Selective Patterned Growth of Silicide Nanowires without the Use of Metal Catalysts

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Nanowires and nanotubes have been intensely studied for their applications in the growing fields of nanoelectronics, nanophotonics, and nanobiotechnology.[1,2] These one-dimensional (1D) nanostructures can simultaneously serve as device and interconnect and are valuable for further device miniaturization in conventional CMOS electrical devices. For these systems to become viable technologies, the assembly or manipulation of nanowires into functional nanosystems is critically important.[3] There are currently two avenues available for assembling functional 1D nanodevices: after synthesis and in situ. Many post-growth techniques require the use of a transferring mechanism such as microfluidic directed flow,[4] Langmuir−Blodgett films,[5] or microcontact printing.[6] In situ techniques for assembly almost exclusively rely on first patterning metal catalyst particles or films (that upon heating will agglomerate to yield particles). Photo,[7] E-beam,[8−10] dip-pen,[11] nanoimprint,[12] and nanosphere[13] lithographies along with microfluidic flow,[14] diblock copolymer masks,[15] and focused ion beam deposition[16] have all been used to pattern catalysts, either colloids or thin films. Because the formation of many nanotubes and nanowires is catalyzed by metal nanoparticles, prepatterned metal particles or films afford patterned growth of 1D nanostructures. Distinctly different from any of the nanowire(tube) patterning techniques above, we report a simple procedure for patterning growth of silicide nanowires without the use of metal catalysts.

Such patterned nanowire growth is enabled by a unique method for synthesizing silicide nanowires from single-source precursors, as we previously reported.[17,18] In this method, metal catalysts, either thin films or nanoparticles, are insufficient and unneccesary for nanowire formation. Instead, the essential feature of the nanowire nucleation and growth mechanism is the presence of a 1−2 nm silicon oxide layer on a clean silicon substrate. We now take advantage of this unique feature to enable a simple patterning method without metal catalysts. The demonstration of patterned nanowire growth, in turn, provides a definitive proof that the correct oxide thickness is the most critical aspect of this unique mechanism.

Recently, there has been considerable interest and some exciting new developments in the transition metal silicide class of nanowires. Methods for synthesizing FeSi nanowires[17,19] and other transition metal monosilicides nanowires[20] have been discovered. FeSi, having highly correlated electrons, is particularly fascinating as the only transition metal compound Kondo insulator. Moreover, the alloy ($Fe_{1-x}Co_xSi$) forms a silicon-based magnetic semiconductor,[21] the nanowires of which, once developed, would open a door to silicon-based nanospintronic devices. Moreover, these silicide nanomaterials can serve as ohmic contacts and interconnects[20,22,23] to silicon nanowire field effect transistors and for a variety of other nanoelectronic applications, such as field emission.[24] All of these applications will benefit from the ability to pattern nanowire growth.

Our approach is illustrated schematically in Figure 1. We first spin-coat photoresist onto a Si substrate coated with 100 nm SiO_2 (Figure 1a). Using standard photolithography, we expose and then develop the regions in which we want nanowires to grow over large areas up to wafer scale (Figure 1b). SiO_2 is removed in these exposed regions by a 65−70 s exposure to a buffered HF solution (Buffered HF Improved, Transene Inc.), Figure 1c. After rinsing and dissolving the remaining photoresist, we regrow a thin layer of SiO_2 back onto the exposed regions by oxidizing the surface with an acidic solution (5:1:1 H_2O:37% HCl:30% H_2O_2 v/v) for 10 min at 70 °C to produce silicon substrates mostly covered by 100 nm SiO_2 having periodic array of holes in which thin (1−2 nm) oxide covers the silicon (Figure 1d).

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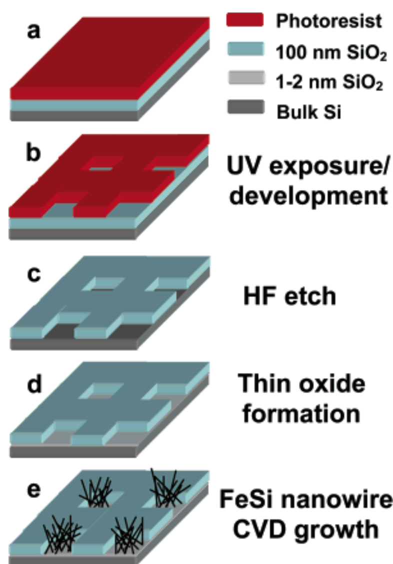

Figure 1. Schematic illustration of the process flow for the patterned growth of FeSi nanowires onto a silicon substrate without the use of metal catalysts.

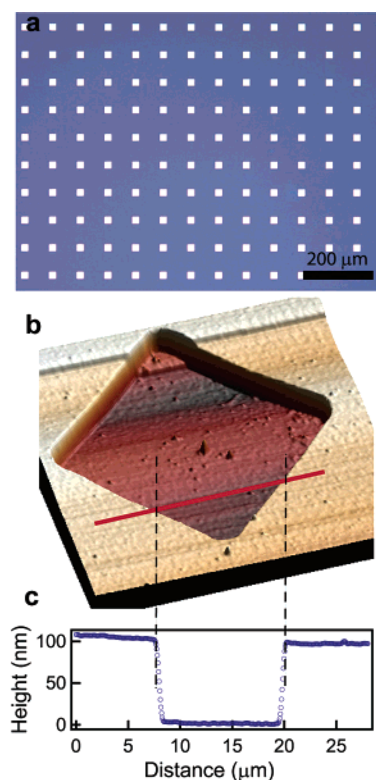

Figure 2. Patterned substrates seen with (a) representative optical image of a substrate before nanowire growth; (b) tapping mode AFM 3-D contour of a trench on the growth substrate; (c) height profile along the red line through the tapping mode image in b.

We confirmed the effectiveness of our substrate treatment through optical microscopy and atomic force microscopy (AFM) imaging of the resulting substrates (Figure 2). Silicon reflects light differently depending on the thickness of SiO_2 layer on the surface, and it is therefore easy to visually check for large thickness differences in optical images (Figure 2a). The starting color of the wafers used is blue, corresponding to approximately 100 nm of SiO_2. The color of silicon with little or no SiO_2 on its surface is gray. Thus, the periodic array of gray squares on a blue background qualitatively shows the trenches as the result of the patterning process shown in Figure 1. Tapping mode AFM was used to prove the differentiation quantitatively and to show the sharp height contrast between the thick and thin regions (Figure 2b). A line profile across the trench shows the depth of the trench to be about 100 nm (Figure 2c). However, HF is an isotropic etchant; the "real" side-wall profile is likely not precipitous but concave into the thick SiO_2 layer and hence undetectable by AFM.

With these silicon-based substrates, selective FeSi nanowire growth can be carried out with the chemical vapor deposition (CVD) of the precursor *trans*-$Fe(SiCl_3)_2(CO)_4$ (Figure 1e).[17] This precursor has been synthesized[25] and used in CVD deposition of FeSi thin films.[26] At temperatures above 400 °C, the decomposition pathway has been determined to be CO and $SiCl_4$ elimination and surface adsorption, followed by Cl_2 desorption and FeSi crystallization.[27] The nanowire growth reaction was performed in a home-built CVD setup in which reaction conditions are controlled by a tube furnace (750 °C), mass flow control of Ar (150 sccm), and a pressure-gauge and feedback valve (200 Torr), as described in detail previously.[17] Through this method, silicide nanowires are grown only in the regions with thin silicon oxide (Figure 1e). Representative SEM micrographs for nanowire growth using various patterns are shown in Figure 3. We are able to pattern nanowires in large area arrays of up to several millimeters across (Figure 3a). The patternable nanowire island sizes range from hundreds of micrometers down to several micrometers with pitches ranging from 10 to 100 micrometers depending on the mask employed. The patterning is uniform and preserves the original shape of the features (Figure 3b). The smallest patternable features achieved with this procedure are about 4 μm, for which only a handful of nanowires grow from each patterned region (Figure 3c). Furthermore, employing various photomasks, we are able to grow nanowires in arbitrary patterns with almost any design both large and small with either a majority (images d and e of Figure 3) or minority (Figure 3f) coverage of nanowires on the growth substrate.

We can explain the basis for this patterned growth using the observations we made while developing these new silicide nanomaterials. As briefly mentioned previously, our new route to transition metal silicide nanowires requires the existence of a thin silicon oxide layer on silicon. We think this oxide layer simultaneously promotes the growth of one-dimensional monosilicide nanowires from the surface and restricts thick films of metal monosilicides from forming. Futhermore, when transition metal silicides are deposited onto substrates coated with thick oxide layers such as SiO_2 or Al_2O_3, not only was nanowire growth not observed but also none of the precursor was found adsorbed or decomposed onto the surface. The solid−vapor surface energy between solid SiO_2 and the vapor from the transition metal silyl carbonyl precursor complexes is sufficiently high that no deposition is witnessed. From these two properties, we

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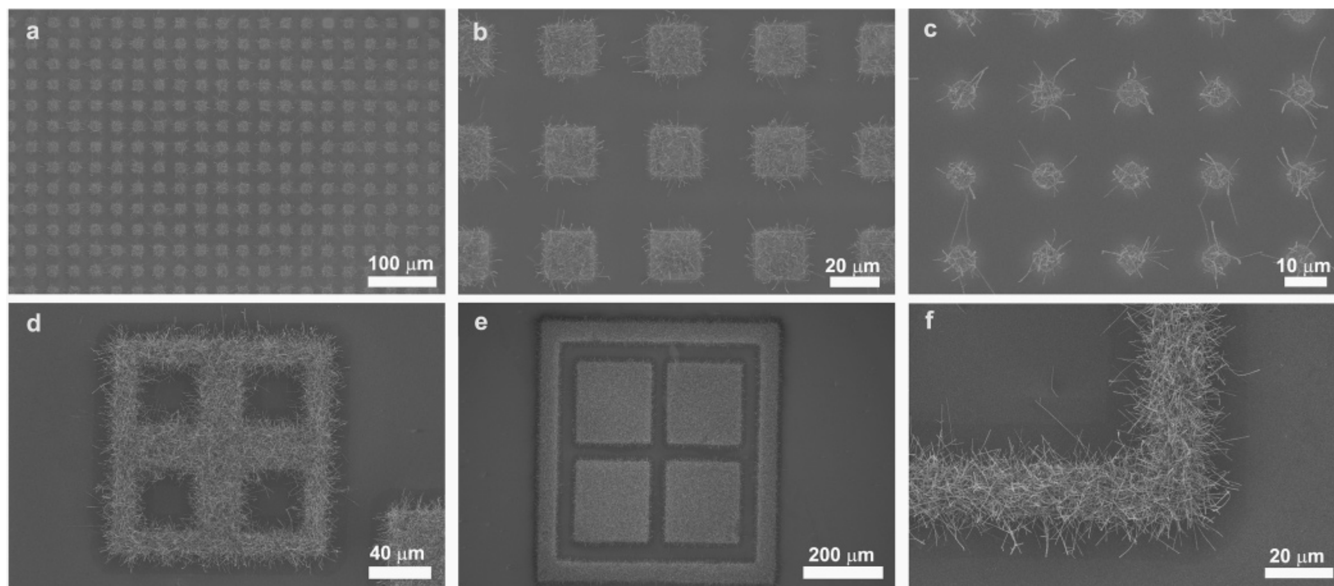

Figure 3. SEM micrographs shown for patterning experiments: (a) for FeSi nanowires formed using arrays of 20 μm width and 40 μm pitch; (b) closer view of a; (c) squares having 4 μm width and 20 μm pitch; and (d−f) other arbitrary shapes and sizes.

were able to design the process outlined in Figure 1. Thin oxides, 1−2 nm or less, are nearly all interface and have different properties from bulk SiO_2−silicon oxides greater than 5 nm thick. For the patterning of nanowires, we found this contrast in thick (>5 nm) and thin (1−2 nm) oxide to be crucial in preventing/enabling anisotropic growth. This demonstration of metal catalyst-free nanowire patterning provides direct proof that oxide thickness is critically important to our FeSi nanowire growth and will likely be common to the patterned growth of other silicide nanowires.

There are, however, some limitations to this approach. Standard photolithography allows us to define feature sizes of about 1−2 μm; however, so far we have only been able to observe patterned nanowire growth with feature sizes down to 4 μm. This first limitation to our method has two possible sources: (1) surface tension between H-terminated silicon and aqueous oxidizing solution that creates an air pocket and prevents oxidation to the required 1−2 nm SiO_2 thickness, and/or (2) enhanced surface diffusion of SiO_2 at the reaction temperature of 750 °C. Silicon hydrophobicity leads to either no oxide or an oxide layer too thin, resulting in only thin film formation and an absence of nanowires in the patterned region. This can be overcome by using dry oxidation methods, such as plasma treatment or UV irradiation. On the other hand, the mobility of SiO_2 presents a rigid boundary for our process. For small exposed regions, SiO_2 can diffuse into the patterned regions at the high growth temperatures employed, resulting in a thicker oxide. This effect could be compensated somewhat by eliminating/reducing oxidation to produce smaller feature sizes. The second limitation is that selective nanowire growth is successful only for thin SiO_2 coverages more than 5% and less than 80%. Coverages that are too low suffer from faster deposition rates to the patterned regions favoring the growth of thin films, whereas coverages that are too large enable nanowire growth to extend over thick oxide regions, even though the nucleation of nanowires is still confined to the established areas. Through this investigation, we are gaining insight into the growth mechanism at play; we now know that the growth surface is very significant, that there is a critical oxide thickness related to the growth mechanism, and that we can change growth conditions to promote/limit nanowire growth. We were also able to observe more closely the surface beneath the nanowires. We believe that a thin film, presumably, of FeSi is forming either after or during nanowire growth, which is likely an important clue to the exact nature of this general mechanism. This information is extremely valuable as we employ this synthetic approach to seek $Fe_{1-x}Co_xSi$ nanowires in addition to nanowires of other interesting transition metal silicides.

In summary, we have demonstrated a simple procedure for patterned growth and assembly of FeSi nanowires onto a silicon substrate without the use of metal catalysts. The general nature of the silicide nanowire growth mechanism will allow for the patterning of many other transition metal silicide nanowires. The ability to selectively grow nanowires in controlled locations is important for many applications such as biological nanosensing, optical-electronic detection, and light-emitting diodes. In addition, the demonstrated patterned growth will be very useful for field emission display applications using stable metallic silicide nanowires.

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