

Ordered Arrays of Silicon Nanowires Produced by Nanosphere Lithography and Molecular Beam Epitaxy

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ABSTRACT

Because of their importance in fundamental research and possible applications in nanotechnology and nanoelectronics, semiconductor nanowires have attracted much interest. In addition to the growth itself, the control of the size and location is an essential problem. Here we show the growth of ordered arrays of vertically aligned silicon nanowires by molecular beam epitaxy using prepatterned arrays of gold droplets on Si(111) substrates. The ordered arrays of gold particles were produced by nanosphere lithography.

The vapor–liquid–solid (VLS) process is regarded as the fundamental mechanism of the growth of crystalline Si nanowires.¹ Different growth techniques have been developed for the fabrication of silicon nanowires: chemical vapor deposition,² pulsed laser deposition,³ and molecular beam epitaxy (MBE).⁴ The growth process is based on the control of small liquid droplets of a metal or alloy where the supersaturation of one component leads to a one-dimensional growth of a nanowire. The liquid alloy remains on the tip of the growing nanowire, and it is fed by the surrounding gas phase with new material. In the case of Si nanowire synthesis, the liquid droplet is an Si–Au eutectic.

Recently, we have demonstrated the fabrication of Si nanowires by MBE,⁵ where gold droplets with significant size distribution and random location were used to promote the VLS growth. The Au droplets were formed by thermal treatment of a thin gold layer deposited in situ. However, an important requirement for device applications is the precise control of the location and the size of the nanowires. While the length of the Si nanowires is determined mainly by the MBE conditions (Si flux, growth temperature, and time), the diameter and the location of the nanowires are controlled by the diameter and the location of the gold droplets. Therefore, the application of lithographic methods for regularly arranged Si nanowires seems to be obvious. In addition to conventional lithography, more and more alternative inexpensive nanolithographic methods are used to

fabricate nanosized patterns.⁶ One of them is the “natural lithography”,^{7,8} later renamed to nanosphere lithography,⁹ in which close-packed monolayers or bilayers of monodisperse spherical particles are used as a lithographic mask. This method has already been applied successfully for the pre patterning of substrates, for example, for the fabrication of magnetic nanoparticles¹⁰ or carbon nanofibers.¹¹ Hochbaum et al.¹² used a soft lithography method to determine regions on the sample where the nanowires should grow and controlled the nanowire diameter and density by using gold colloids.

In previous experiments,⁵ attempting the self-organized growth of Si nanowires, a random distribution of gold droplets with diameters between 40 and 200 nm was used as a template for the growth. However, in this case the nanowires had no sharp size distribution. The utilization of nanosphere lithography in this work overcomes this problem. In the combination with MBE growth, two main preparation features have to be realized: (i) any oxide layer has to be removed before the deposition of Si atoms and (ii) the regular arrangement of the Au droplets should not be disordered, for example, by coalescence. The first feature should guarantee a direct contact between the droplet and the substrate and subsequent epitaxial growth. Even a native oxide layer of about 2 nm would prevent the formation of nanowires.

For all experiments, (111)-oriented Si wafers (As-doped, resistivity of <0.005 Ωcm and P-doped, resistivity of 1–20 Ωcm, respectively) were cut into pieces of 2 × 2 cm².

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Slightly misoriented substrates (about 2°) were used in some experiments to investigate the influence of surface steps on the growth. The substrates were cleaned by the conventional RCA I process to get hydrophilic silicon surfaces, that is, a treatment with a 1:1:5 solution of NH_4OH (25%), H_2O_2 (30%), and water at 80°C for 15 min just before usage.

Monodisperse polystyrene particles (purchased from Microparticles GmbH Berlin) with diameters of 488 (polydispersion index PDI 0.11), 600 (PDI 0.08), 780 (PDI 0.08), 1040 ± 30 , and 1320 ± 40 nm, respectively, were received as a 10 wt % suspension in water. They were further diluted with methanol containing 0.25% Triton X-100. For spheres up to 1040 nm, the corresponding suspensions were then spin-coated onto the wafers according to the technique described by Hultheen et al.⁹ Depending on the particle concentration and the spin speed, monolayers and bilayers of spheres were formed. In contrast to masks of a monolayer of polystyrene spheres, where the deposited metal particles are arranged in a hexagonal two-dimensional lattice with a two-point basis (honeycomb structure), a primitive hexagonal arrangement of the metal clusters is obtained for polystyrene bilayers. It should be mentioned that the periodic arrangement of the polystyrene spheres might be locally disturbed. The most serious defects are grain boundaries. The spin-coating method⁸ could be applied successfully for particles with diameters smaller than 1100 nm. For larger spheres, the layers were prepared by a drying method described by Burmeister et al.¹³

After the formation of the polystyrene layer on the Si substrate, gold was deposited through this mask containing triangular holes between the spheres in a thermal evaporation system (B 30.2, HVT Dresden) at a deposition rate of 0.1 nm/s. The basic pressure in this chamber amounted to 5×10^{-6} mbar. The deposited film thickness was between 10 and 20 nm. After the Au deposition, the polystyrene spheres were removed from the substrate by (i) CH_2Cl_2 in an ultrasonic bath for 2 min and (ii) by a subsequent rinsing in acetone, ethanol, and water.

For the growth of nanowires, the substrates prepatterned with the Au islands were inserted in a RIBER SIVA 45 ultrahigh vacuum MBE chamber. To remove the native oxide from the surface by desorption, the substrates were heated at 810°C for 10 min. This temperature also transformed the triangular gold islands into hemispheres, but it was low enough to keep the arrangement of the islands stable. Temperatures higher than 850°C gave rise to an increasing distortion of the order of the gold particles. After cooling the substrate to 525 or 570°C , the nanowire growth was started by silicon deposition at a flux rate of 0.5 \AA/s and stopped after an initial growth time of 36 min, resulting in nanowires with lengths of about 250 nm. For longer growth times, nanowires with lengths of at least $1 \mu\text{m}$ and aspect ratios up to 10 could be obtained.

The morphology of the samples was investigated by scanning electron microscopy (Philips ESEM XL 30 FEG).

Figure 1 demonstrates the steps necessary for nanowire fabrication in the case of a polystyrene monolayer deposition. The corresponding scanning electron microscopy (SEM)

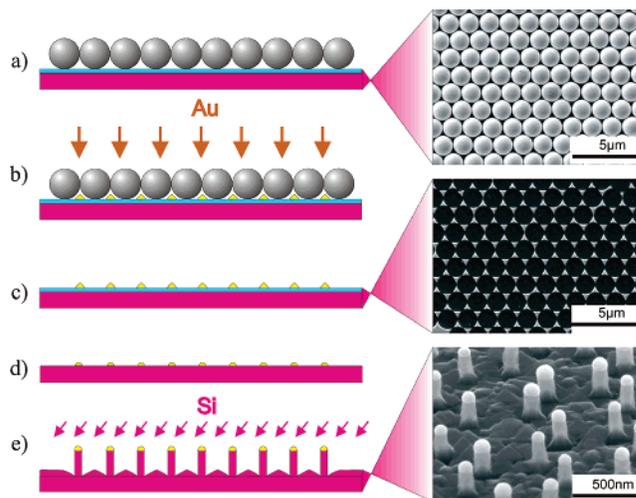


Figure 1. Steps of Si nanowire fabrication. Nanosphere lithography: (a) deposition of a mask of polystyrene particles on a Si(111) substrate covered by a 2-nm-thick oxide layer (blue), (b) deposition of gold by thermal evaporation, (c) removal of the spheres, (d) thermal annealing and cleaning step to remove the oxide layer, and (e) Si deposition and growth of nanowires by MBE. (Right) corresponding SEM micrographs of wafers at different steps: regular monolayer mask and structured gold layer made using 1320-nm polystyrene particles. The Si nanowires were grown with gold templates produced with 600-nm polystyrene particles.

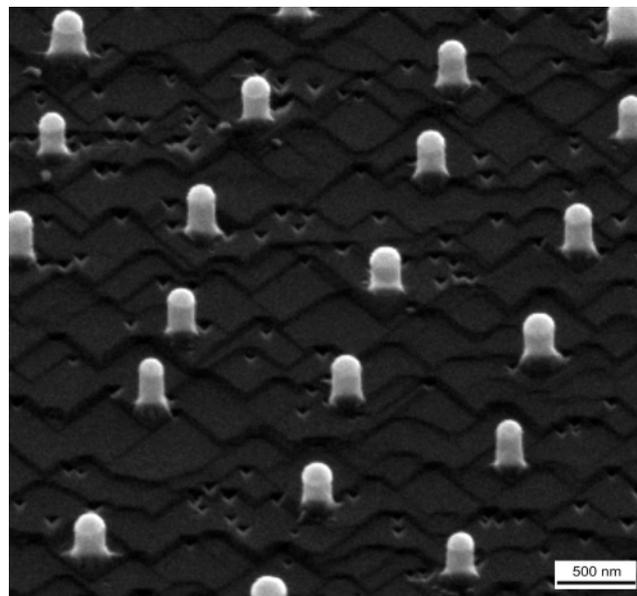


Figure 2. SEM image of a nanowire array obtained on a Si(111) wafer using a bilayer mask of polystyrene particles with an average diameter of 1320 nm. The diameter of the nanowires depends on the size of the Au droplets, which remain on the tips of the wires. During the formation of the nanowires, a thin Si layer also grows on the wafer surface and becomes visible as a steplike structure because of the miscut of about 2° of the (111) wafer used.

micrographs on the right show the monolayer mask (a), the deposited gold structure for 1320-nm polystyrene particles (c), and Si nanowires grown using gold islands produced by 600-nm-diameter particles (e).

Figure 2 shows an SEM image of a region of ordered nanowire growth using Au deposition through a bilayer mask of 1320-nm polystyrene particles. The gold particles on the

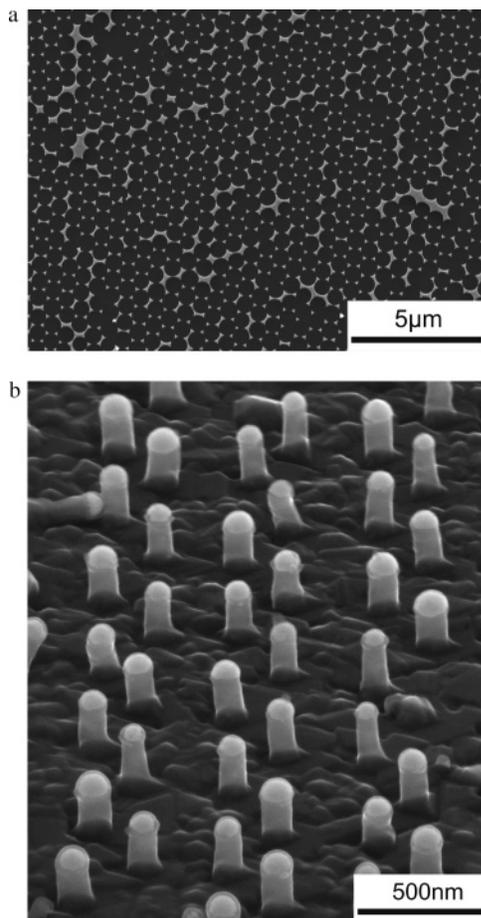


Figure 3. (a) SEM micrograph of an Si wafer (dark) with Au islands (bright). The size distribution of the Au islands resulting from the size distribution of the polystyrene spheres used is clearly visible. (b) Corresponding arrangement of nanowires after MBE growth.

top of the wires can be recognized clearly. The stepped growth on the surface of the substrate visible in Figure 2 is a result of the miscut of the wafer used.

Domains of well-ordered polystyrene spheres of up to $20 \times 20 \mu\text{m}^2$ in a single orientation were obtained with monolayers or bilayers of polystyrene spheres with a diameter of 600 nm. Figure 3a shows gold islands deposited through a single domain polystyrene particle monolayer. Although the order of the spheres is perfect, their size distribution leads to larger gold islands disturbing the perfect long-range order of nanowires and their size distribution. Figure 3b gives a detailed view of Si nanowires grown using such monolayer structures. SEM images were used to analyze the size distribution of gold particles after thermal annealing and the corresponding Si nanowires resulting from monolayer and bilayer masks. The results in Figure 4 show that the diameters of the Si nanowires essentially correspond to those of the gold particles because the maxima of the size distributions of the droplets and the nanowires are found at approximately the same position. Furthermore, we observed that bilayer masks result in smaller diameters of gold particles and the corresponding Si nanowires. The nanowires have a significantly larger diameter distribution than the Au droplets in the case of polystyrene monolayers (see the fwhm values

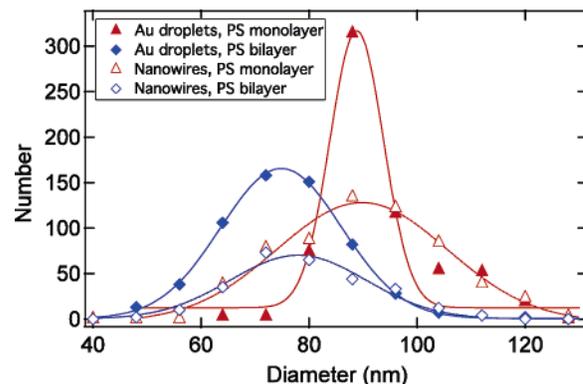


Figure 4. Correlation between the diameter of gold droplets, measured after ex situ thermal annealing at 530 °C and the diameter of Si nanowires. The size distribution of deposited gold droplets (full symbols) and the nanowires grown (open symbols) using a monolayer (triangles) and a bilayer (diamonds) of polystyrene (PS) spheres is shown. The lines show the corresponding Gaussian fits of the number of droplets or nanowires counted by SEM on a wafer. The mean values of the diameters (in nm) are: 89 (Au droplets, PS monolayer), 90 (Si nanowires, PS monolayer), 75 (Au droplets, PS bilayer), and 78 (Si nanowires, PS bilayer). The full width at half-maximum (fwhm) of the fitted curves are (in nm): 7 (Au droplets, PS monolayer), 22 (Si nanowires, PS monolayer), 16 (Au droplets, PS bilayer), and 18 (Si nanowires, PS bilayer).

in the caption of Figure 4). However, a direct comparison of the two curves is difficult because the size of the Au droplets has been measured after ex situ annealing at 530 °C, without removing the native oxide layer. Compared to results obtained with gold colloids¹² for Si nanowires and for nanowires fabricated by electron beam and nanoimprint lithography, respectively, for example, InP,¹⁴ nanosphere lithography gives in our case a larger size distribution (compare the fwhm values of the fitted curves in Figure 4). This is mainly because of the size distribution of the polystyrene spheres used. A higher monodispersity of the polystyrene particles should result in a narrower distribution in the diameters of the grown Si nanowires.

In conclusion, nanosphere lithography was found to be an inexpensive, simple, and fast lithographic tool for the fabrication of regularly arranged gold islands in the nanometer range to obtain ordered arrays of Si nanowires by MBE growth. The native oxide layer has to be removed, for example, by thermal evaporation, to guarantee epitaxial growth. We have shown that it is possible to remove the native oxide layer on lithographically prepatterned substrates after the deposition of gold particles by an in situ thermal annealing step of the silicon wafer while keeping the order of the particles.

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