Initial stages of misfit stress relaxation by rectangular prismatic dislocation loops in composite nanostructures

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Abstract. Theoretical models are proposed for describing the initial stages of misfit stress relaxation in bulk and hollow core-shell nanoparticles and nanowires, and in planar bi- and tri-nanolayers through generation of rectangular prismatic dislocation loops at the inner and outer interfaces. We obtain the changes in the total energy of the system due to the appearance of dislocation loops and calculate the critical conditions of their formation. We also determine the most profitable shape of the loops and the preferred places of their generation. Finally, we choose the nanostructures which are the most stable against dislocation loop generation.

1. Introduction

To date production and applications of nanoparticles, nanowires and nanolayers is one of the most promising areas of nanotechnology. Electronic, magnetic and optical properties of such nanostructures depend on their shape, size, chemical composition, crystal lattice type and the presence of various defects in them. Composite nanoparticles, which represent a significant fraction among the nanoparticles synthesized and studied today, consist of different materials and have many applications in modern optoelectronics, photonics, spintronics, solar cells, sensors, storage devices, catalysis, medicine, etc. [1-3]. Composite nanowires also have excellent electronic and optical properties, so they are used in various devices of optoelectronics, in nanoscale field effect transistors, logic devices, etc. [4,5]. Use of composite nanolayers in engineering systems can give them new properties and functions. One can mention opto- and microelectronic devices, NEMS and MEMS, and various coatings designed to improve the mechanical, tribological, environmental, optical, electrical, magnetic and biological properties of surfaces [6].

Fabrication of composite nanostructures is accompanied by the appearance of misfit stresses caused by the mismatch between crystal lattices and material properties of their components, which leads to substantial changes in their properties. Under some critical conditions, these stresses can relax through development of various defect structures [6-10] or through the destruction of the nanostructures, which explains a special interest to this problem. One of possible relaxation mechanisms is generation and expansion of prismatic dislocation loops (PDLs). The purpose of this work is an approximate calculation and a comparison of critical conditions for the generation of PDLs at the outer and inner boundaries in spherical bulk and hollow core-shell nanoparticles, cylindrical bulk and hollow core-shell nanowires and planar bi- and tri-nanolayers.
2. Models

Consider some typical composite nanostructures which are bulk core-shell nanoparticles and nanowires (Figure 1a,c), hollow core-shell nanoparticles and nanowires (Figure 1b,d), and bi- and tri-nanolayers (Figure 1e,f).

![Figure 1](image)

**Figure 1.** Sketch of composite nanostructures in the form of thin shells (films) 2 on different cores (substrates) 1: (a) bulk core-shell nanoparticle, (b) hollow core-shell nanoparticle, (c) bulk core-shell nanowire, (d) hollow core-shell nanowire, (e) bi-nanolayer, and (f) tri-nanolayer.

The nanostructures are assumed to be elastically isotropic and homogeneous. Further, we suppose that in the nanoparticles and nanowires, the shell thickness is much smaller than the core radius, in which case one can use a planar model of a thin layer on a semi-infinite substrate for correct calculation of strain energies of rectangular PDLs generated in the nanostructures. With these approximations, we find strict analytical formulas for the energy changes accompanied the PDL generation on either core-shell (film-substrate) interface or outer shell (film) surface, and compare these cases in terms of critical misfit parameters with account for the PDL shape. We consider the following three characteristic shapes for the PDLs: (i) extended normally to the interface (NI-loop, Figure 2a), (ii) square (S-loop, Figure 2b), and (iii) extended along the interface (AI-loop, Figure 2c).

![Figure 2](image)

**Figure 2.** Schematics of prismatic dislocation loops of types (a) NI-(1, 2, 3), (b) S-(1, 2, 3), and (c) AI-(1, 2, 3).
3. Results

Our calculations have shown that the Al-loops are the most preferable for all nanostructures under consideration and that the free surface is the most favorable place for generation of these loops. On the other hand, the core-shell (substrate-film) interface is more profitable than the shell (film) free surface for generation of the Ni- and S-loops. The critical misfit for PDLs, which are generated in the core/substrate (shell/film), decreases (increases) with an increase in the shell/film thickness $h$ and with a decrease in the nanoparticle/nanowire radius $R$ or in the bi-nanolayer thickness $H$.

![Figure 3](image_url)

Figure 3. Dependence of the critical shell/film thickness $h_c$ on the misfit parameter $f$ for the case when $r_0 = h_s = 24$ nm, $H_s = 48$ nm, $r_p = 15$ nm and PDLs are generated from the shell/film free surface. Here $r_p$ is the inner radius of hollow core-shell nanoparticles/nanowires, $r$ is the inner radius of bulk core-shell nanoparticles/nanowires, $h_s$ – thickness of bi-nanolayer substrate, $H_s$ – thickness of tri-nanolayer substrate.

Figure 3 shows the dependences of the critical shell/film thickness $h_c$ on the misfit parameter $f$ for the nanostructures under consideration in the most favourable case when PDLs are generated from the shell/film free surface and extend along the interface (Al-2-loops, see Figure 2c). The generation of PDLs in a nanostructure is energetically favorable when the values of $h_c$ and $f$ fall into the area under the curve corresponding to the nanostructure. Therefore, the most stable nanostructure in this sense is the bi-nanolayer, as it is characterized by the smallest area under its curve. The reason is its bending which is an effective channel of misfit stress relaxation. In contrast, the tri-nanolayer (two thin films deposited on both the sides of a planar substrate, see Figure 1f) is the least resistant to the PDL formation. Indeed, when the nanoparticle/nanowire core diameter $2r_0$ is equal to the substrate thickness $H_s$ and the nanoparticle/nanowire shell thickness is equal to the film thickness, the misfit stress in the nanoparticle shell is lower than that in the nanowire shell and lower than that in the film. Further reduction of the misfit stress in the nanoparticle/nanowire shell can be achieved through the formation of a void in its core (Figures 1b,d) [11]. The larger the void radius, the lower the misfit stress in the nanoparticle/nanowire shell and the harder the PDL formation.

To determine the preference of the PDL shape and its generation site in the nanostructures shown in Figure 1, one can use Table 1. The less grade in the table cell the easier formation of the PDL in the corresponding nanostructure. As is seen, PDL generation is easier in the shell of nanowire than in the shell of nanoparticle or in the film of bi-nanolayer. On the other hand, PDL generation is easier in the substrate of bi-nanolayer than in the core of nanowire or nanoparticle. PDL generation in a longitudinal section of nanowire shell is more profitable than that in its cross section, however, for the nanowire core it is vice versa. It is also shown, that for the PDLs generated from free surfaces and extended along interfaces (Al-2-loops), the most stable nanostructure is the bi-nanolayer (grade 11), while the most unstable is the tri-nanolayer (grade 1). The most disadvantageous case for PDL
generation is when square PDLs (S-3-loops) are generated from the interface to the nanowire core in its longitudinal section.

Table 1. Preference of loop shapes and generation sites in different nanostructures

|                            | Loop generation from the interface to the shell/film | Loop generation from the free surface to the shell/film | Loop generation from the interface to the core/substrate |
|---------------------------|-----------------------------------------------------|--------------------------------------------------------|----------------------------------------------------------|
|                           | A1-1  S-1  NI-1                                     | A1-2  S-2  NI-2                                       | A1-3  S-3  NI-3                                         |
| Bulk core-shell nanoparticle | 13    17    16                                   | 6     35    26                                       | 28    34    29                                         |
| Hollow core-shell nanoparticle | -     -     -                                    | 7     -     -                                        | -     -     -                                          |
| Bulk core-shell nanowire (loop in cross section) | 12    15    10                                   | 3     33    23                                       | 25    31    27                                         |
| Bulk core-shell nanowire (loop in longitudinal section) | 9     14    8                                    | 2     32    22                                       | 38    39    36                                         |
| Hollow core-shell nanowire (loop in cross section) | -     -     -                                    | 5     -     -                                        | -     -     -                                          |
| Hollow core-shell nanowire (loop in longitudinal section) | -     -     -                                    | 4     -     -                                        | -     -     -                                          |
| Bi-nanolayer              | 18    20    19                                   | 11    37    30                                       | 21    25    24                                         |
| Tri-nanolayer             | -     -     -                                    | 1     -     -                                        | -     -     -                                          |

Evaluated for \( R = H = 60 \text{ nm}, \ h = 10 \text{ nm}, \ r_p = 15 \text{ nm}. 

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