$f_{shell/substrate} = \alpha_0 c^2 \tag{7}$$

where $\alpha_0$ is a positive coefficient representing the sharpness of the single-welled function.

The second term in free energy functional shown in Eq. (1) is strain energy density $W$ that is defined as

$$W(c) = \frac{1}{2} \sigma_{ij} e^{el}_{ij} \tag{8}$$

$\sigma_{ij}$ is the Cauchy stress tensor, and $e^{el}_{ij}$ is the elastic strain tensor. Elastic strain tensor satisfies the following relationship

$$e^{el}_{ij} = e^{tot}_{ij} - e^*_{ij} \tag{9}$$

where $e^{tot}_{ij}$ is the total strain and $e^*_{ij}$ is the eigenstrain, which arises due to the lattice mismatch between core/shell and the substrate. $e^*_{ij}$ is given by

$$e^*_{ij} = \frac{a_{core/shell} - a_{substrate}}{a_{substrate}} \delta_{ij} \tag{10}$$

where $a$ is the lattice parameter of different parts of the nanowire specified in the subscript and $\delta_{ij}$ is the Kronecker delta. We use a linear interpolation to calculate the lattice mismatch between the core/the shell and the substrate as a function of alloy concentration. Assuming a linear strain-displacement relationship (which is valid for an infinitesimal strain), we solve equilibrium equations to find the total strain. Both the strain-displacement and the equilibrium equations can be found in Ref. [11].

The third term in free energy functional shown in Eq. (1) is interfacial energy that is a function of $\varepsilon^2$ and $c$. In our model, $c$ is a conserved field variable that evolves according to the mass conservation equation

$$\frac{\partial c}{\partial t} = -\nabla \cdot J \tag{11}$$

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