Communication

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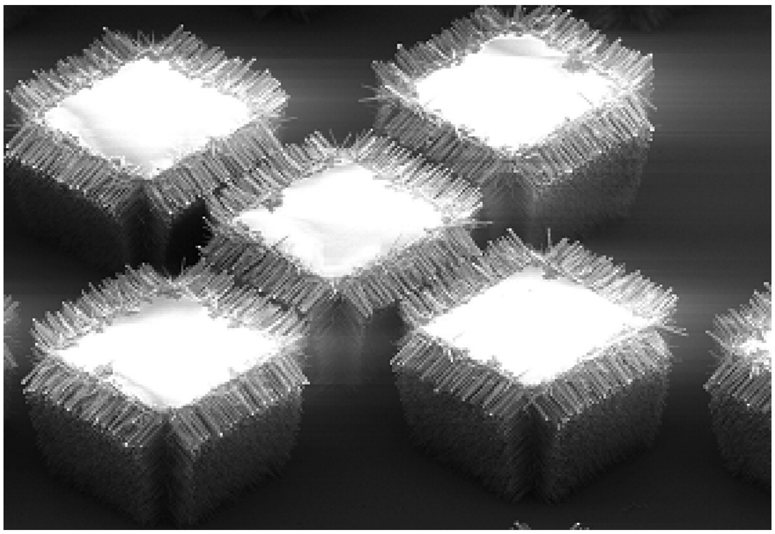

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Selective Growth of Si Nanowire Arrays via Galvanic Displacement Processes in Water-in-Oil Microemulsions

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Semiconductor nanowires are expected to break through the fabrication limitations of the present IC industry and be employed as both interconnects and functional units in electronic, optoelectronic, electrochemical, and electromechanical devices.[1−3] Although significant progress has been made recently in the development of nanowire-based sensors, field effect transistors, and lasers, the synthesis and assembly of nanowires for reproducible mass-fabrication of these devices remain a challenge. Among the bottom-up approaches, the vapor−liquid−solid (VLS) method has attracted much attention for its application in synthesizing single-crystalline nanowires of various compositions in large quantities and its self-alignment capability during the growth of nanowires.[4−7] The diameters of the nanowires synthesized by the VLS method are mainly determined by the size of the metal clusters that serve as the nucleation sites during the initial phase of the nanowire growth.[8]

The ability to control the nanowire size, orientation, and location during growth is critically important, because it allows the growth and assembly of nanowires to be combined into one step, facilitates the subsequent fabrication processes such as the formation of electrical contacts to nanowires, and opens up the design space for novel devices. Most nanowires synthesized via the VLS mechanism have a preferred growth direction. This characteristic can be employed to control the nanowire alignment to the substrate by choosing the proper substrate orientation. For example, Si nanowires grow preferentially along ⟨111⟩ direction, and hence, vertically aligned nanowires can be obtained on Si(111) substrate during a chemical vapor deposition (CVD) process.[9] Laterally aligned Si nanowires have also been obtained on vertical Si(111) sidewalls fabricated on (110)-orientated Si wafers.[10] Typically, the nucleating metal catalysts used in the VLS process are previously synthesized nanoparticles or thin films deposited by physical vapor deposition (PVD), which coat the entire substrate indiscriminately. As a result, the nanowires grow everywhere, making it difficult to fabricate devices. Ideally, the metal catalysts should only be deposited in the locations where the nanowires are desired.

In this communication, we report the use of galvanic displacement processes to selectively deposit Au nanoclusters on Si surfaces for the growth of vertically and laterally aligned Si nanowire arrays. Water-in-oil microemulsions are employed in the galvanic displacement process to control the size of the Au clusters, which in turn control the size of the nanowires synthesized by the VLS method.

The galvanic displacement process has been investigated and employed to deposit Au thin films and nanoclusters on Si surfaces for microelectronics applications.[11−13] The key advantage of this approach is that the metal deposition occurs selectively on Si surfaces and not on other surfaces such as silicon dioxide and silicon nitride (commonly used masks in microfabrication). In a galvanic

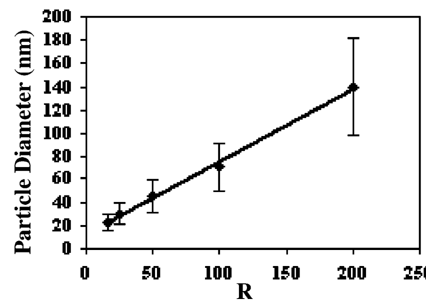

Figure 1. Plot of the Au cluster size in diameter as a function of the microemulsion parameter *R*.

displacement process, gold is deposited on Si through a redox mechanism, in which the Si substrate acts as a reducing agent for gold ions in the solution. Water-in-oil microemulsions have been used in the galvanic displacement process to control the size of Au nanoclusters deposited on Si surfaces.[14] Water-in-oil microemulsions are dispersions of water droplets (reversed micelles) in oil, stabilized by the presence of a surfactant. The size of the micelle is known to be a function of the microemulsion parameter *R*, defined as the ratio of the molar concentrations of water and the surfactant (R = [water]/[surfactant]).[15] The size of the deposited metal clusters in the galvanic displacement process has been found to be determined by the nominal micelle size over a wide range of the microemulsion parameter, *R*.[14] This fact is employed here to control the size of the Au catalyst and, hence, the size of the nanowires synthesized by the VLS method.

Figure 1 plots the diameter of Au clusters deposited on Si(111) substrates by the galvanic displacement process using microemulsions with different *R* values. The mean size of the Au clusters increases roughly from ∼22 to ∼140 nm as *R* increases from 16 to 200. When the galvanic displacement process is performed in water-based solution (i.e., no oil or surfactant), the size of the Au clusters has a wide distribution from 30 to 300 nm, and cluster agglomeration is observed. Figure 2 shows the scanning electron microscopy (SEM) images of vertically aligned Si nanowire arrays grown from Au clusters deposited on Si(111) substrates. The *R* of the microemulsion used in the galvanic displacement process is 16 (a), 25 (b), 50 (c), 100 (d), and 200 (e), respectively. As expected, the diameter of the Si nanowires is determined by the Au cluster size, which serves as the nucleation sites in the initial phase of the nanowire growth. In Figure 2, the Au−Si alloy droplets are clearly seen at the tip of the nanowires after the nanowire growth, which confirms the VLS growth mechanism. Unlike the straight nanowires synthesized in other images, the nanowires grown from the smallest Au clusters deposited in this experiment (about 20 nm) are observed to kink in Figure 2a. This phenomenon has been observed and reported in earlier work.[4] In Figure 2f, the Au clusters used to catalyze the nanowire growth are deposited from water-based

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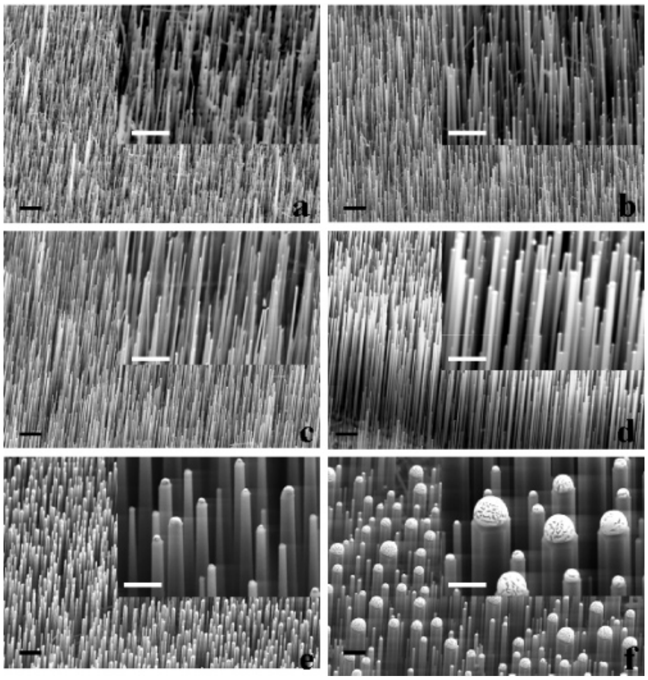

Figure 2. SEM images (with insets of close-up images) of vertically aligned Si nanowire arrays grown from Au clusters deposited on Si(111) substrates. The R parameter of the microemulsion used in the galvanic displacement process is 16 (a), 25 (b), 50 (c), 100 (d), and 200 (e), respectively. Au clusters are deposited from water-based solution in (f). The scale bar is 300 nm.

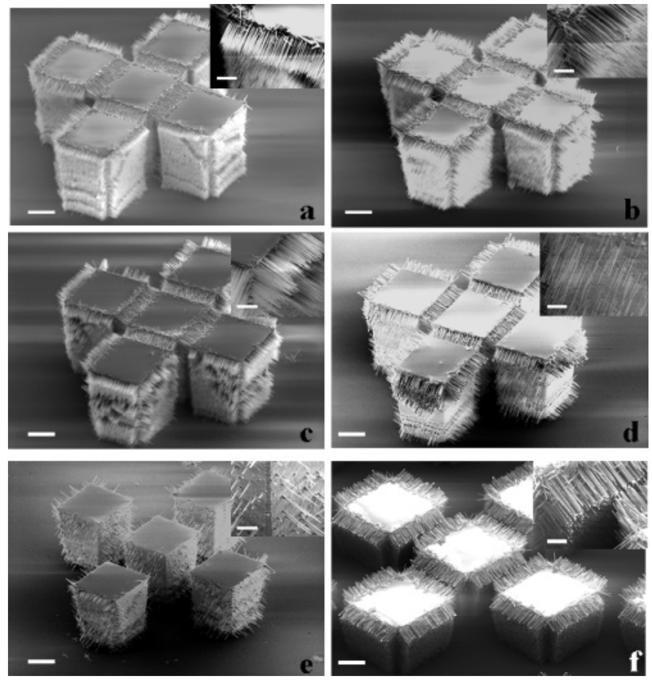

Figure 3. Laterally aligned Si nanowire arrays grown on Si pillars bounded by (111) sidewalls fabricated on (110) SOI substrates. The scale bar is 20 μm. The insets are close-ups of each image with a scale bar of 2 μm. The *R* parameter of the microemulsion used in the galvanic displacement process is 16 (a), 25 (b), 50 (c), 100 (d), and 200 (e), respectively. Au clusters are deposited from water-based solution in (f).

solution (i.e., no microemulsion) and have a broad size distribution. As a result, the diameter of the Si nanowires also has a broad distribution from 30 to 300 nm. The Au irregularly shaped agglomerations form a molten Au/Si alloy in the shape of droplets when the sample is heated, which leads to the shape of the Au/Si alloy tips in Figure 2f.

Figure 3 shows laterally aligned Si nanowire arrays grown on Si pillars with (111)-exposed sidewalls fabricated on (110) silicon-on-insulator (SOI) substrates. The diameters of the nanowires retain a good correlation with *R* parameter of the microemulsions used to deposit Au clusters on the Si pillars. In addition, the nanowires only grow on the Si sidewalls and are absent on both the top and bottom surfaces of the sample, due to the selectivity of the galvanic displacement process.

In summary, it is shown that galvanic displacement processes can be used to achieve selective growth of Si nanowires by the selective deposition of Au catalyst on patterned Si surfaces. This approach combined with water-in-oil microemulsions can be employed to control the size of the nanowires. Vertically and laterally aligned nanowire arrays with controlled nanowire size are demonstrated using this approach. This process provides an effective and relatively simple way to increase the surface-to-volume ratio of micromachined Si structures such as pillars and trenches by several orders of magnitude, which may find applications in microreactor, sensors, and microfluidic and biomedical devices.

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Supporting Information Available: Experimental procedures; schematic illustration of structures fabricated on (110) SOI wafers for the growth of laterally aligned Si nanowire arrays; SEM images of Au clusters deposited on Si(111) substrates by the galvanic displacement process using microemulsions with different *R* values. This material is available free of charge via the Internet at http://pubs.acs.org.

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