Self-assembly of Ag/SiO$_x$ spherules in triangular pattern on strained surface of primary particles

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Spontaneous emergence of nanoscaled structures provides a potential alternative to the conventional bottom-up and top-down fabrication techniques. By a two-step thermal evaporation of mixed Ag$_2$O and SiO$_2$ powder onto sapphire substrate, concentric Ag/SiO$_x$ spherules were assembled into a triangular pattern upon cooling on the spherical surface of large particles, which, of generally a few microns in dimension, were primarily grown with the substrate held at 1270 K. The occasional presence of pentagon or heptagon defect, as required by the spherical geometry of the primary particle, was also recognized. Strain field in the oxide shell arising from expansion mismatch with the silver core seeds the subsequent nucleation events. The triangular pattern of the secondary nanoparticles can be accounted for with a minimized strain energy in the spherical surface. The self-assembled structure of striking uniformity is promising for the generation of a large family of building blocks for device production. © 2004 American Institute of Physics.

FIG. 1. SEM image of Ag/SiO$_x$ deposits of various dimensions on the sapphire substrate.

Self-assembly has turned out to be very promising in preparing highly ordered structures for device production: the emergence of nanoscale features is likely to provide a third way in addition to the conventional bottom-up and top-down fabrication techniques.$^1$ The common strategy for realizing self-assembly is to exploit some mismatched properties in the system-lattice constant, thermal expansion, diffusion rate, and so on. Depending on the mismatched system, the periodicity of the self-assembled structures extends from a few nanometers to a few microns,$^{2,3}$ they thus can meet the requirements for the fabrication of most contemplated quantum devices. Employing lattice mismatch for the growth of semiconductor quantum dots has gradually become a matured technique in the past decade. In planar geometry, quantum dots showing Z-direction registry over ten layers have been reported in several multilayered semiconductor structures.$^{4,5}$ Recently, hollow nanocrystals and yolk-shell structures have been synthesized by using wet chemistry method, where the assembly process is driven by a large difference in diffusion rate.$^6$

In recent times, mismatched thermal expansion has also received increasing attention as an effective mechanism driving self-assembly in layered structures. Upon cooling of thermally expanded films, nonuniform stress accumulates in the layer, which has to be relieved when exceeding a critical value. This results in buckling of the layers giving rise to complex, ordered structures, as has been demonstrated and analyzed by Bowden, Chen and co-workers.$^{3,7}$ The strain field can be manipulated by creating nonplanar substrate topography prior to the growth, from which some more regular patterns are anticipated.

In this letter, we report an application of the strained layer resulting from mismatched expansion. The primary Ag/SiO$_x$ particles of yolk-shell construction would be cooled down, but not so harshly to cause any buckling. The nodal points in the resulting strained layer seed further growth process, giving rise to a triangular pattern of second-
0.8–1.0 μm. These islands are clearly nuclei at initial growth stage—influence of the substrate on the particle geometry is still discernible. The spherical, middle-sized particles are quite uniform in size, with an averaged diameter of 2.5 μm. Accordingly, a smaller density of 1.4 × 10^6/cm^2 was measured. In the image, a bright halo around such particles discloses their yolk-shell structure with silver inside. Thickness of the cell is slightly less than one-third of the particle radius. This yolk-shell structure has been confirmed by our TEM and electron energy loss spectroscopic study of one-dimensional Ag/SiO\_2 capsules in analogy to the samples concerned here. In fact, the segregation of silicon and its oxides to the surface of metal liquid drops has been employed for the fabrication of concentric nanowires.\(^9,10\) The third class is comprised of large particles of complex infrastructure, which bear vivid resemblance to the sunflower showing petal at periphery, spherically curved disk, and regularly arranged seeds. Averaged dimension for these large particles is about 8.0 μm, while the density is 1.3 × 10^7/cm^2, roughly one-tenth of that for the middle-sized ones.

The most striking feature on the large particles is the triangular pattern of spherules on them (Fig. 2). The spherules have the same yolk-shell construction as the mother particle, and they show remarkable uniformity in size with a diameter of ~620 nm. In most part of the curved surface away from the bottom of the underlying large particle, the spherules are arranged in a triangular pattern. A separation of ~830 nm was measured among the nearest neighbors. It is worth noting that also the occasional presence of pentagon or heptagon defect, either centered or not, was identified in Fig. 2, as required by Euler’s rule for the covering of spherical surface with hexagons, remembering that the triangular lattice can be taken as the centered hexagonal one.

Formation of the highly ordered pattern on the large particles can be understood in terms of a two-step growth process. The large particles underlying the ordered pattern are primarily the middle- and small-sized ones, grown when the substrate was held constant at 1270 K. At this stage, super-saturated Ag vapor first nucleates at the substrate, which then provides the sinks for the SiO\_2 clusters. The islands thus formed will coalesce and/or absorb silver atoms and SiO\_2 cluster from the ambient to sustain the growth process. This mechanism is quite advantageous for the synthesis of nanowires.\(^9,10\) Character for this growth stage is the random nucleation sites. In contrast, the patterned spherules can only be self-assembled by conforming to some primary, highly ordered nucleation sites, which we believe to be the strain field induced in the underlying large particles. Recall that the expansion coefficient for Ag is 27.1 × 10^{-6} at 1100 K, say, while that for silicon oxide is about 0.45 × 10^{-6}.\(^11\) Consequently, a large compressive stress is anticipated in the shell when the yolk-shell structure of Ag/SiO\_2 contracts upon cooling from 1270 K. The nearly equi-biaxial stress field, thus also the strained layer, should adopt an ordered pattern so as to minimize the total strain energy in the layer. For spherical geometry, simply based on the symmetry consideration, the most reasonable candidate is the triangular pattern decorated with occasional pentagons or heptagons, in analogy to the checkboard mode in the planar arrangement.\(^7\) The fact that the nodal points of the strained SiO\_2 seed the subsequent growth in the course of cooling was evidenced by one more observations: the pattern of secondary particles is preserved against modified cooling rate. At a slower cooling rate, the spherules continue growing into long rods. The large separation among the spherules indicates the long wave nature of the seeding strain field, as should be the case for the oxide shell far from its critical deformation.

In summary, triangular pattern of Ag/SiO\_2 spherules of remarkable uniformity was grown on the spherical surface of primary large particles. Self-assembled pattern of strained oxide shell caused by mismatched contraction upon cooling provides seeding sites for the subsequent growth of secondary spherules. Evidently, the spherical geometry puts a stronger constraint on the strain field, which can be exploited for the fabrication of highly ordered structures. Yet some questions concerning this synthesis process remain open: what is the critical size of the primary particle desired for the secondary particle growth? Can the self-assembled pattern on an imperfect spherical surface be free from pentagon and heptagon defects, as structural uniformity is essential for the product of high-quality nanoscale quantum devices? These questions can be only answered by further deliberately controlled experiments.

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