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Silicon Nanocrystal Superlattices

Yixuan Yu^[a], Christian A. Bosoy^[a], Dr. Colin M. Hessel^[a], Dr. Detlef-M. Smilgies^[b], and Prof. Brian A. Korgel^[a]

Brian A. Korgel: korgel@che.utexas.edu

^[a]Department of Chemical Engineering, Texas Materials Institute, and Center for Nano- and Molecular Science and Technology, The University of Texas at Austin, Austin, Texas 78712-1062, USA, Fax: (+1)512-471-7060

^[b]Cornell High Energy Synchrotron Source (CHESS), Cornell University, Ithaca, New York 14853, USA

Abstract

Colloidal silicon (Si) nanocrystal superlattices—Nanocrystal superlattices have finally been made of the most commercially relevant semiconductor, silicon. These sterically-stabilized nanocrystals self-assemble into face-centered cubic (fcc) superlattices. Their thermal stability is much more robust than other types of nanocrystal superlattices because of the strong covalent bonding of the hydrocarbon capping layer.

Keywords

Silicon; nanocrystals; self-assembly; colloids; superlattices

Colloidal nanocrystals with precisely controlled size and shape can be assembled into ordered superlattices.^[1–3] Superlattices have been made of a wide range of materials, from semiconductors to metals to insulators, and have been explored for various applications, including sensors,^[4–6] transistors,^[7,8] data storage,^[9] solar cells,^[10] and thermoelectrics.^[11] Nonetheless, colloidal nanocrystal superlattices have not yet been made of one of the most commercially relevant semiconductors, silicon (Si). Here, we report the first colloidal silicon (Si) nanocrystal superlattices. Additionally, we examined their thermal stability and found that they are much more robust than other types of nanocrystal superlattices, retaining their structural order to relatively high temperatures (>350°C) because of the strong covalent bonding of the hydrocarbon capping layer.

Si nanocrystals are interesting for many applications, but especially for optoelectronics requiring light emission. Bulk Si is a poor light emitter due to its indirect band gap, but Si nanocrystals—or quantum dots—can exhibit bright, size-tunable, visible photoluminescence and electroluminescence,^[12] making them suitable as a down-converting phosphor or active emitting material in light-emitting diodes.^[13] Si quantum dots are even being explored as a laser source.^[14] Photovoltaic devices utilizing Si quantum dots have also been proposed^[15] because of their size-tunable optical absorption edge, much higher absorption coefficient and the potential for multiexciton generation (MEG).^[16] Most of these applications require arrays of nanocrystals and there have been efforts to fabricate them. But the collections of Si nanocrystals studied to date have been disordered, usually with a significant size distribution. Some success towards order has been achieved by thermally annealing

Correspondence to: Brian A. Korgel, korgel@che.utexas.edu.

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alternating layers of amorphous Si and SiO₂ to yield periodically stacked monolayers of relatively monodisperse Si nanocrystals in SiO₂, but without positional in-plane order.^[17–19] Here, we report the self-assembly of colloidal Si nanocrystal superlattices with face centered cubic (fcc) order.

Si nanocrystals were synthesized by thermal decomposition of hydrogen silsesquioxane (HSQ) followed with HF etching, thermal hydrosilylation with 1-dodecene and finally a size-selective precipitation. The nanocrystals were dispersed in chloroform and drop cast. Ordering of the nanocrystals was observed by both transmission electron microscopy (TEM) and grazing incidence small angle X-ray scattering (GISAXS), as shown in Figure 1. The GISAXS pattern exhibits both rings and spots that index to an fcc superlattice with a lattice constant of $a_{SL}=15.5$ nm. The occurrence of diffraction spots indicates specific orientations of superlattice domains with respect to the substrate. The spots index to fcc superlattice domains with (111)_{SL} and (100)_{SL} planes parallel to the substrate (i.e., (111) and (100)-oriented). TEM images (as in Figure 1), showed regions of fcc superlattice oriented with (111)_{SL} and (112)_{SL} planes parallel to the substrate. Based on the sizes of the diffraction spots in the GISAXS patterns, these ordered superlattice grains are about 120 nm in diameter (See Supporting Information). The occurrence of the scattering rings in the GISAXS pattern indicates that there are superlattice grains randomly oriented with respect to the substrate as well (See Supporting Information).

Based on the lattice constant of $a_{SL}=15.5$ nm, the nearest neighbour interparticle separation (center-to-center) is 11.0 nm. The Si core diameter of the nanocrystals determined from SAXS measurements of solvent-dispersed nanocrystals was 8.0 ± 1.2 nm (Supporting Information). The length of a fully-extended C₁₂ alkyl chain is 1.7 nm, so the edge-to-edge separation of the nanocrystals (3.0 nm) is slightly less than the twice the length of the fully extended capping ligands (3.4 nm). Based on the volume of the superlattice occupied by ligand, there appears to be a slight excess of free ligand in the superlattice.^[20]

The thermal stability of the Si nanocrystal superlattices was also tested. Figure 2 shows GISAXS of a fcc superlattice of Si nanocrystals as it was heated from 35°C to 375°C. The (111) and (220) diffraction spots are still observed in the GISAXS pattern up to 280°C, although the higher order diffraction spots have disappeared, indicating that some disorder occurs but the superlattice retains its fcc structure. Even up to 375°C—the highest temperature possible in the experimental setup—the Si nanocrystal superlattice showed (111) and (220) diffraction spots, indicating that the nanocrystals remain unsintered. There was, however, a slight contraction in the lattice as it was heated above 280°C due to loss of ligand.

The Si nanocrystal superlattices are much more stable than superlattices of other kinds of nanocrystals. For example, superlattices of dodecanethiol-capped Ag nanocrystal disorder at 180°C.^[21] Superlattices of oleic acid- capped PbSe nanocrystals,^[22] oleic acid-capped PbS nanocrystals,^[23] and dodecanethiol-capped Au nanocrystals^[24] sinter at much lower temperatures of 168°C, 230°C, and 200°C, respectively. The high thermal stability is attributed to the strong covalent Si-C bonded alkane ligand layer on the Si nanocrystals, although it is also possible that partial oxidation of the Si nanocrystals surface during heating in air helps limit sintering. Thermal gravimetric analysis (TGA) of Si nanocrystals (Figure 2F) showed three stages of ligand desorption: (1) evaporation of free ligand at around 190°C; (2) desorption and evaporation of bound ligand between 270°C and 520°C; and (3) significant oxidation of the Si core between 520°C and 800°C.

Figure 3 shows a TEM image of an fcc superlattice of smaller 2.4 nm diameter Si nanocrystals capped with a mixture of 1-dodecene and 1-octadecene. (More TEM images

are provided in supporting information.) From TEM, the (110)_{SL} d-spacing is 4.8 nm, corresponding to a superlattice lattice constant of $a_{SL}=8.3$ nm. From SAXS of solution-dispersed nanocrystals, the Si core diameter is 2.4 ± 0.52 nm. The polydispersity of just over 20% is somewhat surprising since this degree of polydispersity usually prevents ordering; however, there may be a size-selection and purification that occurs during the superlattice formation process. Based on the superlattice dimensions and the nanocrystal diameter, it is clear that there is excess free ligand in the superlattice. This was obvious when drop-casting the nanocrystals. Unlike the larger nanocrystals, the smaller nanocrystals could not be completely dried into a film, even when stored under vacuum at 150°C for 12 hours due to the excess ligand in the sample. As in the case of the larger diameter nanocrystals, excess ligand appears to be important for helping superlattice order, in this case easing the strain in the superlattice that would arise from the relative polydispersity of the nanocrystals.

Colloidal Si nanocrystal superlattices were self-assembled and characterized by TEM and GISAXS. The superlattices exhibit fcc structure for both large (8.0 nm diameter) and small (2.4 nm diameter) nanocrystals. GISAXS showed that a significant amount of superlattice grains had specific orientations with respect to the substrate with (111)_{SL} and (100)_{SL} planes parallel to the underlying substrate. Superlattices with (112)_{SL} planes oriented parallel to the substrate were also observed by TEM. The Si nanocrystal superlattices were found to be very thermally stable, much more than other types of nanocrystal superlattices. Their thermal stability appears to relate to the robust covalent Si-C bonding of the capping ligand layer.

Experimental Section

Si nanocrystal synthesis

Si nanocrystals were prepared following the procedures described by Hessel, et al.^[25,26] 3 g of HSQ (purchased as FOx 16® from Dow Corning Corporation, 16% HSQ by weight in methylisobutylketone) is heated in a flow of forming gas (93% N₂, 7% H₂) at 1100°C or 1250°C for 1 hour to yield a brown glassy product, which is ground with an agate mortar and pestle to a brown powder. The grain size of the powder is reduced further in a wrist-action shaker for 9 hours with 30 g of 3 mm diameter borosilicate glass beads.

300 mg of powder, composed of SiO₂-embedded Si nanocrystals, is suspended in 10 ml of 40% HF and 1.5 ml of 25% HCl and stirred in the dark for 16 hours. Hydride-terminated Si nanocrystals are isolated by centrifugation at 8000 rpm for 5 minutes, and then rinsed twice with 8 ml of ethanol and once with 8 ml of chloroform. The final light brown material is dispersed in 8 ml of 1-dodecene by sonication to form a brown turbid dispersion, which is transferred to a three neck flask and degassed with 3 freeze-pump-thaw cycles. The turbid dispersion is heated at 190°C under N₂ for 18 hours and then allowed to cool to room temperature. The resulting optically clear dispersion is centrifuged at 8000rpm for 5 minutes and the precipitate (unpassivated nanocrystals) is discarded. 20 ml of acetone is added to the supernatant to precipitate the passivated nanocrystals, which are then collected by centrifugation and dispersed in 2ml of hexanes. The passivated nanocrystals dispersed in hexanes are then washed three times by precipitation with ethanol as antisolvent (20 ml) and dispersed in 2 ml of hexanes.

Size-selective precipitation

Ethanol is added dropwise to the hexanes dispersion of Si nanocrystal until dispersion becomes slightly opalescent. The dispersion is then centrifuged at 8000 rpm for 5 minutes and the precipitate (extra large or poorly passivated nanocrystals) was discarded. One more drop of ethanol was added to the supernatant, centrifuged at 8000 rpm for 5 minutes, and the

precipitate was discarded. One more drop of ethanol was added, followed again by centrifugation. The precipitate was discarded. 15 ml of ethanol was then added to the dispersion and centrifuged at 10000 rpm for 10 minutes. The supernatant was discarded (extra small nanocrystals). The precipitate was dispersed in 2 ml of hexanes.

Superlattice formation

The 8.0 nm diameter Si nanocrystals were dispersed in hexanes at 3 mg/ml. 50 μ l of this hexanes dispersion was dried in a vial and then redispersed with 20 μ l of chloroform. The chloroform dispersion was drop-cast onto a silicon substrate for GISAXS. The chloroform dispersion was further diluted and drop-cast onto a Cu TEM grid for TEM imaging. The 2.4 nm diameter Si nanocrystals were dispersed in toluene and drop-cast onto a carbon-coated Ni TEM grid for TEM imaging.

GISAXS and SAXS

GISAXS and SAXS measurements were performed at the D1 beamline of the Cornell High Energy Synchrotron Source (CHESS) using 10 keV photon energy as described by Goodfellow, et al.^[22] and Smilgies, et al.^[27]

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 2.

A–E) GISAXS of a (100)-oriented FCC superlattice of Si nanocrystals as it was heated to the indicated temperature. F) TGA of Si nanocrystals.

Figure 3.

TEM image of an fcc superlattice of 2.4 nm diameter Si nanocrystals capped with a mixture of dodecene/octadene. Inset: Fast Fourier transform (FFT) of the TEM image indexed to an fcc superlattice. The superlattice is oriented with $(111)_{\text{SL}}$ planes parallel to the substrate. The superlattice has a lattice constant of $a_{\text{SL}}=8.3$ nm.