Controlled Formation of Stacked Si Quantum Dots in Vertical SiGe Nanowires

Emily M. Turner,* Quinn Campbell, Joaquín Pizarro, Hongbin Yang, Keshab R. Sapkota, Ping Lu, Andrew D. Baczewski, George T. Wang,* and Kevin S. Jones*

ABSTRACT: We demonstrate the ability to fabricate vertically stacked Si quantum dots (QDs) within SiGe nanowires with QD diameters down to 2 nm. These QDs are formed during high-temperature dry oxidation of Si/SiGe heterostructure pillars, during which Ge diffuses along the pillars’ sidewalls and encapsulates the Si layers. Continued oxidation results in QDs with sizes dependent on oxidation time. The formation of a Ge-rich shell that encapsulates the Si QDs is observed, a configuration which is confirmed to be thermodynamically favorable with molecular dynamics and density functional theory. The type-II band alignment of the Si dot/SiGe pillar suggests that charge trapping on the Si QDs is possible, and electron energy loss spectra show that a conduction band offset of at least 200 meV is maintained for even the smallest Si QDs. Our approach is compatible with current Si-based manufacturing processes, offering a new avenue for realizing Si QD devices.

KEYWORDS: Si quantum dots, Si/SiGe pillars, high-temperature oxidation, vertically stacked QDs

The ability to fabricate quantum dots (QDs) in a controllable manner compatible with current Si-based manufacturing processes is highly desirable for a wide range of applications including quantum computing, optoelectronics, and microelectronics. One way to ensure such compatibility is to implement QDs from the Si/SiGe materials system through the fabrication of SiGe, Ge, and Si QDs. SiGe QD formation has been accomplished on Si(100) surfaces through a variety of patterning and deposition methods as well as through the use of SiGe/Si heterostructures. Ge QDs have also been realized through growth on Si(100) surfaces, as well as through controlled oxidation of SiGe nanostructures. In particular, vertically stacked Ge QDs have been fabricated through SiGe pillar oxidation, with the Ge QD position being controlled via Ge QDs “burrowing” through SiO2 to reach SiN layers. Vertically stacked Si QDs encapsulated in SiO2 have also been fabricated through oxidation of corrugated Si nanopillars, resulting in stacked Si QDs with visible to near-infrared photoluminescence. However, SiO2 is limited as an encapsulating material for some QD microelectronics applications in part due to the insulating nature of oxide.

Si QDs encapsulated in a SiGe host may be particularly useful for applications reliant on charge trapping. Due to the type-II band alignment between Si and compressively strained SiGe, a Si QD encapsulated in SiGe can achieve quantum confinement for one or more electrons, which is desirable for single-electron transistors, single-photon generation/detection, and qubit devices. Further, core–shell Si–Ge nanostructures have been shown to offer enhanced performance for a variety of applications. We propose the fabrication of core–shell Si–Ge QDs encapsulated in a SiGe host nanowire as an intriguing route to tune QD properties in the Si/SiGe materials system.

In this work, we demonstrate the formation of site-controlled, stacked, strained single-crystal Si QDs encapsulated in vertical SiGe nanowires by leveraging an enhanced Ge diffusion process during thermal oxidation of Si/SiGe nanostructures. These Si QDs are tunable in size down to 2 nm, and the fabrication process is compatible with current silicon wafer manufacturing techniques. We also observe a Ge shell surrounding the Si QDs, which we suggest is a thermodynamically favorable result using molecular dynamics and density functional theory. In all QDs examined, electron energy loss spectroscopy (EELS) analysis

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demonstrates a conduction band offset of at least 200 meV, allowing for charge trapping on the QDs.

**Si/SiGe NANOPILLAR FABRICATION**

A Si/SiGe superlattice was grown on a 300 mm n-type Si(100) wafer with alternating layers of 15 nm-thick Si and pseudomorphic Si$_{1-x}$Ge$_x$ layers ($x = 0.3$). Four layers each of Si and SiGe were grown for a total Si/SiGe stack height of 120 nm. Vertical pillars were defined using e-beam lithography and deep reactive ion etching (DRIE), resulting in 120 nm-tall features with initial diameters ranging from 25 to 200 nm (additional details in the Supporting Information). A conventional tube furnace at 900 °C with flowing O$_2$ was used to oxidize each sample for a different amount of time to create a time series. Additional deposited oxide protected the pillars during focused ion beam cross-section preparation and allowed for subsequent removal of all material surrounding the pillars using a wet-chemical etch method developed for cross-sectional transmission electron microscopy (TEM) of 3-D nanostructures.$^{34}$

**Si QD FORMATION VIA HIGH-TEMPERATURE OXIDATION**

The evolution of 60 nm-diameter pillars during oxidation is shown in cross-section using high-angle annular dark-field (HAADF) scanning transmission electron microscopy (STEM) images in Figure 1. After a 5 min oxidation (Figure 1B), a thin SiGe layer forms along the sidewalls of the pillar, resulting in encapsulated Si discs. Increasing oxidation time results in these discs becoming more spherical and decreasing in diameter as shown in Figure 1C. Continued oxidation further reduces the size of these Si dots while still retaining a defined, extended defect-free Si dot interface as shown in Figure 1D. Figure 1E shows STEM energy dispersive X-ray spectroscopy (EDS) Si K mapping of the 20 min oxidized pillar, highlighting the formation of three stacked, single-crystal Si QDs encapsulated in the vertical SiGe nanowire. With this result, we demonstrate the ability to tune the Si dot size through oxidation time. With continued oxidation, we achieve Si QD sizes down to approximately 2 nm in diameter. EELS Si compositional mapping of a 2 nm-diameter Si QD is available in the Supporting Information. We note that the initial diameter of the pillar used for Figure 1B was approximately 20% larger than the other pillars in the series, so while the Ge sidewall behavior is a good representation of the pillar evolution, the absolute diameter of the 5 min oxidation sample is not indicative of 60 nm-diameter pillar oxidation. Also of note, the pillar in Figure 1C was slightly overetched during the DRIE, leading to loss of the topmost Si layer.

The pillar sidewall shape evolves during oxidation, gradually becoming concave as oxidation time continues and affecting the Si QD dimensions. Previous work studying the oxidation of Si nanopillars revealed slower oxidation rates at the top and bottom of pillars due to curvature effects.$^{35}$ A similar
INVESTIGATION OF A Ge SHELL AROUND A Si QD

Interestingly, a bright halo suggesting higher Ge content around the encapsulated Si QD is observed during longer oxidation times as indicated by black arrows in Figure 1F and the illustration in Figure 1H. Other sources besides compositional differences can also cause intensity variation in STEM imaging of crystalline materials, including strain fields and sample thickness variations. While strain is known to affect the contrast in ADF STEM, the intensity changes due to strain are highly dependent on the detector angle. In HAADF STEM images, the intensity changes due to strain are small and the lattice bending due to strain causes decreased, not increased, retardation of the oxidation rate at the top and bottom of the Si/SiGe pillars is observed, leading to encapsulated Si dots that evolve at different rates during oxidation. For example, the top Si dot shown in Figure 1F is slightly larger than the middle dot shown in Figure 1G, likely due to the higher oxidation rate at the middle of the pillar when compared with the top or bottom of the pillar. If necessary, it may be possible to mitigate this effect through a multiple-step oxidation in the self-limiting oxidation regime, such as that done by Ye et al. to reduce variations in Si nanopillar oxidation or by placing the Si layers further from the substrate via a deeper RIE.

SiGe oxidation is known to occur in a similar fashion to Si oxidation, with the new oxide layer forming at the oxide/SiGe interface. Prior studies report a temperature regime from ~800−1000 °C for SiGe oxidation that selectively oxidizes Si, creating a Ge-rich pile-up layer in the SiGe at the SiGe/SiO2 interface. Continued oxidation results in further increase of the Ge concentration in the SiGe. To investigate the composition of our pillars, EDS and EELS analysis were used to reveal Ge concentrations up to 80% in the SiGe after oxidation (compared to the initial 30% Ge concentration). Our nanostructures remain dislocation-free despite the lattice mismatch between Si and Si0.2Ge0.8. A possible explanation is that some strain relaxation has occurred through elastic deformation due to high free surface area of the nanowires, rather than plastic deformation as would be evidenced by dislocations.
favoring the formation of a Ge shell. However, this result should be treated with caution as the energy difference is below the size of typical systematic errors in MD simulations. Further, the interatomic potentials in our MD calculations do not explicitly treat the electronic structure of the chemical bonds comprising the interface. Therefore, we use DFT to make an energetic comparison based on a fully quantum mechanical approach to the electronic structure.

Applying DFT to slices of the atomic configurations realized in the MD simulation, we predict an energy difference of 64 meV/atom, again in favor of the Ge shell case. We calculate the entropic contribution to the free energy at room temperature to be approximately 12 meV/atom in favor of mixing within the Ge shell region, leading to a total free energy difference of approximately 50 meV/atom in favor of Ge shell formation. While this energy difference is still within the methodological uncertainty of DFT, multiple chemical tools parametrized at both a classical and quantum mechanical level indicate that Ge shell formation is, in fact, a thermodynamically favored outcome for these Si QDs.

### STRAIN AND ELECTRONIC STRUCTURE OF SI QDS

The strain present in the Si dot and surrounding material will affect the band structure and band alignment present in these nanostructures, which will in turn affect the utility of these QDs for many device applications. Conventional experimental methods to determine strain from atomic resolution STEM images using geometric phase analysis are frustrated by the embedded nature of the Si QD. To address this, strain values were extracted from the MD calculations, as shown in Figure 3. Stress on the silicon is hydrostatic and tensile while stress on the Ge shell is nonuniform and compressive. Figure 3A shows the inverse relationship between strain of the Si QDs and QD diameter. Error bars account for variations in strain across the Si QDs. Computational stress maps, as seen in Figure 3B,C, reveal that the vast majority of stress on the system is placed on the Si dot and surrounding Ge shell with stress in the surrounding SiGe rapidly approaching zero. The stress map of a 10 nm-diameter Si dot is available in the Supporting Information. As the ratio of the Si dot to SiGe pillar diameter becomes larger, the Si lattice parameters appear to dominate, leading to roughly zero lattice strain in the Si for the 16 and 23 nm-diameter Si dots.

The electronic structure of our strained Si QDs differs significantly from bulk Si due to the presence of both strain and quantum confinement. To investigate this, monochromated EELS inside a 60 kV STEM was used to measure high-resolution Si L\(_{2,3}\) edges for the embedded Si QDs. The near-edge fine structure in these spectra, shown in Figure 4, is a direct measure of the unoccupied conduction band (CB) density of states.\(^{56}\) Figure 4A shows the spin-3/2 component of the L\(_{2,3}\) spectra, after background removal, of the portion of the Si/SiGe nanostructure with only SiGe as well as the portion of the Si/SiGe nanostructure with the embedded Si dot/Ge shell (Supporting Information). Figure 4B is the L\(_{3}\) spectra of just the Si dots, a result of subtracting the SiGe pillar/Ge shell contribution from the Si dot/Ge shell/SiGe pillar spectra. The inflection points, indicated by red markers, give the energy of the conduction band minima (CBM).\(^{57}\) We see a large difference of approximately 350 meV in onset energy between the Si\(_{0.2}\)Ge\(_{0.8}\) pillar and Si substrate spectra, suggesting a type-II band alignment that would allow charge trapping on the Si QDs. We see that the near-edge structures of the Si QDs resemble that of bulk unstrained Si, suggesting that our QDs are under hydrostatic strain and no splitting of CB valleys has occurred.\(^{57}\)

The Si QD energy shift consists of three contributions as illustrated in Figure 5: a strain-dependent shift in the 2p core levels, a strain-dependent shift in the Si Δ valleys, and a shift due to quantum confinement for electrons occupying the Si QDs under a type-II band alignment. The two strain-dependent shifts push the respective energy levels in opposite directions, increasing the relevant transition energy under hydrostatic tensile strain. The effect of confinement also tends to increase the relevant transition energy and only implicitly depends on strain in that the relevant band offsets depend on strain.

To compare with the MD calculations, we estimate the magnitude of the strain in our Si QDs using EELS data. By employing the equation shown in Figure 5, with an estimated 2p core level shift of 6 eV\(^{58}\) and the aggregate shift in the Si ΔCBM due to the dilatation and uniaxial deformation potentials inferred as 4.6 eV,\(^{59}\) we expect that a 1% hydrostatic tensile strain will result in a 106 meV shift in the transition
energy probed by EELS relative to bulk Si. If we neglect the effect of quantum confinement, the strain in our Si QDs calculated using EELS data is shown in Figure 3A. While this estimate of the strain is fairly consistent with the MD calculations for the smaller dots, the strain in the larger dots significantly deviates from the MD calculations. While quantum confinement may play a role in shifting the Si QD L_{2,3} spectra, a lack of direct constraints on the electronic structure of the Ge-rich shell around the Si QDs makes calculating this effect difficult.

To understand the band alignments of the Si QD, Ge shell, and SiGe pillar, we first turn to our EELS measurements, which indicate that the conduction band offset (CBO) between the Si QD and the surrounding SiGe is at least 200 meV. However, we do not know what the relevant offset is between the Si dot and the Ge shell. Further, the inhomogeneous nature of the strain in the Ge shell predicted by our classical MD calculations suggests that the band offset and the valley structure of the relevant conduction band minima in the Ge shell might be highly nonuniform. To estimate how large the Si dot/Ge shell band offset might be, we employ a simple effective mass model in which each region is characterized by a constant potential and the effective mass of a single bulk-like valley (Δ in the Si QD, L in the Ge shell). We fix the CBO between Si and SiGe to 200 meV and allow the offset between Si and Ge to vary to rationalize the observed EELS shift and the strains predicted by classical MD. For the 2 and 5 nm Si QDs, we predict the Ge shell would need to be set 150 meV below and 5 meV below the Si QD, respectively, in order to bind an electron to the QD. Details are given in Supporting Information.

Using this model, we are able to tentatively estimate the strain at approximately 1% for all of our QDs, but further analysis is needed to sharpen our understanding of this system. The strain-dependent 2p core level shift, the CBO between the Si core and Ge shell, and the inhomogeneous nature of the strain in the shell all need to be more precisely constrained. Atomistic tight-binding calculations may be a promising modeling tool to resolve ambiguities in our analysis and to help better understand both the EELS and the opportunities for optoelectronic applications in this novel system.

■ CONCLUSIONS

We demonstrate for the first time that enhanced lateral diffusion of Ge along all sides of Si/SiGe superlattice nanopillars occurs during oxidation, enabling the formation of Si QDs embedded in extended defect-free SiGe nanowires with QD diameters down to 2 nm. In addition, a Ge-rich shell is observed to form around the QD. EELS analysis confirms a
type-II band alignment between the Si QD and the surrounding SiGe pillar, as well as a shift in the Si L2,3 edge that is dependent on the QD size. This L edge shift suggests that the combined effects of strain and quantum confinement cause a reduction in the potential well present in the Si QD. However, the estimated 200 meV potential well is still deep enough to allow trapping of an electron on the Si QD, a key property for memory or logic applications. While the predicted ∼1% strain in our QDs may not be sufficient to shift the Γ and Δ valley bands enough to achieve direct bandgap behavior, the quantized states in the Si QDs may suppress phonon recombination and allow the direct gap behavior to dominate,60,61 but further investigation is needed. The ability to stack a desired number of Si QDs in a SiGe pillar, as well as tune the distance between these dots by changing the initial thickness of the SiGe layers, may allow these Si QDs to interact with one another, which may be useful for quantum computing applications. These techniques could potentially be extended to create novel shapes such as rings, ovals, and crossed wires. Existing processes for device fabrication, such as techniques for establishing contacts to vertical nanostructures,62−64 are compatible with our oxidized Si/SiGe nanostructures. In sum, our demonstrated ability to fabricate site-specific, extended defect-free Si QDs of controllable size could enable a broad array of applications in the field of optoelectronics, QD memory and logic devices, and quantum computing.

ASSOCIATED CONTENT

1 Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.nanolett.1c01670.
Sample preparation, STEM EELS, SICSTEM simulations, MD calculations, and theoretical electronic structure calculations (PDF)

AUTHOR INFORMATION

Corresponding Authors
Emily M. Turner − Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611, United States; orcid.org/0000-0001-7210-7606; Email: emilyturner@ufl.edu
Kevin S. Jones − Department of Materials Science and Engineering, University of Florida, Gainesville, Florida 32611, United States; Email: kjones@eng.ufl.edu
George T. Wang − Advanced Materials Sciences Department, Sandia National Laboratories, Albuquerque, New Mexico 87158, United States; orcid.org/0000-0001-9007-0173; Email: gtwang@sandia.gov

Researchers
Quinn Campbell − Quantum Computer Science Department, Sandia National Laboratories, Albuquerque, New Mexico 87158, United States; orcid.org/0000-0003-1377-3769
Joaquín Pizarro − Department of Computer Engineering, University of Cádiz, Puerto Real 11519, Spain
Hongbin Yang − Department of Chemistry and Chemical Biology, Rutgers University, Piscataway, New Jersey 08854, United States; orcid.org/0000-0002-0998-6944
Keshab R. Sapkota − Advanced Materials Sciences Department, Sandia National Laboratories, Albuquerque, New Mexico 87158, United States; orcid.org/0000-0001-8581-4211

Ping Lu − Department of Materials Characterization and Performance, Sandia National Laboratories, Albuquerque, New Mexico 87158, United States
Andrew D. Baczewski − Quantum Computer Science Department, Sandia National Laboratories, Albuquerque, New Mexico 87158, United States

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.nanolett.1c01670

Author Contributions
E.M.T, K.S.J, and G.T.W. conceived the concept and design of the experiment. E.M.T fabricated and processed the Si/SiGe pillars, K.R.S. assisted in quantum device discussions. J.P. provided SICSTEM simulations of the Si dot/Ge shell/SiGe pillar system. H.Y. collected EELS spectra and composition maps for a range of Si/SiGe pillars. Q.C. and A.D.B. provided theoretical analysis, including MD and DFT simulations. P.L. gathered aberration-corrected HAADF STEM images as well as EDS data. The manuscript was written through contributions of all authors, and all authors have given approval to the final version of the manuscript.

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Notes
The authors declare no competing financial interest.
DFT and MD input files are available upon request.

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ABBREVIATIONS

BOX, buried-oxide; CBM, conduction band minimum; CBO, conduction band offset; DFT, density functional theory; DRIE, deep reactive ion etch; EDS, energy dispersive X-ray spectroscopy; EELS, electron energy loss spectroscopy; HAADF, high-angle annular dark-field; MD, molecular dynamics; QD, quantum dot; SGOI, SiGe-on-insulator; STEM, scanning transmission electron microscopy; TEM, transmission electron microscopy

REFERENCES


