Published in final edited form as:

Nano Lett. 2012 September 12; 12(9): 4757–4762. doi:10.1021/nl302190e.

Misfit-guided self-organization of anti-correlated Ge quantum dot arrays on Si nanowires

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Abstract

Misfit-strain guided growth of periodic quantum dot (QD) arrays in planar thin film epitaxy has been a popular nanostructure fabrication method. Engineering misfit-guided QD growth on a nanoscale substrate such as the small curvature surface of a nanowire represents a new approach to self-organized nanostructure preparation. Perhaps more profoundly, the periodic stress underlying each QD and the resulting modulation of electro-optical properties inside the nanowire backbone promise to provide a new platform for novel mechano-electronic, thermoelectronic, and optoelectronic devices. Herein, we report a first experimental demonstration of self-organized and self-limited growth of coherent, periodic Ge QDs on a one dimensional Si nanowire substrate. Systematic characterizations reveal several distinctively different modes of Ge QD ordering on the Si nanowire substrate depending on the core diameter. In particular, Ge QD arrays on Si nanowires of around 20 nm diameter predominantly exhibit an anti-correlated pattern whose wavelength agrees with theoretical predictions. The correlated pattern can be attributed to propagation and correlation of misfit strain across the diameter of the thin nanowire substrate. The QD array growth is self-limited as the wavelength of the QDs remains unchanged even after prolonged Ge deposition. Furthermore, we demonstrate a direct kinetic transformation from a uniform Ge shell layer to discrete QD arrays by a post-growth annealing process.

Keywords

Quantum dot; misfit strain; heterostructures; epitaxy; core/shell nanowires

In growth of pseudomorphic semiconductor thin film heterostructures, when the top layer grows beyond a critical thickness, large misfit-strain due to lattice mismatch will unavoidably lead to rough surfaces, formation of QDs and as thickness increases, the introduction of dislocations and faults due to strain relaxation^{1,2}. These defects are undesirable in electrical and optical device applications as they act as scattering sites, recombination centers, and leakage path. Considerable efforts have been spent minimizing strain relaxation in heterostructure growth.^{3–5} In recent years core/shell nanowire (NW) heterostructures have attracted increasing attention as they are more accommodating to high misfit strain than planar thin films without relaxation. The radius of curvature of the small

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Supporting information available

High resolution TEM images of Ge QDs and amorphous Ge shells grown on the Si nanowire core. Calculation of the wavelength of Ge QD arrays as a function of core diameter and thermodynamic activation energy of Ge adatoms surface diffusion. This material is available free of charge via the Internet at <http://pubs.acs.org>.

diameter core surface is expected to alleviate the strain in the shell layer, allowing thicker critical thickness for a wide range of coherent shell material growth without formation of dislocation and other defects.^{6,7} Indeed, epitaxial core/shell and core/multishell heterostructure NWs of IV, III–V, II–VI and transition metal oxide materials have been successfully synthesized^{8–13}. The advent of nanoscale heterostructure semiconductors, such as quantum dots^{14,15} and core/shell nanowires^{8–10} has provided an unprecedented opportunity towards engineering accurate and scalable devices at an atomistic scale for applications in photonics^{11,16}, electronics^{12,17}, and biosensors^{18,19}.

Still, even with a small diameter nanowire, for very large misfit strain between two materials such as Ge on Si (4.2%), the critical thickness for epitaxial shell growth is no more than a few nanometers⁶, beyond which a change in shell morphology is commonly observed. Multiple grain boundaries and roughened surfaces may form due to strain relaxation, similar to the case on a bulk substrate.^{4,20} Interestingly, recent studies on thick Ge shell deposition on ~50 nm diameter Si NWs have discovered an instability from uniform shells and formation of individual Ge islands²¹. Compared with earlier reports of uniform Ge shell growth on small, 10–15 nm diameter Si NW cores¹², these results suggest a strong influence from the core diameter on the morphologies of the shell layer. The individual Ge islands are reminiscent of the self-organized Ge/Si quantum dots widely investigated in planar growth due to their interesting quantum confined electronic structures.^{22–24} The transition of shell layer growth mode into QDs is a result of interplay of surface and strain energies that is unique in a thin and flexible nanowire substrate. Unlike in a traditional planar growth substrate, a small diameter nanowire core is thin enough to allow the strain distribution on one side to influence the strain on the opposite side of the cylindrical substrate. Recent theoretical studies by Schmidt et.al.²⁵ and Wang et.al.²¹ have shown that at certain diameters, misfit strain in core/shell nanowires can propagate along the length of the wire and self-organize into a periodic pattern to minimize total strain energy.^{10,26} They used a surface perturbation model to describe a series of morphological instability growth modes after deposition of Ge on a Si NW backbone.^{21,25} The model predicts that initial instability of the shell layer deposition would lead to formation of periodic QD arrays in one of several unique growth modes (Fig. 1 top), with the core size being the key determining factor of the QD morphology. Such misfit strain-guided epitaxial islands not only present a new type of periodic nanostructure, but also serve as periodic nanostressors to the core nanowire backbone thus providing a unique opportunity towards strain-engineered materials with novel mechano-electronic properties for applications in, for example, thermoelectronic, and optoelectronic devices.

Experimentally, while periodic Ge QD array structures have been reported on both surfaces of thin Si nanomembranes²⁷, most studies of Ge deposition on Si NWs have focused on homogeneous shell growth^{8,9,11,12,17,28–30} with few reports on observation of the predicted periodic surface instability.^{18,20,27} Herein we report the first systematic study of misfit-guided QD growth based on CVD growth of Si/Ge core/shell nanowires with a variety of core diameters. Regular periodic arrays of coherent Ge QDs are formed and interestingly, anti-correlated QDs growth is observed for ~20 nm core diameter, consistent with theory. The wavelength of QD array is inversely proportional to core diameter while insensitive to growth time due to pinning of QDs with the periodic strain field. Lastly, a surface kinetics-driven transformation of uniform Ge shells to QD arrays is demonstrated ex-situ by thermal annealing at higher temperatures. Such strain-guided growth opens up a new avenue towards growth of self-organized nanoscale heterostructures.

Following the model by Schmidt et.al.²⁵, Fig. 1 illustrates several predicted growth modes of Ge shell on a Si NW core when uniform shell growth becomes unstable followed by preferential growth towards islands/QDs. Ge growth on Si surface is prone to form islands

rather than a thin film under the Stranski-Krastanow (S-K) growth mechanism. This is because of a large 4.2% lattice mismatch between Ge and Si and the need to minimize surface and edge energy.^{7,31,32} The morphology of the shell instability in Fig. 1 is defined by perturbation of the outer shell layer thickness $R = R_s + \delta \cos(qz) \cos(n\phi)$ where R_s is the unperturbed outer radius of a uniform core-shell nanowire, δ is the amplitude of the perturbation, and q and n are the wave numbers in axial (z) and azimuthal (ϕ) direction.

Fig. 1 bottom shows schematically the nonuniform strain distribution inside the Si NW backbone at mode $n = 1$. In this example, a Ge island pseudomorphically formed on the top side creates tensile strain within the Si substrate immediately underneath it due to the larger lattice of Ge compare to Si (+ signs). This in turn leads to compressive strain in Si at the bottom side (– signs), much in the same way as the convex and concave surfaces of a bent pipe. As a consequence further Ge deposition and QD formation at the bottom side will tend to avoid the compressively strained (–) surfaces while preferentially grow at the tensile strained (+) region, resulting in an anti-correlated zig-zag organization of Ge dots on Si in order to reduce the total elastic energy of the system.^{33,34}

In our experiment Si/Ge core/shell nanowires were grown on Si (100) substrate using silane (SiH_4 , 2%) and germane (GeH_4 , 2%) diluted in hydrogen as precursor gas sources in an LPCVD system (ET2000, Firstnano). Gold colloids (Ted Pella) with diameters ranging from 10 to 80 nm were dispersed on the Si substrate as catalyst seeds. The Si nanowire core was grown at 470 °C for 25 min with total pressure of 100 Torr ($P_{\text{silane}} = 2$ Torr) followed by Ge shell/QD growth with total pressure of 40 Torr under a selection of growth temperatures and durations. During the transition from Si to Ge growth, small amount of silane ($P_{\text{silane}} = 0.45$ Torr) was flowed to prevent gold diffusion from the catalyst to the nanowire sidewall. Temperature, pressure, Si core diameter, and Ge shell/QDs growth time were varied extensively to explore Ge shell/dots morphology.

TEM analysis of the as-grown Si/Ge nanowires heterostructures shows prominently uniform Si NWs with Ge islands on their surface (Fig. 2a, b). The Ge islands or QDs appear darker in contrast compared to the Si backbone due to its higher elemental weight. In Fig. 2c, high-resolution TEM image shows that each QD consists of dislocation-free heteroepitaxial growth of single crystal Ge on Si. The corresponding fast Fourier transform (FFT) pattern (Fig. 2d) shows that the Si NW grows along the $\langle 110 \rangle$ direction and exhibits two clearly distinguishable peaks at the $[1\bar{1}0]$ direction, normal to the Ge/Si interface (inset of Fig. 2d). The twin diffraction peaks indicate a clean epitaxy between the Ge and Si lattices similar to those reported previously in Ge/Si core/shell NWs^{12,35}.

Significantly, we find that the choice of core diameters has a strong influence on morphology of Ge QDs on Si NW substrate. Fig. 2a and 2b show TEM images of Si/Ge core/shell NWs grown with 20 nm gold colloids as catalysts. The measured core diameter of each nanowire is 20 and 21 nm respectively and both nanowires have periodic arrays of anti-correlated Ge islands or QDs decorated along the circumference in an alternating fashion corresponding to the $n = 1$ mode in Fig. 1b. The average wavelengths of Ge QD arrays (as defined in Fig. 1) are $L = 56.6$ and 53.3 nm respectively. These results are strongly indicative of the previously proposed anti-correlated organization of Ge dots on nanoscale Si NW substrates due to the periodic correlation of strain field in the nanowires.

In the case of nanowires grown with smaller, 10 nm diameter catalysts, however, the morphology of the Ge deposition is distinctively different. Fig. 2e shows two thin nanowires with 13 nm and 11 nm diameter backbone on which instead of discrete Ge QDs covering both sides, wider Ge islands are formed and they are found on a single side of Si surface only. In addition, the nanowires exhibit a bending curvature with the Ge on the convex

surfaces (Fig. 2e). Such bending can be attributed to the high flexibility of these thin nanowire cores.³⁶ At such small diameter, the core substrate itself is close to or even less in thickness than the thickness of the Ge shell deposition, hence most of the strain energy is accommodated by bending stress within the core.

At the other end of the spectrum, as we focus on much larger diameter Si NW cores (Fig. 2d), the arrangement and density of Ge dots resemble island growth on planar substrates, covering all exposed surfaces around the circumference of the core and without clear angular or axial correlation among island location distributions. These represent higher order growth modes ($n \geq 2$) in Fig. 1d because with large core diameter the correlating effect of strain field across the core NW diameter is no longer significant enough to produce the correlated pattern of Ge dots.

To gain quantitative insight into the self-organization of QDs on the Si nanowire substrates we collected and analyzed images from a variety of diameter-dependent morphologies of QD arrays. For this purpose, two key growth parameters, core diameter and Ge deposition time were extensively varied and TEM analysis was used to perform a statistical study on the wavelength of QD arrays.

Table I summarizes the core diameter dependence of Ge shell growth morphologies. Three groups of nanowires were included based on initial growth of Si NW with catalyst Au colloids of 10, 20 and 40 nm. For samples with the smallest diameter ($D < 15$ nm), single-side Ge growth mode with Ge deposition on only one side of the Si NW is found on a majority (90%) of the nanowires. Among these single-side growth samples most (80%) exhibit bending curvature similar to that in Fig. 2e. Only one small diameter sample was found with Ge QDs on opposite side of the circumference in either $n = 0$ or $n = 1$ geometry. For medium range diameter samples ($15 \leq D \leq 30$ nm), however, we find a predominant distribution (84%) of $n = 1$ mode growth, while none shows $n = 0$ behavior. Lastly, the largest diameter nanowires in this study ($D > 30$ nm) uniformly exhibit higher index mode ($n \geq 2$) growth with the core surrounded by Ge dots on all sides. The fact that surface morphologies or growth modes of the Ge QDs are sensitively defined by the core diameter is strong indication of the role of growth substrate diameter in directing the correlation of misfit-strain across the circumference and is directly supportive of previous theoretical calculations^{21,25,31}. The diameter dependence can be qualitatively understood by considering that the ability to form regular arrays of correlated QDs on the nanowire surface closely relies on the strain field correlation across the nanowire backbone (Fig. 1 bottom panel), therefore the larger the core diameter, the weaker the effect of strain on one side of the nanowire will propagate to affect the opposite side. At 84%, 90% and 100% for each diameter groups, such large, near-uniform distribution of certain growth modes suggests a novel route towards self-organization of QD nanostructures driven by minimization of strain energy in nanoscale heterostructures.

Among each of the different growth modes, we also investigated the effect of core diameter on the wavelength of Ge QDs. In particular, Fig. 3a shows in the case of anti-correlated ($n = 1$) nanowires the wavelength L is nearly insensitive to core diameter at 20~50 nm but increases rapidly with smaller D . These observations are also in good agreement with theoretical calculation (solid line, Fig. 3a) of the shell instability using first order perturbation²⁵ (see supporting information). Therefore with careful control of the nanowire core diameter, one can rationally tune the QD wavelength as a new route toward nanomaterial design.

Besides simple $n = 1$ mode, we collected a large set of data of Ge QD wavelength versus core diameter from all observed growth modes ($n = 0$ and above) that also include various

Ge growth time from 3.5 to 20 minutes. Here the Si core nanowires were grown with 10~40 nm gold catalyst. The resulting L vs. D trend is plotted in Fig. 3b and reveals interestingly an inverse relationship between L and D . The trend is consistent with that from previous theoretical calculations^{21,25,31} and strongly reinforces the picture of the controllability of self-organized QDs by strain engineering within specific core diameters.

Another striking finding from the statistical analysis of Ge QD wavelength L is the lack of dependence with increased Ge deposition time. As can be seen in Fig. 3b, despite Ge deposition time being varied nearly 6 times from 3.5 minutes to 20 minutes, there is no significant difference in L vs. D . That is, with longer growth time each individual QDs may grow in size but maintain spaced according to the strain field distribution and will not converge into each other. This echoes previous observations in planar S-K growth of Ge on Si, where it is found that during extended growth, smaller islands tend to disappear while larger island continue to ripen, leading to a low island density rather than the islands merging into each other forming a continuous film.^{32,37} To put this into our perspective on nanowire substrates, we focused on one specific group of 20 ± 2 nm core diameter nanowires to characterize the size evolution of standalone Ge QDs as a function growth time and to see whether they will merge with each other to form a continuous Ge layer upon a long Ge deposition. Fig. 4a–c show the time evolution of Ge QDs on Si NW for a series of growth batches each with a different Ge deposition time (3.5, 5 and 10 minutes). These images show clearly that QDs grow larger in both width and height direction upon a longer Ge deposition: from Fig. 4a to c, the average QD heights increase from 2.6 ± 0.6 , 6.3 ± 2.3 , to 8.5 ± 2.4 nm while the average QD widths increase from 18 ± 1.4 , 27 ± 3.4 , to 30.5 ± 8.3 nm respectively (Fig. 4d). High resolution TEM images show that individual Ge QD shapes evolve from a small dome shape to a much taller and wider nanocrystal island with a large number of high-index facets as the Ge grows thicker (Fig. S1). Yet, as the size of each QD grows larger, the wavelength L (indicated between two black arrows) remains unchanged (Fig. 4e) regardless of growth duration (Fig. 4a to c: 50.3, 51.7, and 48.8 nm respectively). The QD formation remains discrete and is limited by the periodic strain distribution even after up to 20 minutes of Ge deposition. The self-limited growth of the QD array via the alternating tensile and compressive stress suggests that inner-nanowire strain engineering has the potential as a robust and reliable assembly driving force.

While our observation is consistent with the instability growth models from the perturbation method which considers thermodynamic energy minimization within the context of deposition influx of Ge atoms^{20,21}, we can further extend our experiment to explore the possibility of kinetic surface evolution to create misfit strain-driven QD arrays directly from an existing nanowire with uniformly coated Ge shells. For this purpose, we first grew 20 nm diameter Si NWs followed by Ge shell deposition at a lower temperature of 290 °C compared to previous growth conditions. TEM reveals no formation of QDs. Instead, an amorphous Ge shell with a relatively uniform surface is grown throughout the entire length of the Si nanowires as shown in Fig. 5a and Fig. S2. In all, 2–3 nm of Ge shell was grown with 20 minutes deposition time at such a low temperature (Fig. 5a). Subsequently, post-growth anneal at a higher temperature have transformed these smooth Ge shell into $n = 1$ QD arrays (Fig. 5b). The results suggest that at high anneal temperatures, Ge adatoms on the surface of the amorphous shell will diffuse kinetically on Si surface forming a regular QD array to minimize total free energy. To quantitatively analyze the effect of temperature on morphological evolution of the Ge shell, we focus on the normalized shell roughness amplitude $\delta/R = (R_{max} - R_{min})/(R_{max} + R_{min})$ where δ and R are the amplitude of shell thickness perturbation and the outer radius of the unperturbed core/shell nanowire respectively. The minimum and maximum nanowires radius R_{min} and R_{max} along the entire length of the wire is used to calculate δ and R as a function of annealing temperature (Fig. 5c). In Fig. 5b and its inset, (δ/R) increases from 0.15 to 0.25 as temperature is raised from

440 °C to 500 °C, with the Ge islands thickness increasing and the remaining amount of inter-island Ge material decreasing. Overall, as temperature T increases ($1000/T$ decreases), the roughness δ/R is seen to increase sharply and the morphology transitions from a smooth Ge shell, to a rippled, semi-roughened surface, to eventually discrete QDs. This is summarized in Fig. 5c and its inset. From fitting existing equations on kinetic growth (see supporting information) we deduced the activation energy to be 0.67 eV which is in agreement with previous study on Ge adatom diffusion on Si surface.³⁸

In summary, we report the first systematic experimental study of correlated QD array on nanowires and their diameter dependence. By varying growth parameters, we provided a comprehensive picture on self-organized and self-limited growth behavior of misfit-driven QDs on the nanowire substrate. First, the core diameter of nanowire plays an important role in determining the morphology mode shape and wavelength of Ge QD arrays. Secondly, growth-time dependent comparison on the Ge shell morphology reveals that the QD wavelength exhibits self-limiting characteristics. Furthermore, we have demonstrated ex-situ Ge QD array transformation from existing uniform shells by a post-growth annealing process. Compare to other self-organization or template techniques for nanostructure growth, we found that strain in nanostructure substrates presents another thermodynamic and kinetic driving force towards self-limited formation of periodic nanostructures without the need for lithography. Depending on the magnitude of misfit strain, it can naturally be extended to a wide range of heterostructure material systems.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We acknowledge the use of the UCSD Cryo-Electron Microscopy Facility which is supported by NIH grants to Dr. Timothy S. Baker and a gift from the Agouron Institute to UCSD. This work is supported by the NSF CAREER Award (ECCS-0955199) and the UCSD startup fund. J.X. acknowledges support from the Hellman Fellowship.

References

1. Hsu PS, Young EC, Romanov AE, Fujito K, DenBaars SP, Nakamura S, Speck JS. Appl Phys Lett. 2011; 99:081912.
2. Bourret A, Adelmann C, Daudin B, Rouviere JL, Feuillet G, Mula G. Phys Rev B. 2001; 63:245307.
3. Zubia D, Hersee SD. J Appl Phys. 1999; 85:6492.
4. Goldthorpe IA, Marshall AF, McIntyre PC. Nano Lett. 2008; 8:4081. [PubMed: 18954126]
5. Eaglesham DJ, Cerullo M. Phys Rev Lett. 1990; 64:1943. [PubMed: 10041534]
6. Raychaudhuri S, Yu ET. J Appl Phys. 2006; 99:114308.
7. Li X, Yang G. J Phys Chem C. 2009; 113:12402.
8. Hu Y, Churchill HOH, Reilly DJ, Xiang J, Lieber CM, Marcus CM. Nat Nano. 2007; 2:622.
9. Cui LF, Ruffo R, Chan CK, Peng H, Cui Y. Nano Lett. 2008; 9:491. [PubMed: 19105648]
10. Guo JY, Zhang YW, Shenoy VB. ACS Nano. 2010; 4:4455. [PubMed: 20681529]
11. Qian F, Li Y, Grade ak S, Park HG, Dong Y, Ding Y, Wang ZL, Lieber CM. Nat Mater. 2008; 7:701. [PubMed: 18711385]
12. Lauhon LJ, Gudiksen MS, Wang D, Lieber CM. Nature. 2002; 420:57. [PubMed: 12422212]
13. Hayden O, Agarwal R, Lu W. Nano Today. 2008; 3:12.
14. Milliron DJ, Hughes SM, Cui Y, Manna L, Li J, Wang L-W, Paul Alivisatos A. Nature. 2004; 430:190. [PubMed: 15241410]
15. Bruggemann C, Akimov AV, Scherbakov AV, Bombeck M, Schneider C, Hofling S, Forchel A, Yakovlev DR, Bayer M. Nat Photonics. 2012; 6:30.

16. Galland C, Ghosh Y, Steinbruck A, Sykora M, Hollingsworth JA, Klimov VI, Htoon H. *Nature*. 2011; 479:203. [PubMed: 22071764]
17. Xiang J, Lu W, Hu Y, Wu Y, Yan H, Lieber CM. *Nature*. 2006; 441:489. [PubMed: 16724062]
18. Cho NH, Cheong TC, Min JH, Wu JH, Lee SJ, Kim D, Yang JS, Kim S, Kim YK, Seong SY. *Nat Nano*. 2011; 6:675.
19. Patolsky F, Zheng G, Lieber CM. *Anal Chem*. 2006; 78:4260. [PubMed: 16856252]
20. Pan L, Lew KK, Redwing JM, Dickey EC. *Nano Lett*. 2005; 5:1081. [PubMed: 15943447]
21. Wang H, Upmanyu M, Ciobanu CV. *Nano Lett*. 2008; 8:4305. [PubMed: 19367801]
22. Takagahara T, Takeda K. *Phys Rev B*. 1992; 46:15578.
23. Tersoff J, Teichert C, Lagally MG. *Phys Rev Lett*. 1996; 76:1675. [PubMed: 10060489]
24. Wang KL, Dongho C, Jianlin L, Chen C. *Proc IEEE*. 2007; 95:1866.
25. Schmidt V, McIntyre PC, Gosele U. *Phys Rev B*. 2008; 77:235302.
26. Taraci JL, Hytch MJ, Clement T, Peralta P, McCartney MR, Jeff D, Picraux ST. *Nanotechnology*. 2005; 16:2365. [PubMed: 20818019]
27. Huang M, Ritz CS, Novakovic B, Yu D, Zhang Y, Flack F, Savage DE, Evans PG, Knezevic I, Liu F, Lagally MG. *ACS Nano*. 2009; 3:721. [PubMed: 19209871]
28. Xiang J, Vidan A, Tinkham M, Westervelt RM, Lieber CM. *Nat Nano*. 2006; 1:208.
29. Cao BQ, Zuniga-Perez J, Boukos N, Czekalla C, Hilmer H, Lenzner J, Travlos A, Lorenz M, Grundmann M. *Nanotechnology*. 2009; 20:305701. [PubMed: 19584419]
30. Tian B, Zheng X, Kempa TJ, Fang Y, Yu N, Yu G, Huang J, Lieber CM. *Nature*. 2007; 449:885. [PubMed: 17943126]
31. Wang YU, Jin YM, Khachatryan AG. *Acta Mater*. 2004; 52:81.
32. Wang LG, Kratzer P, Scheffler M, Moll N. *Phys Rev Lett*. 1999; 82:4042.
33. Yang B, Liu F, Lagally MG. *Phys Rev Lett*. 2004; 92:025502. [PubMed: 14753943]
34. Ni Y, He LH. *Appl Phys Lett*. 2010; 97:261911.
35. Zhao Y, Smith JT, Appenzeller J, Yang C. *Nano Lett*. 2011; 11:1406. [PubMed: 21417251]
36. Zhu G, Yang R, Wang S, Wang ZL. *Nano Lett*. 2010; 10:3151. [PubMed: 20698630]
37. Ling WL, Giessel T, Thurmer K, Hwang RQ, Bartelt NC, McCarty KF. *Surf Sci*. 2004; 570:L297.
38. Kim HJ, Zhao ZM, Liu J, Ozolins V, Chang JY, Xie YH. *J Appl Phys*. 2004; 95:6065.

Figure 1. (Top) Schematic of possible surface instability modes of Ge shell on Si core nanowires. Homogeneous Ge shell and four different types of inhomogeneous growth modes are shown: $n = 0, 1, 2$, and 5 . (Bottom) Alternating coherent strain distribution inside the core is shown as + (tensile) and – (compressive) signs for an $n = 1$ mode growth. The QD wavelength L is defined as the periodic distance between QDs on the same side of the wire.

Figure 2.

TEM images of Ge QDs on Si nanowires. Both Si core and Ge QDs were grown at 470 °C. a) and b) Representative TEM images of anti-correlated quantum dots with 20 ± 2 nm core diameters. c) High resolution TEM showing the defect-free single crystal Si core and Ge island. d) FFT of the TEM image in c). Note that the $[0\bar{1}1]$ and $[1\bar{1}0]$ FFT spots are composed of twin peak signals (lower inset). e) and f), morphology of Ge dots on small (11~13 nm) and large (> 50 nm) Si cores. Scale bar, 50 nm for a), b), d), and e) and 5 nm for c).

Figure 3.

Wavelength of Ge QD array as a function of Si core diameter. Each point indicates the average distance between two Ge dots on the same side of one particular nanowire obtained from TEM images. Error bars represent the standard deviation obtained from measurements along the length of each nanowire. a) Statistic analysis and fitting result at the anti-correlated mode $n=1$. Arrows in the inset indicate selected QDs and their relative positions. Scale bar, 50 nm. Solid line corresponds to the calculation result of perturbation theory with the following parameters: Shear modulus²² ($G = 80$ GPa), Poisson ratio²² ($\nu = 0.3$), surface free energy²¹ ($\gamma = 1.5$ Jm⁻²), surface stress²¹ ($\tau = 1.5$ Nm⁻¹) and misfit ($m = 0.042$). See supporting information for details. b) Statistical summary of the general trend of core diameter dependent QDs wavelength for five batch of nanowire samples with different Ge growth time. The growth modes include all the modes observed and is not limited to $n = 1$.

Figure 4.

Evolution of Ge QDs as a function of growth time. a) – c) TEM images showing anticorrelated array of Ge QDs at different Ge growth time; 3.5, 5, and 10 min from left to right. d) and e) Summary of width, height and wavelength of Ge QDs as a function of growth time. Inset of e) TEM image of 20 min growth of Ge QDs. Error bars indicate the standard deviation from mean size of QDs on each nanowire. Scale bars, 20 nm.

Figure 5.

Effect of post growth anneal on morphological transition of Ge shell. a) Uniform Ge shell growth on Si core at 290 $^{\circ}\text{C}$ for 20 minutes. b) Effect of different annealing temperature. Main panel: sample annealed at 500 $^{\circ}\text{C}$ after Ge shell growth at 290 $^{\circ}\text{C}$ for 20 minutes. Inset, 440 $^{\circ}\text{C}$ for 20 minutes. c) Transition of Ge shell roughness amplitude δ/R as a function of inverse temperature $1000/T$. Inset shows the same δ/R data (red) plotted in semi-log scale vs. $1000/T$ and a theoretical fit (blue line, see supporting information). Scale bars, 20 nm.

Table IStatistical summary of Ge shell morphology versus core diameter D .

Core diameter		$D < 15$ nm	$15 \leq D \leq 30$ nm	$D > 30$ nm
Morphology	Single-side	90%	12%	-
	$n = 0$	5%	-	-
	$n = 1$	5%	84%	-
	$n = 2$	-	4%	100%
Number of samples		20	25	14