Influence of strain distribution on the morphology evolution of a Ge/GeO_2 core/shell nanoparticle confined in ultrathin Al_2O_3 thin film by surface oxidation*

Zhang Ying(章 英)[a], Huang Hong-Hua(黄红华)[a], Liu Xiao-Shan(刘晓山)[a], Luo Xing-Fang(骆兴芳)[a], Yuan Cai-Lei(袁彩雷)[a]†, and Ye Shuang-Li(叶双莉)[b]

[a] *Laboratory of Nanomaterials and Sensors, School of Physics, Electronics and Communication, Jiangxi Normal University, Nanchang* 330022, *China*
[b] *Institute of Microelectronics and Information Technology, Wuhan University, Wuhan* 430072, *China*

(Received 26 June 2014; revised manuscript received 16 October 2014; published online 30 January 2015)

The influence of strain distribution on morphology evolution of Ge/GeO_2 core/shell nanoparticle confined in ultrathin Al_2O_3 thin film by surface oxidation is investigated. A finite-element simulation is performed to simulate the morphology evolution of the confined Ge/GeO_2 core/shell nanoparticle under the influence of the local strain distribution. It indicates that the resultant oxidation-related morphology of Ge/GeO_2 core/shell nanoparticle confined in ultrathin film is strongly dependent on the local strain distribution. On the other hand, the strain gradients applied on the confined GeO_2 shell can be modified by the formation of polycrystalline GeO_2 shell, which has potential application in tailoring the microstructure and morphology evolution of the Ge/GeO_2 core/shell nanoparticle.

Keywords: strain, deformation, nanoparticles

PACS: 77.80.bn, 91.55.Mb, 78.67.Bf **DOI:** 10.1088/1674-1056/24/3/037701

1. Introduction

Recently, group-IV semiconductor nanoparticles confined in thin films have received increasing attention due to their unique optical properties and potential applications for Si-based optoelectronic[1,2] and electronic memory devices.[3,4] However, a substantial strain can be induced for the nanoparticles confined in a host matrix.[5,6] This strain has a pronounced influence on the microstructure[7,8] and morphology[9,10] of nanoparticles, leading to various physical properties of the nanoparticles.[11,12] On the other hand, with the device scaling down, when the size of the confined nanoparticle and the thickness of the host thin films are of the same order of magnitude, it can be easy for nanoparticles to be deformed by the applied compressive strain, which also has a significant influence on the properties of nanoparticles.[10,13]

Moreover, the properties of nanomaterials such as optical and electrical properties, mechanical stability, and phase-transition mechanics, can be designed by manipulating size, shape, structure, etc.[12,14–16] In particular, nanoparticle heterostructures are an emerging subclass of nanomaterials where two or more chemically distinct components are brought together.[17] For example, a core-shell nanoparticle can expand single-component nanoparticles to hybrid nanostructures with discrete domains of different materials arranged in a controlled fashion, resulting in integrated functionalities. Furthermore, with the dimension and material parameters of individual component optimized independently, even entirely novel properties via the coupling between different components can be found. In view of the scientific importance of the core-shell nanoparticles, it is not surprising that a wide variety of approaches for their synthesis have been reported.[18–21] Specifically, the surface oxidation method has attracted much attention because it can be utilized as a simplistic route to obtain core/shell nanostructures.[22,23] However, the understanding on the mechanisms and kinetics of morphology evolution of confined core/shell nanoparticles formed by surface oxidation method is still very limited. Therefore, there is a strong motivation to pursue theoretical calculation approaches to investigate the morphology evolution mechanism of core/shell nanoparticles confined in ultra-thin films.

Our previous research work has demonstrated that a substantial compressive strain can be induced during the growth process of nanoparticles confined in a host matrix. The strain can change the bond lengths and induce a structural phase transition of confined nanoparticles,[8,10,12] tailoring the optical properties significantly.[24] For the core/shell nanostructure, the passivation effect of GeO_2 shell can dramatically reduce the surface state density on the surface of the Ge core. In contrast, confined growth at the nanoscale may introduce substantial strain field,[25,26] leading to extra strain-relaxing surface states at the heterostructure interface. In this paper, Ge/GeO_2 core/shell nanoparticles confined in ultrathin Al_2O_3 thin film are used as a typical material structure system to study the influence of the strain distribution on the mor-

*Project supported by the National Natural Science Foundation of China (Grant Nos. 11164008, 51461019, 51361013, 11174226, and 51371129).
†Corresponding author. E-mail: clyuan@jxnu.edu.cn
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phology evolution. A finite-element (FE) simulation is performed to simulate the morphology evolution of the confined Ge/GeO_2 core/shell nanoparticles under the influence of the local strain distribution. This indicates that the strain can be relaxed greatly through the disordered areas at cracks in the GeO_2 shell. Thus, the applied strain by the matrix has no significant influence on the microstructure of Ge/GeO_2 core/shell nanoparticles. It has been found that the resultant oxidation-related morphology of Ge/GeO_2 core/shell nanoparticles confined in ultrathin film is strongly dependent on the microstructure of a GeO_2 shell.

2. Simulation

FE calculation is a versatile computer simulation technique that is used for continuum modeling of deformation in materials.[18] The simulations account for many materials' properties, including elastic anisotropy, thermal expansion, and an object's three-dimensional shape. Therefore, in order to investigate the influence of strain on the morphology evolution of confined core/shell nanoparticles, an FE simulation is performed to simulate the morphology evolution and the dynamic strain distribution of Ge/GeO_2 core/shell nanoparticle in ultrathin Al_2O_3 film formed by the surface oxidation method. In the simulation, the FE model for the strain generation is based upon the following assumptions: a spherical, linear-elastic Ge/GeO_2 core-shell nanoparticle is confined in isotropic and linear elastic Al_2O_3 matrix. During the surface oxidation process, oxygen atoms from either the atmosphere or from the internal diffusive migration within the film contribute to further formation of the GeO_2 structures, leading to volume expansion of Ge/GeO_2 core shell nanoparticle. Assuming that the Al_2O_3 matrix cavity is small enough, the compressive strain on the Ge/GeO_2 core/shell nanoparticle can be induced by the volumetric difference, which may arise from the matrix atoms, not being able to move rapidly enough to accommodate the growing Ge/GeO_2 core/shell nanoparticle. The strain distributions are changed with the thermal expansion mismatch due to the growth of the Ge/GeO_2 core/shell nanoparticle. Since the size of Ge/GeO_2 core/shell nanoparticle and the thickness of the ultrathin Al_2O_3 film are of the same order of magnitude, in the FE calculation, the Al_2O_3 matrix is considered to be infinite in the lateral side and bottom directions of the Ge/GeO_2 core/shell nanoparticle, while the Al_2O_3 matrix is finite in the top direction of Ge/GeO_2 core/shell nanoparticle. Therefore, in our model, fixed displacement boundary conditions are imposed at the lateral side and the bottom surface, while the top surface is allowed to expand freely. In this paper, we simulate the surface oxidation process of the Ge/GeO_2 core/shell nanoparticle. At the beginning stage, the size of Ge core and the thickness of GeO_2 shell is 8 nm and 2 nm, respectively. During the growth process, the Ge core shrinks while the surrounding GeO_2 shell becomes thicker. The size of Ge core decreases to 6 nm and 4 nm, while the thickness of GeO_2 shell increases to 4 nm and 6 nm. The Young's moduli are 103, 43.3, and 360 GPa for Ge, GeO_2, and Al_2O_3, while the Poisson's ratio are taken to be 0.26, 0.28, and 0.24 for Ge, GeO_2, and Al_2O_3, respectively.

3. Results and discussion

Figure 1 shows the cross-sectional strain distributions of confined Ge/GeO_2 core/shell nanoparticle at different surface oxidation stages. The colors and figures represent strain intensity and strain value, respectively. Obviously, the compressive strain is applied on the Ge/GeO_2 core/shell nanoparticle by the Al_2O_3 matrix because of the volume expansion by surface oxidation. During the surface oxidation, the Ge core shrinks while the surrounding GeO_2 shell becomes thicker. The simulation results indicate that the Ge core experiences homogeneous stain, while the strain applied in the GeO_2 shell distributes inhomogeneously and the strain intensity gradually increases. It should also be noted that the compressive strain applied at the bottom surface of the GeO_2 shell is stronger than that at the top surface, which can be due to the fact that some strain can be relaxed through the expansion of the Al_2O_3 matrix above the Ge/GeO_2 core/shell nanoparticle when they are very close to the Al_2O_3 film surface. Moreover, with the surrounding GeO_2 shell being thicker, it can be found that the strain intensity gradually increases and the strain energy tends to increase. Strain gradients induced in the confined GeO_2 shell during the oxidation can have a significant influence on the morphology evolution of Ge/GeO_2 core/shell nanoparticle.

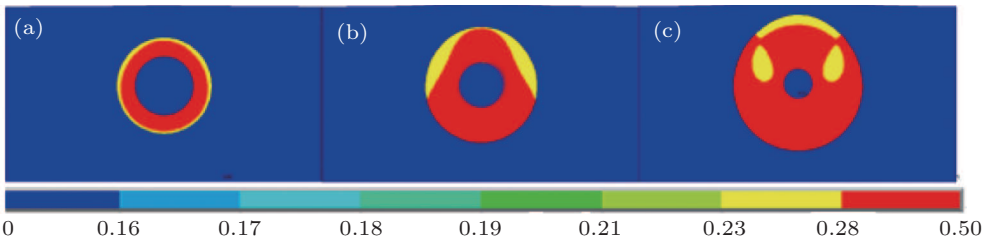


Fig. 1. (color online) Cross-sectional strain distributions of confined Ge/GeO_2 core/shell nanoparticle at different surface oxidation stages: (a) the original stage, (b) the middle stage, (c) the later stage.

Figure 2 presents the simulated morphology evolution of the cross-sectional morphologies of a confined Ge/GeO_2 core/shell nanoparticle at different oxidation stages with the strain influences taking into account. In these simulations, it has been found that during the surface oxidation, even the Ge core shrinks, and the shape of Ge core still remains spherical. In contrast, the surrounding GeO_2 shell becomes thicker and the shape of GeO_2 shell has been deformed into an ellipsoid, which can be due to the fact that a part of strain is relaxed through the expansion of the Al_2O_3 matrix above the Ge/GeO_2 core/shell nanoparticle when they are very close to the Al_2O_3 film surface. Finally, an ellipsoidal GeO_2 nanoparticle can be formed due to the surface oxidation.

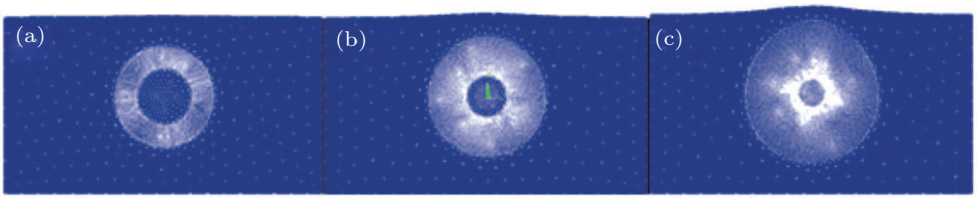


Fig. 2. (color online) Simulated evolution of the cross-sectional morphologies of a confined Ge/GeO_2 core/shell nanoparticle at different oxidation stages: (a) the original stage, (b) the middle stage, (c) the later stage.

On the other hand, the strain gradients in the confined GeO_2 shell during the oxidation can be modified by the microstructure of the Ge/GeO_2 core/shell nanoparticle, which can also tune the morphology evolution. Therefore, the strain distributions of confined Ge/GeO_2 core/shell nanoparticle with polycrystalline GeO_2 shell have to be analyzed. Figure 3 presents the cross-sectional strain distributions of confined Ge/GeO_2 core/shell nanoparticle with polycrystalline GeO_2 shell at different surface oxidation stages. Obviously, it can be found that the strain gradients applied on the polycrystalline GeO_2 shell are much less than that at GeO_2 shell in Fig. 1. The compressive strain applied on the polycrystalline GeO_2 shell is also much weaker than that at the GeO_2 shell in Fig. 1. The weakened compressive strain indicates that the strain has been relaxed due to the appearance of the disorder areas at the boundaries of GeO_2 nanocrystallites. Correspondingly, this modified strain can have a different influence on the morphology evolution of Ge/GeO_2 core/shell nanoparticle from that shown in Fig. 2.

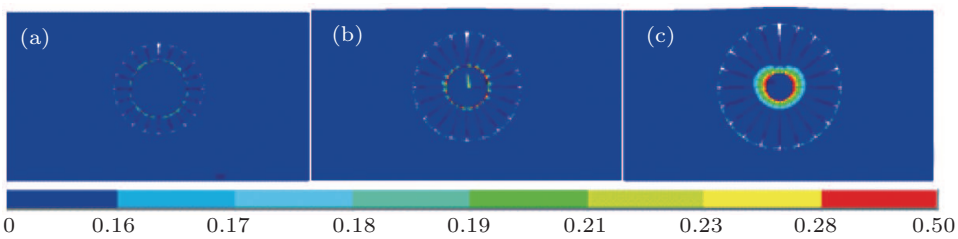


Fig. 3. (color online) Cross-sectional strain distributions of confined Ge/GeO_2 core/shell nanoparticle with polycrystalline GeO_2 shell at different surface oxidation stages: (a) the original stage, (b) the middle stage, (c) the later stage.

Figure 4 illustrates the simulated evolution of the cross-sectional morphologies of a confined Ge/GeO_2 core/shell nanoparticle with polycrystalline GeO_2 shell at different oxidation stages with the strain influences taking into account. It can be found that, during the surface oxidation, the shape of confined Ge/GeO_2 core/shell nanoparticle still remains spherical, and even the Ge core shrinks and the surrounding GeO_2 shell becomes thicker, leading to no observable deformation in the Ge/GeO_2 core/shell nanoparticle as shown in Fig. 4. The simulated results are consistent with our previous experimental results.[23] Finally, at the last oxidation stage, a spherical GeO_2 nanoparticle can be formed.

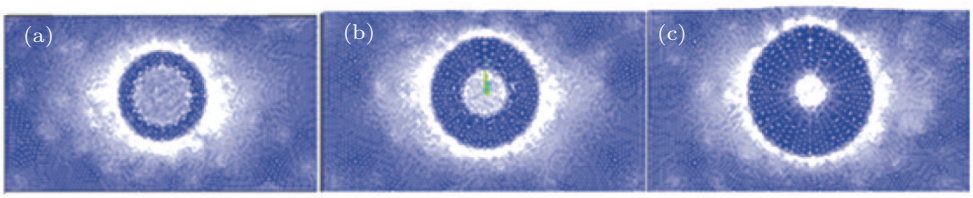


Fig. 4. (color online) Simulated evolution of the cross-sectional morphologies of a confined Ge/GeO_2 core/shell nanoparticle with polycrystalline GeO_2 shell at different oxidation stages: (a) the original stage, (b) the middle stage, (c) the later stage.

4. Conclusion

An FE simulation is performed to simulate the morphology evolution of Ge/GeO_2 core/shell nanoparticles confined in ultrathin Al_2O_3 thin film under the influence of the local strain distribution. This indicates that the resultant oxidation-related morphology of Ge/GeO_2 core/shell nanoparticle confined in ultrathin film is strongly dependent on the microstructure of the GeO_2 shell. The strain gradients applied on the confined GeO_2 shell can facilitate the deformation of GeO_2 shell and the formation of polycrystalline GeO_2 shell, tailoring the microstructure and morphology evolution of the Ge/GeO_2 core/shell nanoparticle.

References

[1] Talbot E, Larde R, Gourbilleau F, Dufour C and Pareige P 2009 *Europhy. Lett.* **87** 26004

[2] Stavarache I, Lepadatu A M, Stoica T and Ciurea M L 2013 *Appl. Surf. Sci.* **285** 175

[3] Tiwari S, Rana F, Hanafi H, Hartstein A, Crabbé E F and Chan K 1996 *Appl. Phys. Lett.* **68** 1377

[4] Bonafos C, Carrada M, Benassayag G, Schamm-Chardon S, Groenen J, Paillard V, Pecassou B, Claverie A, Dimitrakis P, Kapetanakis E, Ioannou-Sougleridisb V, Normandb P, Sahuc B and Slaouic A 2012 *Mater. Sci. Semicond. Process* **15** 615

[5] Wellner A, Paillard V, Bonafos C, Coffin H, Claverie A, Schmidt B and Heinig K H 2003 *J. Appl. Phys.* **94** 5639

[6] Chew H G, Zheng F, Choi W K, Chim W K, Foo Y L and Fitzgerald E A 2007 *Nanotechnology* **18** 065302

[7] Johnson C L, Snoeck E, Ezcurdia M, Rodríguez-Gonzalez B, Pastoriza-Santos I, Liz-Marzan L M and Hÿtch M J 2007 *Nat. Mater.* **7** 120

[8] Yuan C L, Ye S L, Xu B and Lei W 2012 *Appl. Phys. Lett.* **101** 071909

[9] Pratt A, Lari L, Hovorka O, Shah A, Woffinden C, Tear S P, Binns C and Kröger R 2014 *Nat. Mater.* **13** 26

[10] Yuan C L, Jiang Z X and Ye S L 2014 *Nanoscale* **6** 1119

[11] Smith A M, Mohs A M and Nie S 2009 *Nanotechnology* **4** 56

[12] Yuan C L, Liu Q and Xu B 2011 *J. Phys. Chem. C* **115** 16374

[13] Jiang Z X, Yuan C L and Ye S L 2014 *RCS Adv.* **4** 19584

[14] Andrievski R A 2014 *J. Mater. Sci.* **49** 1449

[15] Peng Y J, Zhang S P, Wang Y H and Yang Y Q 2008 *Chin. Phys. B* **17** 1674

[16] Fan G H, Qu S L, Guo Z Y, Wang Q and Li Z G 2012 *Chin. Phys. B* **21** 047804

[17] Cozzoli P D, Pellegrino T and Manna L 2006 *Chem. Soc. Rev.* **35** 1195

[18] Portilla L and Halik M 2014 *ACS Appl. Mat. Inter.* **6** 5977

[19] Zeleňáková A, Zeleňák V, Michalík Š, Kováč J and Meisel M W 2014 *Phys. Rev. B* **89** 104417

[20] Kwak K, Cho K and Kim S 2014 *Appl. Phys. Lett.* **104** 103303

[21] Lei Z W, Liu M, Ge W, Fu Z P, Reinhardt K, Knize R J and Lu Y L 2012 *Appl. Phys. Lett.* **101** 083903

[22] Yuan C L 2010 *J. Phys. Chem. C* **114** 2124

[23] Yuan C L and Lee P S 2008 *Nanotechnology* **19** 355206

[24] Yuan C L, Chu J G and Lei W 2010 *Appl. Phys. A: Mater. Sci. Process* **99** 673

[25] Newton M C, Leake S J, Harder R and Robinson I K 2010 *Nat. Mater.* **9** 120

[26] Gilbert B, Huang F, Zhang H, Waychunas G A and Banfield J F 2004 *Science* **305** 651