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Oxide-Free Three-Dimensional Germanium/ Silicon Core—Shell Metalattice Made by High-Pressure Confined Chemical Vapor Deposition

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ABSTRACT: Metalattices are crystalline arrays of uniform particles in which the period of the crystal is close to some characteristic physical length scale of the material. Here, we explore the synthesis and properties of a germanium metalattice in which the ~70 nm periodicity of a silica colloidal crystal template is close to the ~24 nm Bohr exciton radius of the nanocrystalline Ge replica. The problem of Ge surface oxidation can be significant when exploring quantum confinement effects or designing electronically coupled nanostructures because of the high surface area to volume ratio at the nanoscale. To eliminate surface oxidation, we developed a core—shell synthesis in which the Ge



metalattice is protected by an oxide-free Si interfacial layer, and we explore its properties by transmission electron microscopy (TEM), Raman spectroscopy, and electron energy loss spectroscopy (EELS). The interstices of a colloidal crystal film grown from 69 nm diameter spherical silica particles were filled with polycrystalline Ge by high-pressure confined chemical vapor deposition (HPcCVD) from GeH₄. After the SiO₂ template was etched away with aqueous HF, the Ge replica was uniformly coated with an amorphous Si shell by HPcCVD as confirmed by TEM-EDS (energy-dispersive X-ray spectroscopy) and Raman spectroscopy. Formation of the shell prevents oxidation of the Ge core within the detection limit of XPS. The electronic properties of the core-shell structure were studied by accessing the Ge 3d edge onset using STEM-EELS. A blue shift in the edge onset with decreasing size of Ge sites in the metalattices suggests quantum confinement of the Ge core. The degree of quantum confinement of the Ge core depends on the void sizes in the template, which is tunable by using silica particles of varying size. The edge onset also shows a shift to higher energy near the shell in comparison with the Ge core. This shift along with the observation of Ge–Si vibrational modes in the Raman spectrum indicate interdiffusion of Ge and Si. Both the size of the voids in the template and core-shell interdiffusion of Si and Ge can in principle be tuned to modify the electronic properties of the Ge metalattice.

KEYWORDS: chemical passivation, silica nanoparticle template, high-pressure deposition, core–shell structure, oxide-free Ge, three-dimensional nanostructure, interconnected polycrystalline Ge

S trongly coupled and coherently connected semiconductor nanoparticles offer the possibility of bandlike electron transport in combination with size-dependent electronic and optical properties.^{1,2} At the nanoscale, obtaining such delocalized electronic states requires an interconnected network of nanoparticles and a passivated surface. Meta structures with extended electronic states have been realized in nanoparticle/quantum dot superlattices that have a small interparticle distances, which are typically accessed synthetically by ligand stripping and/or exchange.^{3–11} These structures can provide enhanced performance in electronic transistors, thermoelectric, optoelectronic light-emitting devices^{1,2,12–14} and electrode materials for batteries.^{15,16}

Even with ligand modifications, however, it is challenging to integrate particle interconnectivity, periodicity, and quantum confinement into one system. This problem has motivated

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Figure 1. Schematic diagram of the steps involved in core-shell metalattice synthesis.

other synthetic approaches to 3D interconnected periodic structures at the nanoscale, especially the synthesis of mesoporous structures by hard or soft templating methods.^{17,18} Recently Liu *et al.* reported an approach to synthesizing completely connected, atomically crystalline three-dimensional metal structures using high-pressure confined chemical fluid deposition and silica nanoparticle colloidal crystal templates.^{19,20} Using the vapor-phase counterpart of this technique, high-pressure confined chemical vapor deposition (HPcCVD), we are now infiltrating semiconductors into the nanoscale voids of the silica template.^{21,22,23} These inverse structures, defined as metalattices, inherit the void structure of the template to form an interconnected periodic lattice.

As in other nanoscale structures, the interior surface of a semiconductor metalattice is a significant contributor to its electronic structure and physical properties. In this paper, we explore core—shell synthesis as a way to chemically passivate a Ge metalattice surface. As a group IV semiconductor, Ge has potential applications in electronics. However, despite its high carrier mobility and large exciton Bohr radius relative to Si, its integration into devices has been limited due to its complex surface oxidation chemistry.^{24–26}

Depending on the oxidation conditions and the Ge surface exposed (100, 111), Ge forms Ge^{1+} , Ge^{2+} , Ge^{3+} , or Ge^{4+} or even a mixture of different oxides.²⁷⁻³⁰ These native oxide layers on Ge are not stable and do not form a defect-free interface. Passivation techniques developed so far for Ge nanostructures such as thin films, wafers, and wires can be broadly classified into two kinds of techniques. The first are methods that terminate the surface with a Ge-M covalent bond, where M can be hydrogen, a halogen (Cl, Br, I), or an alkyl group,³¹⁻³⁸ and the second involves a core-shell approach that passivates the surface by forming a shell around the Ge core.³⁹⁻⁴³ Surface modification inside a metalattice is more challenging in comparison to wires, films and nanocrystals due to the interconnected structure, high curvature, and high surface area to volume ratio. This added complexity makes it difficult to extend covalent passivation methods to metalattices. Most of the covalent passivation methods involve intermediate steps that etch the sample or high temperature annealing, which could result in metalattice collapse, delamination from the supporting substrate, or a rough passivated surface. The core-shell approach, which has been employed in Ge heterostructures, nanowires and nanoparticles,

provides a conformal coating for passivation. In addition to passivation, the core-shell structures also enable band gap engineering, modulation doping, and multifunctionality.

The core-shell approach has been implemented in semiconductor nanocrystals *via* both solution and gas phase deposition methods.^{3,43-46} In 2017, Hunter *et al.*⁴³ reported the synthesis of Ge nanocrystals with Si shells using a nonthermal plasma method, which enabled more control of the core and shell dimensions in comparison to solution processes. Because of the versatility of the core-shell approach with structures and surfaces and its ability to integrate with the HPcCVD technique, we have applied it here to metalattices. In this paper, we demonstrate the chemical passivation of Ge metalattices by forming a Si shell and study the effect of the Si shell on the oxidation state/chemical composition of the Ge core. While the use of Si shells for Ge passivation is well established for 2D and 1D nanostructures, we present here the chemical passivation of a 3D interconnected Ge nanostructure using a Si shell.

Core-shell metalattices were synthesized by sequential infiltration of Ge and Si into silica templates using HPcCVD (see Figure 1), which provides access to the nanoscale voids in the template⁴⁷ and also creates a uniform and conformal shell on the Ge core. The effect of chemical passivation/ modification of Ge nanocrystals/films on their electronic structure has been commonly probed by absorption or photoluminescence (PL) spectroscopy. In the absence of bulk defects and unpassivated surface states, quantum confinement effects in nanoscale Ge can be characterized by mapping the shifts in absorption edge or PL peak positions as has been reported in several earlier studies.^{18,48-51} Core-shell metalattices did not show sharp emission features that could be attributed to Ge nanocrystals of specific sizes. Instead, broad photoluminescence was observed above the band gap energy (Figure S4), possibly due to the presence of Ge nanocrystals that have many different degrees of quantum confinement. Therefore, to probe the electronic structure at the local level in the metalattice we accessed the Ge 3d edge using electron energy loss spectroscopy (EELS) in the transmission electron microscope. This technique has been used before to probe electronic structure and bonding in a number of materials at nanometer resolution.⁵² In our system, EELS coupled with Raman spectroscopy to characterize the interdiffusion of Ge and Si atoms at the core-shell interface, provides information



Figure 2. (a) TEM image with energy-dispersive X-ray spectroscopy (EDS) maps of the Ge–Si core–shell structure showing formation of the interconnected Ge structure within a Si shell. (b) High-resolution TEM image showing (i) the crystalline Ge core, amorphous Si shell, and etched silica sphere regions; (ii) magnified region from the Ge core showing Ge lattice fringes; (iii) fast Fourier transform (FFT) of the Ge core region.

about the electronic effects of dimensional confinement and core-shell interdiffusion in the Ge metalattice.

RESULTS AND DISCUSSION

The synthesis of a core-shell metalattice is a multistep process as discussed in the Methods and illustrated in Figure 1. The silica sphere template is etched away using aqueous HF between the sequential deposition of Ge and Si. This step serves the dual purpose of template removal and termination of the Ge surface with Ge-H bonds. Even though the hydrideterminated Ge surface is stable for only a short time (maximum a few hours),⁵³ it protects the surface from oxidation prior to shell formation. Both Ge and Si are infiltrated in their amorphous forms by HPcCVD. The Ge core is annealed after the Si shell is added to ensure formation of a conformal coating. Because Ge crystallizes at a lower temperature than Si, we could selectively crystallize only the Ge core by rapid thermal annealing. TEM EDS shown in Figure 2 confirms the formation of the core-shell metalattice, and high-resolution TEM shows the amorphous Si shell and polycrystalline Ge core. X-ray diffraction (XRD) of the coreshell metalattice film also confirms the crystallinity of the Ge core (Figure S3). We observed that the width of the Ge (111) peak is approximately twice the instrumental line width, obtained from a corresponding peak of a crystalline Si standard

as shown in Figure S3. The broadening and asymmetry of the Ge peak are a function of nanocrystallite size and Si-Ge lattice mismatch-induced strain in the structure. According to the Scherrer formula (see the Supporting Information), the width of the Ge (111) reflection corresponds to a crystalline domain size of \sim 47 nm, which is about twice the size of the largest voids in the 69 nm silica sphere template (\sim 29 nm) and much larger than the diameter of the necks between voids, which is ~11 nm. This indicates that the crystalline domains extend beyond a single meta-atom. In addition, there is significant strain in the Ge lattice, as evidenced by the shift and asymmetry of the Ge-Ge Raman peak (Figure 3), and this effect contributes to the X-ray line broadening. Thus, the relatively narrow peak width of the Ge (111) reflection implies crystalline domains that extend across at least several interconnected meta-atoms in the core-shell structure.

In addition to TEM, we used Raman spectroscopy to gain insight into the structural composition of the core-shell structure. Figure 3 shows a comparison of a Ge-Si core-shell metalattice with the corresponding Ge metalattice and a CVD grown Ge film. We observe a first-order optical phonon mode for Ge-Ge at ~300 cm⁻¹ for all three Ge structures—thin film, metalattice, and core-shell—indicating successful infiltration of Ge (Table S1). In addition to the Ge-Ge mode, optical phonon modes for Ge-Si and Si-Si are also present in



Figure 3. (a) Raman spectrum at different steps of the sample preparation. The sharp Ge–Ge peak at \sim 300 cm⁻¹ indicates the presence of crystalline Ge in the metalattice. (b) Raman spectrum of the core–shell metalattice. The appearance of a Ge–Si band at \sim 390 cm⁻¹ indicates possible interdiffusion of Si and Ge.

the core-shell metalattice. The shapes of the peaks (sharp *vs* broad) confirm the presence of polycrystalline Ge and an amorphous Si shell, in agreement with the TEM images.

Following initial structural characterization of the core-shell metalattice, we investigated the possible presence of Ge oxide in the structure using XPS as shown in Figure 4. Oxidation of the exposed metalattice surface containing both Ge and Si was expected as the sample was not stored in an inert atmosphere. However, after in-situ ion milling of the top layer (20 nm), no Ge oxide signal was detected. We do not observe any Ge oxide in the structure within the detection limit of XPS. Si, on the other hand, shows the presence of an oxide after ion milling. This can be attributed to the oxidation of the protective Si shell, which upon exposure to air forms a native oxide layer and passivates the material against further oxidation of metalattice. Another source of silicon oxide could be from the silica nanoparticles. We have observed partial etching in these samples in some regions using both SEM and TEM. This means the residual SiO2 particles could also be contributing to the oxide in the XPS spectrum.

As noted above, one of the major challenges in implementing Ge in electronic devices or in even studying the fundamental properties of Ge nanostructures is the oxidation and reconstruction of the Ge surface, which leads to defect formation. The preparation of an oxide-free Ge metalattice allows us to investigate the effect of structural confinement and the Si shell on the local electronic properties of the Ge metalattice. Since the measured PL spectrum was broad (Figure S4), possibly due to different degrees of confinement at different sites within the macroscopic collection area, we used EELS to study the structure at microscopic level. With the energy and spatial resolution of EELS in the electron microscope, it is possible to obtain the Ge 3d edge energies locally at different sites in the metalattice.

The Ge metalattice conforms to the void structure of the silica nanoparticle template as shown in Figure S2 and maintains the long-range order of the template as observed in the small-angle X-ray scattering (SAXS) pattern (Figure S5). The Ge replica of the close-packed silica sphere lattice can be conceptually divided into meta-atoms and meta-bonds (MA and MB), where the meta-atoms are formed in the tetrahedral/ octahedral voids of the silica nanoparticle template and the meta-bonds correspond to the thin connections between these voids. We were able to selectively probe the Ge 3d edge at MA and MB sites as shown in Figure Sa.

A small shift of ~ 0.2 eV in the 3d edge onset between the MA and MB regions was observed (Table S2). This shift in the edge onset should be interpreted cautiously due to the several contributing parameters that include structural confinement, defects, and strain. Earlier studies by Hanrath et al.⁵⁴ and Batson et al.⁵⁵ on Ge nanowires and Si clusters, respectively, have found a size-dependent variation in the edge onset mapped by EELS, which is characteristic of the quantum confinement that has been seen in other studies of Ge quantum dots and nanowires.^{18,48–51,56} At the microscopic level, we also expect to see a variation in the degree of confinement of Ge in the metalattice due to the different sizes of the voids in the template from which it is formed. In a template composed of 69 nm diameter silica spheres, the void sizes range from 11 to 29 nm, providing different degrees of confinement for crystalline Ge, which has an exciton Bohr radius of 24 nm.⁵¹ This structural confinement by the template affects the average size of the Ge crystalline domains in the MA and MB sites and thus can contribute to the variation in the edge energy. The shift toward higher energy with decreasing void size is consistent with quantum confinement. The two types of voids labeled as MA sites in Figure 5a cannot be distinguished in the 2D image, but we speculate the trend on the basis of void size. However, structural confinement may not be the only factor determining the size of the Ge crystalline domains. Several other factors including the rate and type of nucleation and growth could also affect their size and thus the edge onset. We observe a comparable shift in the same types of sites across several samples, possibly due to variation in the average size of the crystalline domains as influenced by these other factors.

Even though structural confinement could be a significant contributor to the blue shift in edge onset, other factors in a polycrystalline core—shell system such as grain boundaries and interfacial strain may also contribute. We accessed the Ge 3d edge at different positions from core to shell to understand the local effects of the Si shell and its interaction with the Ge core. Figure 5b shows an average spectrum representing each of



Figure 4. High-resolution Ge 3d and Si 2p X-ray photoelectron spectra of core-shell metalattice before and after *in situ* ion milling top 20 nm film. The dotted lines represent fitting for respective peaks.



Figure 5. Normalized EELS spectra of the Ge 3d core-edge at (a) different sites in the metalattice structure. The spectra are stacked to highlight the shift in the inflection point (inset shows representative MA and MB sites) and (b) different points in the core/shell structure (inset shows representative core, interface, and shell points with a magnified view of the points). Scale bar in the magnified image is 25 nm.

these sites. The Ge edge at sites 1 and 2 does not show any shift in onset energy indicating no change in the oxidation state or bonding of Ge in the core. However, as we progress into the shell, there is a shift of $\sim 0.2-0.3$ eV in the edge onset (Table S3). We speculate that a change in the chemical environment

of Ge and strain at the interface can lead to these shifts. Earlier studies of core–shell Ge–Si nanocrystals have also noted a blue shift in the absorption edge onset due to strain.⁴³ Ge and Si have a lattice mismatch of ~4\%,⁴⁰ and it has been shown that lattice mismatch-induced strain is often compensated by

interdiffusion of Ge and Si.^{40,57–60} The shift in the Ge 3d edge in close proximity to the shell and the presence of a Ge–Si vibrational mode in the Raman spectrum indicate the possibility of interdiffusion leading to a change in the bonding environment of Ge. Since the shift in the Ge 3d edge occurs at sites close to or in the shell, we believe that the Ge–Si region is localized at the interface/shell and not in the Ge core.

From the trends in the EELS data, we identify two parameters that can be used to tune the electronic properties of the Ge-Si core-shell metalattice. The first parameter is the size of the voids in the template, which are defined by the size of the silica spheres used. The void size controls the degree of confinement of Ge and hence the band gap and distribution (discreteness) of electronic states. With a large exciton Bohr radius (24 nm), it is possible to confine Ge using the silica templating method. The shell and core interaction serve as a second parameter. The shell thickness and controlled interdiffusion of Ge and Si have been used previously in nanostructures to modify the strain and alloy composition at the interface, providing control of the band offset, band gap and charge carrier distribution in the material.^{39,40,43,58,61} The confinement of both electrons and holes in an oxide free Ge nanostructure can be realized in a core-shell metalattice and in principle can be tuned to affect the charge carrier mobility.

CONCLUSION

Crystalline semiconductor metalattices have been synthesized by combining HPcCVD and silica nanoparticle assembly. In this study, we have demonstrated a core-shell approach for chemical passivation and obtain an oxide-free Ge metalattice. A uniform Si shell infiltrated using HPcCVD around the Ge core prevents oxide formation as confirmed by XPS. Further structural characterization performed using TEM, Raman, and XRD confirms the formation of a core-shell structure with an amorphous Si shell and a polycrystalline Ge core. Microscopic details of structural confinement and the effect of the Si shell on the Ge core were explored locally using EELS. We observe a blue shift in the Ge 3d edge with decreasing void size, indicating the possibility of quantum confinement in the metalattices, which arises from the structure of the template. Mapping of the 3d edge along the core-shell interface indicates a chemically uniform core and possible interdiffusion of Ge and Si, as also evidenced in Raman spectra as the formation of Ge-Si bonds near the shell. The HPcCVD method enables the formation of a uniform Si shell on the Ge core, which protects it from oxidation. EELS data from the core-shell structure suggest that the degree of quantum confinement can be controlled by adjusting the size of the template spheres and the interdiffusion of Ge and Si at the core-shell interface in order to tune the band gap and charge carrier distributions. In addition, the core-shell approach demonstrated here can, in principle, be extended to different semiconductor material systems as core and shell for controlled tuning of electronic structure.

METHODS

Silica Nanoparticle Template Synthesis. Monodisperse spherical silica nanoparticles (diameter 69.2 \pm 3.2 nm, Figure S1) were synthesized using the method of Watanabe *et al.*⁶⁷ A colloidal solution of as-synthesized silica nanoparticles was diluted 10× for deposition. Double-side polished undoped silicon wafers (University Wafers) of ~280 μ m thickness and $\langle 100 \rangle$ orientation were cut into 3

cm \times 1 cm pieces. Before deposition, the silicon wafer pieces were treated with freshly prepared piranha solution (3:1 concentrated H₂SO₄: 30% v/v H₂O₂) for 15–20 min. (Caution: Piranha solution is corrosive to skin and can react explosively with organic substances.) The wafers were then copiously rinsed with water followed by ethanol and were dried in a stream of air. The diluted nanoparticle suspension was deposited on the Si wafers in open plastic vials at controlled temperature and humidity (40 °C at 80% RH) as described earlier by Russell *et al.*⁶⁸ Then 8 mm \times 5 mm pieces were diced from the films obtained at the end of 2 weeks for metalattice infiltration. The thickness of these nanoparticle films, as measured by SEM, varied from 240 to 850 nm depending on the vertical position on the substrate. A representative SEM image of the silica nanoparticle template is shown in Figure S1.

Core–Shell Metalattice Synthesis. The synthesis of a coreshell metalattice is a three-step process involving infiltration of Ge into the interstitial voids of the template followed by template etching and finally infiltration with Si to form the shell. HPcCVD was used for both Ge and Si infiltration steps. In the HPcCVD process, high pressure ensures that the mean free path of precursor molecules is on the order of a few nanometers, enabling them to penetrate the nanoscale voids of the silica template prior to decomposition on the walls. Spatial confinement of the precursor molecules results in the formation of a smooth film because it inhibits vapor-phase homogeneous nucleation of Ge or Si. The process for synthesizing the core–shell metalattice is described briefly below.

Germane (GeH₄) at a partial pressure of 5-10% in helium carrier gas at a total pressure of 20-35 MPa was used as the Ge precursor. Spatial confinement was ensured by placing U-shaped stainless-steel spacers of 25 μ m thickness between adjacent template pieces in the HPcCVD reactor. Amorphous germanium was deposited at a temperature of 325 °C for 1-3 h depending on the gas pressure and concentration. After the interstitial voids were completely filled by germanium, the germanium overlayer on top of the metalattice was removed by deep reactive ion etching (DRIE) in a chlorine plasma. The metalattice was then treated with 3% hydrofluoric (HF) acid solution in water for 4 min to etch away the silica nanospheres. (Caution: HF is highly reactive, hazardous, and corrosive.) The metalattice was then rinsed with deionized water and dried using acetone. Immediately following this etching step (within 20 min), a silicon shell was deposited in the germanium metalattice at 400 $^\circ\mathrm{C}$ using HPcCVD with silane (SiH₄) as the precursor in helium carrier gas. Silicon deposition was carried out for 30-60 min, depending on the gas pressure and concentration, to form a thin shell around Ge. The germanium core was crystallized afterward using rapid thermal annealing (RTA) at 550 °C for 120 s to promote rapid crystallization without fusion of the metalattice or significant oxygen contamination by diffusion into the structure. Figure S2 shows a Ge metalattice obtained after infiltration and etching of silica template.

Characterization. Scanning Electron Microscopy. Silica nanoparticles and the templates were imaged and sized by using a Zeiss SIGMA VP-FESEM and ImageJ software, respectively.

X-ray Diffraction. XRD on core-shell metalattice films and a Si reference sample was performed on a Malvern Panalytical Xpert Pro MPD, and the analysis was performed using Jade and Origin software.

TEM and EELS. A FEI Helios Nanolab 660 FIB/FESEM was used for TEM sample preparation. STEM images and EDS maps were collected using a Talos F200X scanning/transmission electron microscope equipped with a XEDS detector at 200 kV accelerating voltage. A double aberration corrected Titan Transmission Electron Microscope with Gatan GIF and a monochromator was used for STEM-EELS. The accelerating voltage was 80 kV with a spot size of 14 nm and an energy resolution of ~0.14 eV. A C3 aperture of 50 μ m and C2 aperture of 150 μ m were used for data acquisition with a dwell time for 10 ms for each spectrum. EELS analysis was performed in Digital Micrograph and OriginPro. The background from the plasmon peak at ~16 eV was subtracted to obtain the Ge 3d edge onset on a flat baseline. A constrained power law equation,⁶⁹ y(x) =a((x + m)(-r)) + b, where *a*, *b*, *r*, and *m* are fitting parameters, was used to fit the background, and the background-corrected spectra were compared (Figure S6). The inflection point was chosen as the edge onset.

Raman Spectroscopy. Raman spectra were collected using an ND-MDT confocal Raman (Renishaw) spectrometer. An excitation wavelength of 532 nm was used at 1 mW with a 100× objective, and the signal was collected by using a Peltier-cooled Andor CCD detector. The exposure time was limited to 20 s to prevent damage to the sample. The spectra were collected at multiple spots to confirm the uniformity of the sample.

X-ray Photoelectron Spectroscopy. XPS experiments were performed using a Physical Electronics Versa Probe II instrument equipped with a monochromatic Al K α X-ray source ($h\nu = 1,486.7$ eV) and a concentric hemispherical analyzer. Measurements were made at a takeoff angle of 45° with respect to the sample surface plane. This resulted in a typical sampling depth of 3–6 nm (95% of the signal originated from this depth or shallower). The sample was ion milled (20 nm) *in situ* to obtain a freshly cleaned surface for compositional analysis. The Si 2p and Ge 3d spectra were curve fitted into metallic and oxidized forms using CasaXPS software (version 2.3.19rev1.0k). The Si 2p spectra were fitted with 3/2 and 1/2 spin orbit doublets with peaks constrained for identical full-width-at-halfmaximum (fwhm), peak area (2:1) and an offset of +0.607 eV. The Ge 3d spectra were also fitted with matching fwhm, a 3d 5/2 to 3/2 peak area ratio of 3:2 and offsets of +0.59 eV.

Photoluminescence Spectroscopy. Measurements were made inside a cryostat (Janis Research ST-300R) using a continuous liquid nitrogen flow and illumination with a 785 nm laser diode (Coherent OBIS) operated at 50 mW with a spot size of \sim 2 mm diameter. The Ge film sample was illuminated by 640 nm diode laser operated at 100 mW. The emitted light was collected from a \sim 400 um diameter spot through a long pass filter (900 nm) and measured in a spectrometer (Horiba iHR320) with an InGaAs array (Horiba Symphony). Data are proportional to the photon flux by calibration through the same optical setup with a calibrated light source (Ocean Optics LS-1-cal).

Small Angle X-ray Scattering. Synchrotron SAXS measurements were performed at beamline 12-ID-B at the Advanced Photon Source, Argonne National Laboratory. An X-ray beam with energy of 14 keV and a spot size of $200 \times 100 \ \mu m^2$ was used, with 1s exposure time. The 2D pattern was collected in transmission mode on Pilatus 2 M detector.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c03559.

SEM image of the silica nanoparticle template (Figure S1), SEM images of a Ge metalattice after template removal and core-shell metalattice (Figure S2), XRD of the core-shell metalattice (Figure S3), photoluminescence spectra of core-shell metalattice (Figure S4), 2D and 1D SAXS patterns of a Ge metalattice after template removal (Figure S5), and background subtraction of EELS spectra (Figure S6). Peak position and fwhm of the Ge-Ge mode in Raman spectra (Table S1). Average values and standard deviations of Ge 3d edge onsets at different sites (Table S2 and S3) (PDF)

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Author Contributions

P.M. and P.M. designed the study in consultation with T.E.M., N.A., J.V.B., and N.C.G. P.M., P.M., H.Y.C., N.N.N., A.G., B.L., L.R.D.J., and M.W. carried out the experimental work, and all authors contributed to the analysis of the data. The manuscript was drafted by P.M. and P.M. and edited by T.M. and N.A.

Notes

The authors declare no competing financial interest. ∇ (J.V.B.) Deceased October 26, 2019.

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