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AXIAL MISFIT STRESS RELAXATION IN CORE-SHELL NANOWIRES WITH HEXAGONAL CORE VIA NUCLEATION OF RECTANGULAR PRISMATIC DISLOCATION LOOPS

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Abstract. A theoretical model of axial misfit stress relaxation in core-shell nanowires with hexagonal cross section of the core through the nucleation of prismatic dislocation loops is suggested. Different nucleation sites of the loops in core-shell nanowires are considered. The energy change caused by the loop nucleation is calculated. The critical condition for the onset of the loops is given and analyzed in detail. The most favorable sites in nanowires and the optimal loop shape are defined.

Keywords: core-shell nanowires, misfit stress relaxation, prismatic dislocation loops

1. Introduction

In the last two decades, heterogeneous nanowires (NWs) have been extensively used in various spheres due to their advanced optical and electronic properties [1-3]. The core-shell NWs are of special interest for designing such modern devices as photodetectors [1-5], gas nanosensors [1,3,6-8], solar cells [3,9-11], etc. Reliability of these devices strongly depends on the state of the NW interfaces including their shape, lattice mismatch and presence of defects [12,13].

The variety of NW interface and surface shapes is determined by the crystallographic structure; for instance, the materials with a wurtzite (WZ) structures take the hexagonal shape [3,14], while zinc blende (ZB) structures take the rectangular shape [15]. Another factor influencing the reliability of devices is misfit strains and stresses caused by the difference between lattice parameters, thermal coefficients and chemical inhomogeneities of the materials composing the NWs. When these strains and stresses reach certain critical levels, the plastic relaxation occur through the formation of misfit defects usually deteriorating the functional properties of NWs. Stress relaxation in core-shell NWs has long been the subject of both experimental [16-18] and theoretical [19-22] researches.

The experiments [16-18] clearly indicate that dislocation mechanisms contribute a lot at the initial stages of plastic relaxation in composite NWs. In the paper [16], misfit dislocations of different types in NWs with InAs-cores and GaAs-shells were observed. The ensembles of

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straight edge dislocations located along the hexagonal sidewalls of the cores were considered as responsible for relaxation of the radial stress in the shells, while the prismatic dislocation loops (PDLs) located in parallel cross sections were considered as responsible for reducing the axial stress in NWs. Another work [17] was devoted to the relaxation mechanisms in InAs/GaAs core-shell NWs with growth direction [001] in ZB and [0001] in WZ structures investigated by transmission electron microscopy. The misfit dislocations, placed around the cores and relaxing the axial stress, were observed in both {111} planes in NWs with ZB structure and (0001) plane in NWs with WZ structure. In similar research [18], the dislocation loops were observed to nucleate on the interfaces in ZnO/ZnMgO multilayer NWs with WZ structures and glide in prismatic and pyramidal planes. Apparently, at the initial stages of relaxation, these misfit dislocations can nucleate on the free surfaces and interfaces of the composite NWs close to stress concentrators, such as straight edges, and subsequently expand within cores and shells herewith producing equilibrium dislocation configurations [16-18].

By now, few theoretical models of misfit stress relaxation in core-shell NWs have been suggested (see, for example, Refs. [19-22]). The energetic approach has been widely used for defining the critical parameters of relaxation processes. According to this method, the energy change between the initial defect-free interface state and the final partly relaxed state with a misfit defect is calculated. In work [19], the stress relaxation mechanism through the formation of a straight misfit edge dislocation along the core-shell interface was studied. Two other works [20,21] were devoted to the models of axial stress relaxation in core-shell NWs due to formation of a circular PDL around the core. The models proposed in [19-21] allow one to determine the critical parameters of misfit stress relaxation, including critical shell thickness and critical misfit parameter of the composite. The initial stages of misfit stress relaxation in bulk and hollow core-shell NWs via nucleation of small PDLs on free surfaces and interfaces, and subsequent extension into either cores or shells were analyzed in paper [22]. The assumption of small shell thickness compared with NW radius allowed the authors to solve the problem for rectangular PDLs nucleated at flat interfaces and surfaces. It was shown, in particular, that the PDLs nucleating on the outer free surface and extending into the shell are the most energetically favorable carriers of misfit stress relaxation in such NWs.

The aforementioned models [19-22] (as all others) have a significant disadvantage. They treat the core-shell NWs as axisymmetric cylindrical heterostructures that makes it much easier to calculate the critical conditions for generation of misfit dislocations. This approach neglects the effect of stress concentration caused by straight edges of polyhedral cores on the stress relaxation process. Besides, it cannot be used for describing the relaxation mechanism which includes dislocation glide along flat faces of the interface. Thereby considering structural features of real core-shell NWs, such as the faceting of the cores and shells, is important for developing theoretical models of stress relaxation, which are aimed at predicting the stability of these nanostructures against formation of misfit defects.

The lack of work considering the influence of flat boundaries and straight edges on the relaxation process in core-shell NWs is mainly connected with a limited number of existing analytical solutions of the boundary value problems of the classical theory of elasticity for a cylinder containing the polyhedral inclusions subjected to eigenstrains. To the best of our knowledge, there are a few analytical solutions of this kind [23-25] obtaining by complex variable approach. In particular, analytical solutions of the boundary value problems for elastic cylinders containing the inclusions in form of long square prisms symmetrically placed with respect to the free cylindrical surface and subjected to two-dimensional and three-dimensional dilatation eigenstrains were found in [23] and [24], respectively. In paper [25], the solution for an eccentric inclusion in the form of a long rectangular prism, subjected to one-dimensional cross dilatation eigenstrain, was obtained. The first solution [23] is given in an implicit form of complex combinations of stress tensor components. The second solution

[24] is given by explicit expressions for the stress tensor components in the form of trigonometric series. In the third work [25], the stress components are given in a closed analytical form as combinations of elementary functions.

Recently, we have proposed a theoretical model of misfit stress relaxation through the nucleation of PDLs in the cross section of a core-shell NW with the core in form of a long parallelepiped placed symmetrically with respect to the cylindrical surface of the NW [26]. Indeed, the cores in the form of long parallelepiped are common for core-shell NWs with a ZB structure. However, investigating the critical conditions of misfit stress relaxation in core-shell NWs with a WZ structure, which usually take the form of hexagonal prism, requires the development of new mathematical means such as misfit stress state caused by the hexagonal core in a NW. We have solved recently a boundary value problem in the classical theory of elasticity for a cylinder containing the inclusion in the form of a long hexagonal prism subjected to a three-dimensional dilatation eigenstrain [27]. The stress field of the inclusion was found by superposition of stress fields caused by straight dilatational lines [28] continuously distributed over the cross section of the inclusion, with using the corresponding solution of the boundary value problem for such a dilatation line in a cylinder [27]. These solutions give new opportunities for studying the processes of misfit stress relaxation in core-shell NWs with different cross sections of the core.

In the present work, we apply our analytical solution [27] to developing a theoretical model of initial stages of misfit stress relaxation through the nucleation of PDLs in different sites of the hexagonal core in a core-shell NW. In doing so, we determine the critical parameters of this process, the most favorable sites for PDL nucleation and optimal shapes of the PDLs, thus evaluating the interface shape effect on the relaxation process in core-shell NWs.

2. Model

Consider an elastic core-shell NW of radius R with a hexagonal core (the core side is denoted as L) which is symmetrically placed with respect to the free cylindrical surface of the NW (Fig. 1). The core and shell materials are supposed to have the same elastic constants but different crystal lattice parameters a_c and a_{sh}, respectively ($a_c > a_{sh}$). In this case, the coherent state of the interface induces hydrostatic compression in the core and tangential tension in the shells which are in direct proportion with the misfit parameter $f = 2\,(a_c - a_{sh}) / (a_c + a_{sh})$.

Under certain conditions, the coherent interface can relax through the nucleation of various defects. We presume the nucleation of rectangular PDLs in different sites of the NW cross section (Fig. 1) as follows: (i) in the middle of interface side with expansion within the shell (PDL-1); (ii) at the free surface far from core corners with expansion within the shell (PDL-2); (iii) in the middle of interface side with expansion within the core (PDL-3); (iv) at the free surface in front of core corners with expansion within the shell (PDL-4).

According to the energy approach [19-22,26], the energy change ΔE due to nucleation of a PDL-k $(k = 1,2,3,4)$ reads:

$$\Delta E = E_{st} + E_c + E_{int}, \tag{1}$$

where E_{st} is the strain energy of the PDL-k, E_c is the dislocation core energy of the PDL-k, and E_{int} is the interaction energy between the PDL-k and the misfit stress in the NW.

Following the authors [22,26], we assume that the PDL sizes $2a$ and $2c$ are much smaller than the NW radius R. Then the strain energy E_{st} can be expressed as [29]:

$$E_{st} \approx \frac{Db^2T}{2}, \tag{2}$$

where $D = G/[2\pi(1-\nu)]$, G is the shear modulus, ν is the Poisson ratio, b is the Burgers vector magnitude for the PDL, T is the effective length of the PDL perimeter, which is determined in details in [29].

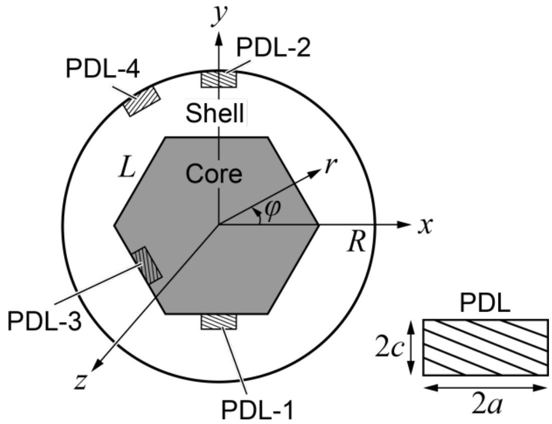

Fig. 1. Sketch of a cross section of the core-shell NW, where possible sites of nucleation of rectangular PDLs with sizes $2a \times 2c$ are indicated

The core energy of a rectangular PDL-k is approximated by [30] as:

$$E_c^1 = E_c^3 \approx 4(a+c)\frac{Db^2}{2}, \quad \text{for } k = 1 \text{ and } 3; \tag{3}$$

$$E_c^2 = E_c^4 \approx 4(a/2+c)\frac{Db^2}{2}, \quad \text{for } k = 2 \text{ and } 4. \tag{4}$$

The interaction energy E_{int} can be found as the work spent to generate the PDL-k in the axial misfit stress σ_{zz}:

$$E_{int} = -b\int_{-a}^{a} dy' \int_{-c}^{c} \sigma_{zz} dx', \tag{5}$$

where x' and y' are the Cartesian coordinates with the origin in the center of the PDL-k, and σ_{zz} is given by [27]

$$\sigma_{zz} = 2C\left(\left[{}^{\infty}\Psi_{zz} + {}^{*}\Psi_{zz}\right]_{m=\sqrt{3}/3,\,t=-R_0}^{m=-\sqrt{3}/3,\,t=R_0} \Big|_{y_0=0}^{y_0=\sqrt{3}R/2} + \left[{}^{\infty}\Psi_{zz} + {}^{*}\Psi_{zz}\right]_{m=-\sqrt{3}/3,\,t=-R_0}^{m=\sqrt{3}/3,\,t=R_0} \Big|_{y_0=-\sqrt{3}R/2}^{y_0=0} \right), \tag{6}$$

$${}^{\infty}\Psi_{zz} = -\frac{\pi}{2}\mathrm{sgn}\frac{y-y_0}{x-k\,y-c}, \tag{7}$$

$${}^{*}\Psi_{zz} = -\cos\psi\left[q^2\cos(2\theta+\psi) + \frac{4}{p^2}\left(\sin(2\phi+\psi)\ln\sqrt{p^2q^2 - 2pq\cos(\phi-\theta)+1} + \right.\right.$$
$$\left.\left.\cos(2\phi+\psi)\arctan\frac{pq\sin(\phi-\theta)}{1-pq\cos(\phi-\theta)} \right)\right], \tag{8}$$

where $C = Gf(1+\nu)/[2\pi(1-\nu)]$, $p = r/R$, $q = \rho/R$, $\rho^2 = x_0^2 + y_0^2$, $\theta = \arctan[y_0/x_0]$, $\psi = \arctan[m]$, (x_0, y_0) and (ρ, θ) are the Cartesian and polar coordinates of a hexagonal corner, m is the slope of the line imaging a hexagonal side of the core, and t is the coordinate of the intersection of this line with the y-axis. With Eqs. (6) to (8), the interaction energy E_{int} were calculated numerically within the Wolfram Mathematica software. Thus, we determined all the terms determining the energy change ΔE by Eq. (1).

3. Results and discussion

As an example, we consider the InAs/ZnS core-shell NW with misfit $f = 0.107$, outer radius $R = 100b$, core side $L = 0.7R$, and modulus of the Burgers vector $b = 0.38$ nm. The maps of the energy change ΔE due to the nucleation of rectangular PDLs in these NWs are shown in Fig. 2. As is seen from Fig. 2a, the nucleation of a PDL-1 becomes energetically favorable

$(\Delta E < 0)$ when it takes the shape of square with the side larger than $\sim 6b \approx 2.3$ nm. The nucleation of a similar loop in the InAs core (PDL-3) is energetically favorable at even much smaller sizes of the loop (Fig. 2c).

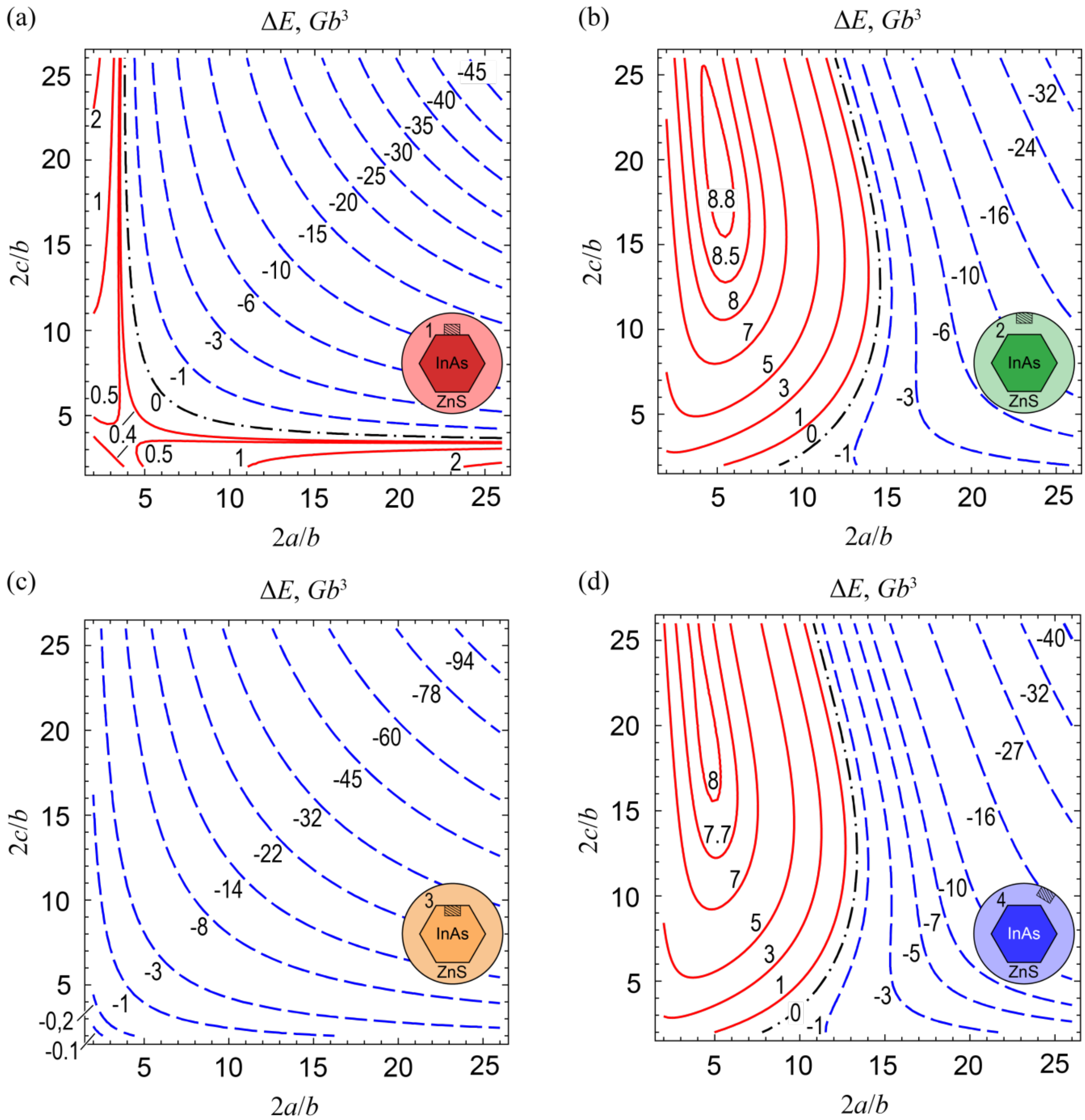

Fig. 2. Maps of the energy change ΔE in the space of normalized sizes of PDLs $2a/b$ and $2c/b$ for the InAs/ZnS core-shell NW with $R = 100b$, $L = 0.7R$, $f = 0.107$, $b = 0.38$ nm, $\nu = 0.25$ in the case of (a) PDL-1, (b) PDL-2, (c) PDL-3, and (d) PDL-4. The energy values are given in units of Gb^3. The insets show the types of PDLs

In contrast, the nucleation of PDL-2 and PDL-4 on the ZnS shell surface is energetically favorable if they take a rectangular shape elongated along the surface (see Fig. 2b and 2d). In these cases, the smallest possible sizes of PDL-2 and PDL-4 are approximately 3×0.8 nm^2 and 3.5×0.8 nm^2, respectively. Thus, the analysis of the energy maps (Fig. 2) shows that the shape of PDLs has an impact on the possibility of their nucleation, as is also the case with cylindrical [22] and parallelepipedal [26] cores.

Using the condition $\Delta E < 0$, we can conclude that a PDL-k can nucleate if the misfit parameter f exceeds a critical value f_c which is given by [22,26]:

$f_c = -(E_{st} + E_c) / E'_{int}$, (9)

where $E'_{int} = E_{int} / f$.

Figure 3 shows the dependences of the critical misfit f_c on the length L of the core side, which have been calculated for three different shapes of the PDLs-k: square (Fig. 3a), elongated along a normal to the NW free surface (Fig. 3b), and elongated along the NW free surface (Fig. 3c). These plots demonstrate critical conditions for different PDLs and allow one to define the most preferable shapes and nucleation sites of the PDLs, based on the idea that the less critical misfit value is, the more preferable the PDL is [22,26]. Then the intersection points of the curves $f_c(L)$ indicate a change in relative preference of PDLs.

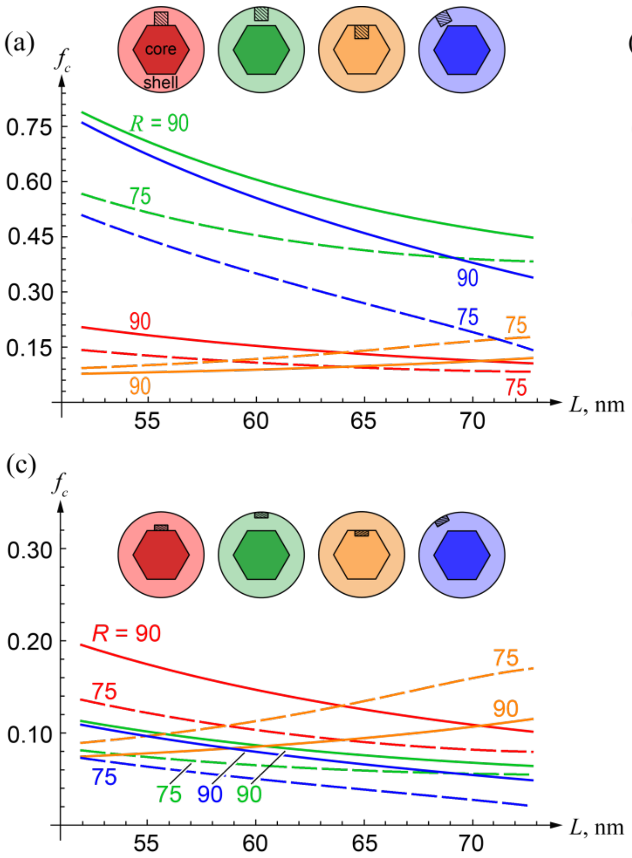

Fig. 3. Dependence of the critical misfit f_c on the core side L for different values of the radius R (in nanometers) at $b = 0.3$ nm and $\nu = 0.3$ for (a) $c/a = 1$, $c/b = 2$; (b) $c/a = 5$, $a/b = 2$; and (c) $c/a = 0.2$, $a/b = 10$. The insets show the type of PDLs

As is seen from Fig. 3, the qualitative behavior of the curves $f_c(L)$ is determined by the sites of PDL nucleation. For PDLs expanding within the cores (shells), the critical misfit value f_c increases (decreases) with the core side L. One can also see that, in the case of small shell thickness (the case of larger L in Fig. 3), the nucleation of PDLs-4 elongated along the free surface is the most preferable mechanism of relaxation. However, with increasing the shell thickness (decreasing L), the curves $f_c(L)$ indicate potential nucleation of PDLs of other types and shapes in the NWs.

Using plots in Fig. 3 with corresponding plots in work [26], we can compare the critical misfit values for the onset of similar PDLs in core-shell NWs with square [26] and hexagonal (the present work) cross sections of the core. It is seen from Fig. 3b that the nucleation of PDL-3 in a NW of radius $R = 90$ nm, with hexagonal cross section of the core of side length $L = 60$ nm, becomes possible at $f_c \approx 0.08$, while the nucleation of a similar PDL in a NW of the same radius, with square cross section of the core of the same side length, becomes possible at $f_c \approx 0.06$ [26]. Therefore, we can conclude that core-shell NWs with hexagonal cross section of the core are more stable against nucleation of PDLs-3 than those with square cross section of the core.

4. Conclusions

A theoretical model is suggested, which describes the misfit stress relaxation in core-shell NWs with hexagonal cross section of the core through the nucleation of small rectangular PDLs of three different shapes in four different sites of the NW cross section. It is shown that the PDLs, which nucleate at the shell free surface in front of a core corner, are the most preferable PDLs for the NWs with relatively thin shells, while the PDLs, which nucleate at the core/shell interface and expand within the core, are the most preferable PDLs for the NWs with relatively thick shells. It is also shown that, depending on the values of the main parameters of the NW (its radius R, the length L of the core side, and the critical misfit value f_c), the relaxation mechanisms can change. This concerns, for example, the shape of nucleating PDLs and the site of their nucleation in the cross section of the NW. Our analysis of the core shape effect on relaxation process in core-shell NWs with hexagonal and square [26] cross sections of the core shows that, in the case of PDLs nucleating at the core/shell interface and expanding within the core, NWs with hexagonal cross sections of the core are more stable against nucleation of PDLs than NWs with square cross sections of the core.

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