

Confined in-fiber solidification and structural control of silicon and silicon–germanium microparticles

Alexander Gumennik^{a,b,c,1}, Etgar C. Levy^{a,b,1}, Benjamin Grena^{a,b,d,1}, Chong Hou^{a,b,d}, Michael Rein^{a,b,d,2}, Ayman F. Abouraddy^e, John D. Joannopoulos^{a,b,f,2}, and Yoel Fink^{a,b,d}

^aResearch Laboratory of Electronics, Massachusetts Institute of Technology, Cambridge, MA 02139; ^bInstitute for Soldier Nanotechnologies, Massachusetts Institute of Technology, Cambridge, MA 02139; ^cDepartment of Intelligent Systems Engineering, Indiana University Bloomington, Bloomington, IN 47408-2664; ^dDepartment of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139; ^eCREOL, The College of Optics and Photonics, University of Central Florida, Orlando, FL 32816; and ^fDepartment of Physics, Massachusetts Institute of Technology, Cambridge, MA 02139

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Crystallization of microdroplets of molten alloys could, in principle, present a number of possible morphological outcomes, depending on the symmetry of the propagating solidification front and its velocity, such as axial or spherically symmetric species segregation. However, because of thermal or constitutional supercooling, resulting droplets often only display dendritic morphologies. Here we report on the crystallization of alloyed droplets of controlled micrometer dimensions comprising silicon and germanium, leading to a number of surprising outcomes. We first produce an array of silicon–germanium particles embedded in silica, through capillary breakup of an alloy-core silica-cladding fiber. Heating and subsequent controlled cooling of individual particles with a two-wavelength laser setup allows us to realize two different morphologies, the first being a silicon–germanium compositionally segregated Janus particle oriented with respect to the illumination axis and the second being a sphere made of dendrites of germanium in silicon. Gigapascal-level compressive stresses are measured within pure silicon solidified in silica as a direct consequence of volume-constrained solidification of a material undergoing anomalous expansion. The ability to generate microspheres with controlled morphology and unusual stresses could pave the way toward advanced integrated in-fiber electronic or optoelectronic devices.

multimaterial fibers | microparticles | confined solidification | silicon–germanium spheres | stressed silicon

Controlling the microstructure or state of stress of microparticles and nanoparticles is often key to attaining the desired properties for a specific application (1–5); however, the ability to do so is strongly limited by the synthesis method. For instance, nonspherically symmetric distributions of inorganic materials are difficult to achieve from bottom-up approaches (4–7). Likewise, controlling the state of stress or strain of semiconductor particles is challenging in unconstrained nucleation-and-growth synthesis methods. However, Janus particles of silicon–germanium (SiGe) could potentially find applications as microswimmers or nanoswimmers owing to asymmetric absorption properties (8), as well as in infrared photodetectors or solar cells for increased infrared absorption (9). Stressed silicon particles, on the other hand, could be used for bandgap tunability in photonic or optoelectronic devices (10–12).

In the past few years, thermally drawn multimaterial fibers have emerged as a unique platform for top-down scalable fabrication of microparticles to nanoparticles over a broad range of materials, through controlled in-fiber capillary breakup of the fiber components (13–15). In the case of polymers or chalcogenide glasses, structural control of the particle can be achieved by constructing complex cores at the preform level, which is later broken up in the fiber state to form structured particles (13). However, in the case of traditional semiconductor materials such as silicon and germanium, the same method cannot be applied because of the low viscosity and high solubility of the materials in the molten state (16). As a result, components of the core intermix during fiber

drawing or breakup, and the initial core structure is lost. Another route needs to be used to go beyond those limitations.

The solidification of SiGe and pure silicon and germanium has been the subject of a large number of studies in different types of configurations and geometries (16–20). First of all, both the alloy and pure materials are known to expand upon solidification, owing to their diamond cubic structure, such that constrained solidification should be associated with pressure buildup. Second, despite complete solubility of silicon and germanium in both solid and liquid states, the phase diagram of SiGe displays a large miscibility gap, with a higher solubility of germanium in the liquid state (16). At slow enough solidification rates, the initial nuclei are silicon-rich, thereby rejecting germanium into the melt. As solidification proceeds, more and more germanium is rejected into the melt, and a nonuniform distribution of germanium arises because of slow diffusion of solute in the solid phase. Naively, directional solidification of SiGe in a strong thermal gradient could lead to Janus morphologies. However, it is well known that germanium rejection in the liquid tends to create strong compositional gradients driving constitutional supercooling of the alloy, leading to growth of dendritic or cellular morphologies (17, 18, 21–24). Therefore, in practice, stable solidification front propagation and Janus morphologies are difficult to achieve.

Here we show that we can use a flame breakup approach to produce compositionally segregated particles, referred to as Janus particles of SiGe, in a scalable manner. We suppress constitutional

Significance

Water freezing into ice has a number of fascinating outcomes: Dendritic solidification of water results in beautiful snowflakes, a sealed bottle of beer shatters in a freezer, and ice covering salty oceans at the poles is salt-free due to compositional segregation. A silicon–germanium (SiGe) material system, ubiquitous in microelectronics, is surprisingly similar to water in its solidification behavior. Quenching of molten SiGe microdroplets sealed inside a glass fiber leads to dendritic morphology, with potential use in solar cells. Slow cooling induces compression of these spheres to tens of thousands of atmospheres, potentially changing the band structure of these materials. Moreover, slow solidification results in compositionally segregated SiGe Janus particles, useful for high-frequency microelectronic and nanorobotic applications.

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¹A.G., E.C.L., and B.G. contributed equally to this work.

²To whom correspondence may be addressed. Email: mlrein@mit.edu or joannop@mit.edu.

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supercooling by slow feed speeds of the fiber into the flame. We can also recrystallize the particles postbreakup using a combination of a CO₂ and diode laser, enabling accurate control over cooling rate as well the ability to reorient the Janus particles' axis. In addition, confined solidification of silicon leads to hydrostatic pressure buildup in the particles because of the anomalous expansion, which we demonstrate through both birefringence and Raman spectroscopy measurements.

Results

Our general method starts with the fabrication of a fiber consisting of a crystalline semiconductor core surrounded with a silica cladding, through the preform-to-fiber thermal drawing process (14, 25, 26). Here, we focus on cores made of silicon, germanium, or a mixture of both. Once drawn, the fiber is fed at a velocity v_f through a flame that locally heats the core and the cladding above their melting and softening temperatures, respectively, and induces local capillary breakup of the semiconductor core into a liquid droplet surrounded by silica (14), as illustrated in Fig. 1A. As the fiber exits the flame, it cools down. Because both silicon and germanium have melting points below the softening point of silica, the cladding hardens first and creates a smooth hermetic spherical vessel surrounding the molten semiconductor droplet. Subsequently, the droplet solidifies in a temperature gradient imposed by the flame, and the solidification front (denoted by ξ in Fig. 1A) is expected to propagate from the colder side toward the hotter side, in the absence of constitutional supercooling.

We have experimentally demonstrated lateral solidification of SiGe droplets by fabricating an array of axially oriented SiGe Janus particles from a Si_{0.5}Ge_{0.5} core fiber (Fig. 1A). Backscattered Mode Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS) mapping of the fabricated Si_{0.5}Ge_{0.5} spheres suggest that the SiGe distribution has a distinct axial dependence, oriented along the fiber axis (Fig. 1B–D). The SiGe map in Fig. 1D clearly shows that the sphere is a Janus particle having a Si-rich lobe and a Ge-rich lobe. The quantitative analysis of EDS shows that the Si:Ge ratio in the Si-rich lobe is roughly 5:2 (Fig. 1F), similar, yet not identical, to what is expected from the respective isothermal quasi-static segregation coefficient for Si_{0.5}Ge_{0.5} melt resulting from the SiGe phase diagram (16) (Fig. 1E). A detailed theoretical derivation of the Ge and Si redistribution in the solid sphere is given in *SI Analytical Derivation for the Ge Content Distribution in the Solid Phase* and Fig. S1, where we assume that the solidification front remains stable and propagates axially. A good agreement is found between experimental and theoretical composition distributions (Fig. 1F).

The discrepancy between the model and the data noticeable in the Si-rich lobe can be explained by the fact that the initial solidification occurs through fast dendritic growth as opposed to slow and stable solidification, which our model assumes. We assume the unstable growth of the initial transient regime to be governed by both thermal and constitutional supercooling. As solidification proceeds in the confined droplet, both mechanisms for instability will lose magnitude. Indeed, the release of latent heat from partial solidification can lead to the temperature in the liquid increasing close to the melting point of the alloy—a phenomenon known as recalescence (27, 28)—by definition reducing thermal undercooling. Second, because of the finite volume, rejection of germanium from the solid gradually decreases the silicon content in the liquid region, which is expected to suppress constitutional supercooling by effectively increasing the critical velocity (29).

Clearly, the stability of the solidification front propagation is a requirement to obtain axial germanium distribution. If cooling conditions were such that the solidification front in the droplet was indeed unstable throughout the sphere volume, the resulting spheres would likely display cellular or dendritic microstructures

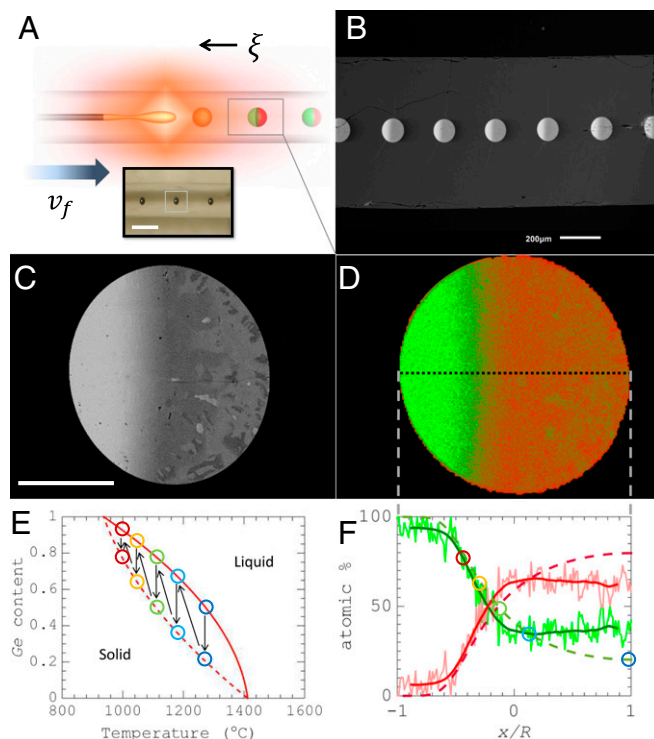


Fig. 1. Si_{0.5}Ge_{0.5} heterostructured cellular composition structure particle fabrication. (A) Schematics of fabrication process of the Janus particles array. (Inset) The generated SiGe spheres within the silica fiber. (Scale bar, 500 μm .) (B) SEM measurement in backscattered mode of the polished fiber along its axis showing a fiber-embedded array of Janus particles. (C) A single sphere cross-section SEM backscattered mode measurement. Brighter areas correspond to a higher Ge concentration. Traces of an unstable liquid–solid interface during the beginning of the crystallization are observed on the right side of the sphere, and gradual distribution is observed from the middle of the sphere to its left side. (Scale bar, 50 μm .) (D) SiGe ratio EDS map of the median cross-section of a Si_{0.5}Ge_{0.5} sphere embedded in a silica fiber, resulting from overlaid maps of Si (in red) and Ge (in green). (E) The SiGe equilibrium phase diagram: the liquidus (solid line) and the solidus (dashed line) are described. The process of the Ge rejection during the solidification of a Si_{0.5}Ge_{0.5} binary alloy is schematically described: The solidification starts at about the point (50%Ge, 1,287 $^{\circ}\text{C}$), marked by a blue circle on the liquidus, and the solidification is described by the vertical arrow to the point (20%Ge, 1,287 $^{\circ}\text{C}$), marked by a blue circle on the solidus (dashed line). As the solidification propagates, Ge is rejected to the liquid phase, and the Ge content in the melt increases while the melting temperature decreases. The resulting increase of the Ge content in the liquid phase due to the solidification is described by the diagonal arrow from the blue circle on the solidus to the cyan circle in the liquidus. As the isothermal solidification propagates, the Ge content in the melt approaches unity, and the melting temperature approaches that of a pure Ge. (F) The graph depicts SiGe atomic content distribution along the dashed line in D. The solid light green/red lines correspond to a single pixel linescan, that is, a 0.7- μm -wide analysis area. The solid dark green/red lines correspond to the same linescan with a 14.7- μm -wide analysis area, and are calculated by having the 2D image in D filtered using a 10-pixel-radius disk. The measured data are overlaid with the theoretical result calculated from the solidification front propagation (dashed red/green). The expected Si and Ge concentration along the sphere median is calculated assuming that the solidification front remains stable and propagates axially. The data were extracted along the dotted line that is described in D. For each circle on the theoretically calculated spatial Ge content distribution (green dashed line), there is a corresponding circle with the same color on the solidus line described in E, such that the spatial x coordinate of the sphere can be associated with the corresponding solidification temperature via the Ge content. The process results in Janus particles, one lobe of which is 5:2 of Si:Ge, and the other is Ge, with a boundary about 20 μm wide between them.

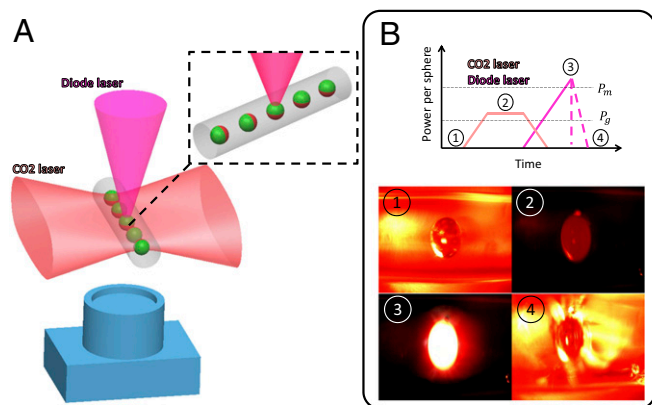


Fig. 2. Laser-induced solidification experimental setup. (A) Schematic description of the experimental setup, consisting of a diode laser beam at 808 nm and two CO₂ laser beams at 10.6 μ m. The silica cladding of the fiber is transparent at the diode laser wavelength but absorbs in the CO₂ wavelength. This experimental setup enables control over the initial sphere temperature and its cooling rate. (Inset) The particle axis reorientation by the laser. (B) (Top) Schematic description of the heating and cooling processes of each sphere. The CO₂ preheating stage is used to prevent cracks during the sphere heating by preheating and softening the silica cladding first. The power thresholds for the silica softening by the CO₂ laser and for the sphere melting by the diode laser are represented by P_g and P_m , respectively. (Bottom) Images of the sphere during the stages described by the graph, showing the sphere before the experiment (1), during the preheating of the silica (2) followed by the main heating of the sphere (3), and after the sphere temperature decreases back to the room temperature (4).

with no particular orientation (17, 18, 20, 30). Despite promising results, the flame setup does not allow sufficient control over the cooling kinetics and thermal gradient direction, and we have therefore used a technique of laser-induced recrystallization, allowing us to not only study more precisely the effect of the cooling conditions but also control the axis of the Janus particle within the fiber. A similar setup was recently used by Coucheron et al. (20) to control the microstructure of SiGe core fibers.

Here, a postbreakup particle is illuminated perpendicularly to the fiber axis by a focused diode laser beam at a wavelength of 808 nm, with a spot size of about 50 μ m. To prevent the cracking of the cladding, which might occur as a result of the release of stresses stored in the silica cladding, we uniformly preheat and soften it with a CO₂ laser (Fig. 24). The absorption length of silica and silicon at 808 nm is about 1.5 m and 12.5 μ m, respectively. Therefore, the diode laser radiation is expected to be transmitted by the silica cladding but to be absorbed by the particle, which heats up. Once the particle is molten, the laser power is gradually reduced and the particle cools down and recrystallizes, while exposed to a thermal gradient defined by the diode laser direction. The process is schematically represented in Fig. 2B. By controlling the laser shut-off rate, we can effectively control the cooling conditions and the magnitude of the imposed temperature gradient.

We have recrystallized spheres of Si_{0.75}Ge_{0.25} and Si_{0.95}Ge_{0.05} under different laser shut-off rates, as shown in Fig. 3. Spheres recrystallized by abrupt laser diode shut-off led preferentially to cellular structures with no axial distribution, whereas spheres recrystallized at low shut-off rates displayed Janus morphologies aligned along the diode laser direction. We can therefore dictate the microstructure of SiGe particles by controlling the shut-off rate of the laser, as well as reorient the axis of the Janus particles by choosing the diode laser direction. Furthermore, we noticed apparent striations in the germanium concentration for Si_{0.95}Ge_{0.05} samples, with a periodicity around 15 μ m. Such fluctuations are common in the growth of SiGe from both Czochralski and

Bridgman processes (31–33). Generally these striations show a 10- to 15- μ m periodicity independent of growth conditions, and commonly attributed to fluctuations in growth velocity associated with time-dependent temperature fluctuations at the interface that can be due to convection or fluctuations in solid-phase conductivity (31–33). Here we believe a similar mechanism is at play.

To explain the overall microstructures' dependence on the laser shut-off rate, we need to understand what affects the constitutional supercooling of SiGe in our solidifying droplets. In general, constitutional supercooling arises when solute rejection in the liquid creates steep concentration gradients near the solidification front, leading to a situation where the actual temperature ahead of the front is lower than the liquidus temperature near the interface, which drives instability (29, 34). This concentration profile occurs if the diffusion of solute in the liquid is slow compared with the solidification velocity, thus resulting in strong gradients at the interface. Hence qualitatively slow shut-off rates would lead to slower solidification and a higher chance of suppressing constitutional supercooling, which is consistent with the observations. Tiller et al. (21) developed a model to compute a critical solidification front velocity above which a binary alloy will develop constitutional supercooling. Later, Mullins and Sekerka (22) enriched the model to take into account effects of interfacial tension and thermal conductivity differences. However, these models only deal with solidification of alloys with no boundaries. Here our system is a confined droplet in thermal contact with a silica cladding, for which most of the Tiller et al. and Mullins and Sekerka assumptions fall short.

Therefore, we have taken a semiquantitative approach instead, to try to predict the outcome as a function of the laser shut-off rate in our specific geometry. We used numerical simulations to estimate the temperature field and solidification front velocity for different shut-off rates in a pure silicon droplet, and

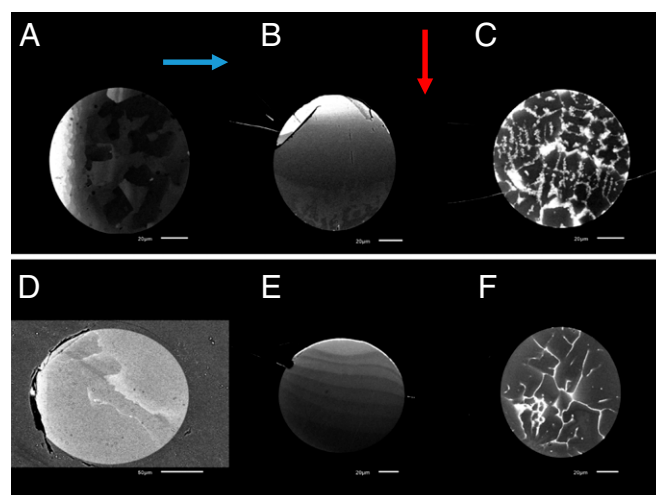


Fig. 3. Controlling the structure of SiGe microspheres. (A and D) Flame-induced and (B and E) laser-induced stable solid-liquid interface solidification of (A and B) Si_{0.75}Ge_{0.25} and (D and E) Si_{0.95}Ge_{0.05} binary alloy microspheres. The blue and the red arrows show the fiber movement direction through the flame in A and the laser illumination direction in B, respectively. The fiber velocity was 10 μ m/s. The monotonic Ge distribution that is observed in the top regions of spheres in B and E is consistent with a stable liquid-solid interface during the solidification front propagation, after the initial dendritic transient regime. The cooling rates in the results in B and E were 0.04 W/s and 3 W/s, respectively. (C and F) The cellular sphere morphology structure when the laser intensity was shut off abruptly; the cooling rate is dominated by heat diffusion rate from the sphere to the environment. The initial laser intensities in the results presented in B, C, E, and F were 2.6 W, 2 W, 1.8 W, and 2 W, respectively.

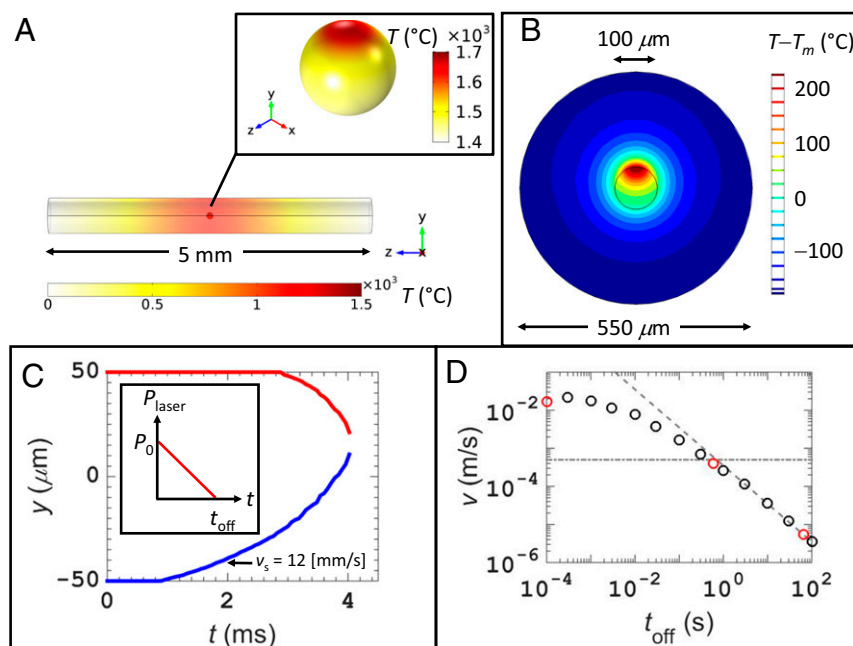


Fig. 4. Theoretical computation of the solidification front propagation velocity. (A) The calculated steady-state temperature of the 3D geometry that was modeled: a 100- μm -diameter Si sphere, encapsulated within a 550- μm -diameter silica fiber section of 5 mm. The sphere center coincides with the axis origin. A heat source condition was set in the sphere domain to simulate the absorption of $P_0 = 2 \text{ W}$ intensity radiation focused on a 50- μm -diameter spot, wavelength of 808 nm and directed in the $-y$ direction. (Inset) The temperature of the entire sphere is above the Si melting temperature. (B) The temperature of a cross-section along the sphere center. (C) The solidification front propagation as a function of time along the line $(x = 0, y, z = 0)$. The solidification front propagation is a result of a time-dependent calculation, in which the steady-state solution that is described in A and B is set as the initial condition, and in which the heat source intensity decreases linearly from $P_0 = 2 \text{ W}$ to 0 during a shut-off time $t_{\text{off}} = 3 \text{ ms}$ (Inset). The initial solidification front propagation velocity equals 12 mm/s. (D) The calculated dependence of the solidification front propagation velocity on the shut-off time (circles). The dashed line is given by $v = 7 \cdot R_s / t_{\text{off}}$, where R_s is the sphere radius. The dash-dotted line corresponds to the effective diffusion velocity and is given by $v = D / R_s$, where $D = 2.5 \cdot 10^{-8} \text{ m}^2/\text{s}$ is equal to the diffusion coefficient of Ge in Si (41). The red marked circles correspond to cooling rates of $2 \cdot 10^4 \text{ W/s}$, 3 W/s (similar to the cooling rate that was obtained in Fig. 3E), and 0.04 W/s (similar to the cooling rate that was obtained in Fig. 3B).

compared them with the estimated germanium diffusion rate in the melt from a scaling argument (Fig. 4). A detailed description of the numerical simulations is presented in *SI Numerical Simulation of the Solidification Front Propagation Velocity* and Table S1. As expected from our discussion, slow cooling leads to much slower solidification than diffusion and, consequently, to a stable nonsupercooled solidification. On the other hand, rapid laser shut-off (shut-off time less than 10 ms) causes the solidification rate to exceed the germanium diffusion rate, which would promote constitutional supercooling (34). In both cases, the experimental results are consistent with the predicted behaviors.

Our qualitative model has several shortcomings. Namely, we perform the thermal simulation for a droplet of pure silicon. A more realistic approach should take into account the germanium content, which affects the thermal properties of the solid and liquid phases, the latent heat, and the freezing point of the liquid. We expect that the solidification front velocity will be affected, and likely will decrease as the liquid freezing point decreases at higher germanium content for a given set of external cooling conditions, thereby, in fact, promoting stability due to the confinement.

The in-fiber confined solidification of particles has interesting consequences not only for the morphologies of SiGe alloys but also for their stress state. The presence of stress was indicated by cracks in thin-cladding fibers systematically appearing in the silica surrounding individual particles after solidification of the droplets (see *SI Cracked Fiber Due to Stress Buildup* and Fig. S3). As mentioned, both SiGe and pure silicon and germanium expand upon solidification. When the postbreakup droplets reach the solidification temperature, they are restricted to their liquid volume by the relatively stiff surrounding silica cladding. The anomalous

expansion upon solidification thus causes the droplets to strain the surrounding silica and to develop internal compressive stress (Fig. 5A), much like a water bottle in the freezer. We studied this effect in pure silicon to avoid complexities arising from nonuniform germanium distribution such as nonuniform volume expansions. Assuming a state of uniform stress in the spheres, we can compute its magnitude. The detailed calculation can be found in *SI Homogeneous Solidification Scenario* and Fig. S2, and it leads to a uniform hydrostatic stress of 2.9 GPa in solidified silicon droplets, independent of their diameter. These calculations do not take into account any possible plastic deformation of the silica cladding, which would limit the magnitude of the stresses.

The resulting strain in silica can also be quantified optically through a photoelastic measurement. The strain field in silica alters its refractive index and causes the material to become birefringent, which we can observe using cross-polarizers (Fig. 5C). Contrary to the region around the spheres, the intact section of the core remains unstressed (refer to *SI Evaluation of Stress in the Silica Cladding Surrounding the Sphere by Crossed Polarizers Technique*, Figs. S4–S7, and Table S2 for details). The birefringence pattern around the spheres displays a fourth-order rotational symmetry as well as multiple Michel–Levi rings (35) (Fig. 5D). By taking into account the photoelastic coefficients of silica, we can compute the expected birefringence patterns for arbitrary stresses at the silica/semiconductor interface (see *SI Evaluation of Stress in the Silica Cladding Surrounding the Sphere by Crossed Polarizers Technique*, Figs. S4–S7, and Table S2 for details of the calculations) and evaluate the surface stress by matching the number of rings with the experimental patterns (Fig. 5E). This method enables us to define the range of surface stresses coherent with a given number of rings. For a 35- μm -diameter Si droplet, the surface stresses were

Flame Breakup. The breakup of the SiGe core was performed using a hydrogen–oxygen torch with outlet diameter of 0.020” and by feeding the fiber through a flame resulting from 0.4 L/min flow of H₂ and 0.15 L/min flow of O₂ at an offset of 15 mm from the torch outlet.

The breakup of the Si core was achieved by feeding a fiber through the flame produced by a flow of 0.3 L/min and 0.2 L/min of H₂ and O₂, respectively.

Laser Recrystallization. Controlled recrystallization of spheres was obtained by feeding a fiber containing spheres through a laser heating setup. The fiber was heated locally by focusing an illumination from a fiber-coupled diode laser emitting light with a peak wavelength of 808 nm and a CO₂

laser. The diode was operated in a pulsed mode with a pulse rate of 5 kHz, controlled by a function generator, where the duty cycle was precisely tuned through a Labview program, to induce a controlled solidification rate.

For further details on the experimental methods, see [Supporting Information](#).

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