Orthogonal Self-Assembly of Interconnected One-Dimensional Inorganic and Organic Nanostructures on the Si(100) Surface

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Silicon-based molecular electronics has attracted significant attention recently due to the potential for interfacing traditional semiconductor technology with novel molecular devices.[1-5] Among the many organic functionalization schemes demonstrated on silicon,[6] a variety of molecules including several olefins and aldehydes undergo self-directed growth on the Si(100)−2×1:H surface,[7-15] leading to the formation of one-dimensional organo-silicon nanostructures that are oriented parallel and/or perpendicular to silicon dimer rows. The self-assembly of these molecular nanostructures allows for fabrication in a parallel manner over macroscopic areas. While organic molecules impart useful electronic and chemical functionality, additional inorganic materials (e.g., metallic interconnects) are required to realize molecule-based integrated circuit technology.

In this paper, we report a general scheme for forming orthogonal, interconnected inorganic and organic one-dimensional nanostructures using self-assembled inorganic nanowires and organic molecular chains on the Si(100) surface. Although ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) is used to interrogate these nanostructures, it is important to note that they are formed without intervention of the STM tip, thus enabling parallel formation over macroscopic areas. The chemical functionality of organic molecules, electrical and optical properties of inorganic nanostructures, and the ubiquitous use of silicon in microelectronic technology suggest multiple possible applications and future directions for the surface chemistry demonstrated here.

As a proof of principle, bismuth was chosen as the inorganic component since Bi spontaneously forms uniform nanowires perpendicular to silicon dimer rows on the Si(100)−2×1 surface.[16-20] Bi nanowires are stable at room temperature due to an accompanying subsurface reconstruction in the Si substrate.[17] They can also be used to template the growth of additional metals such as Ag[21] and In.[22] Styrene was selected for the organic molecule since it undergoes self-directed growth parallel to the silicon dimer rows, thus enabling orthogonal intersection with the Bi nanowires. In addition to being the first molecule to show self-directed chain growth on the Si(100)−2×1:H surface initiated at dangling bond sites,[7] the electronic properties of one-dimensional arrays of styrene have been studied[23] and atomically registered heteromolecular nanostructures have been constructed using styrene.[24] To integrate the Bi and styrene structures, the clean Si(100)−2×1 areas surrounding the Bi nanowires must be H-passivated without significant perturbation to the Bi nanowire template.

The experiments were conducted at room temperature in a home-built UHV STM.[25] The n-type Si(100) substrates were prepared in UHV to produce the clean Si(100)−2×1 reconstruction (see Supporting Information). Bi metal (99.9999%, ESPI) was then evaporated onto the substrate held at 570 °C. The substrate was further annealed at 570 °C to promote the formation of Bi nanowires.[18,20] The anneal resulted in the surface pictured in Figure
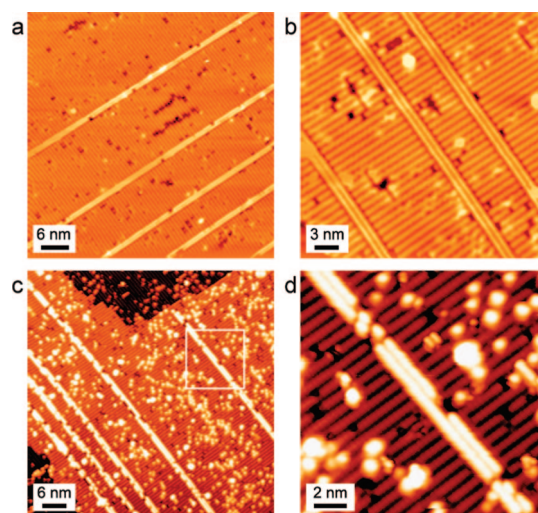

Figure 1. UHV STM images of the silicon surface with Bi nanowires prior to styrene growth. (a) Si(100)−2×1 surface with Bi nanowires after deposition and annealing. (b) Close up image of the Bi nanowires. (c) After H-passivation, the Bi nanowires remain largely undisturbed, while the surrounding surface shows Si dangling bonds (small protrusions). (d) Close up image of the area marked by the square in image (c). Tunneling conditions: −2 V sample bias, 0.1 nA setpoint current.

1a, which shows pristine Bi nanowires surrounded by the clean Si(100)−2×1 substrate. In Figure 1b, the Bi nanowires are seen to consist of two parallel protruding rows, which correspond to two rows of Bi dimers.[17,20]

By H-passivating the Si dangling bonds surrounding the Bi nanowires, their transport properties are improved due to a reduction in leakage current,[19] and a surface suitable for the self-assembly of styrene molecule chains is created. Passivation was achieved using atomic hydrogen generated from a W filament heated to 1350 °C at a distance of 6 cm from the sample, whose temperature was held at 350 °C. While previous reports have suggested that the Bi nanowires are completely resistant to atomic H,[26,27] we found that at high doses of H the Bi nanowires begin to show increasing numbers of missing atom and missing dimer defects, and eventually most of the Bi atoms from the nanowires dewet and form small islands or clusters (see Supporting Information). Therefore, care was taken to control the atomic H dose such that the Bi nanowires remained largely intact, while sufficiently passivating the Si surface with a suitable concentration of dangling bond sites at which styrene chain growth can be initiated. Typical hydrogen doses were 840 Langmuirs (L), where 1 L is a dose of 1×10^{-6} Torr for 1 s. Figure 1c−d show the sample surface following the passivation process. The Bi nanowires appear topographically higher since the H-passivation reduces the electronic density of states of the surrounding substrate. The small protrusions are Si dangling bonds,
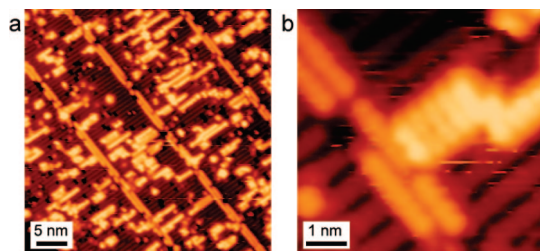
Figure 2. UHV STM images of intersecting Bi nanowires and styrene chains. (a) Large scale image showing the coverage of Bi and styrene. (b) High resolution image of an intersection between a Bi nanowire and a styrene double chain. Individual styrene molecules in the chain are resolved, and two protrusions are observed at the point of contact with the Bi nanowire. Tunneling conditions: sample biases (a) −2.0 V, (b) −2.5 V, setpoint current 0.1 nA for both images.

while the slightly larger protrusions are likely Bi atoms that have segregated into clusters after dewetting from the nanowires.

Styrene undergoes a chain reaction on the Si(100)−2×1:H surface when the C=C group reacts at a Si dangling bond site to form a covalent Si−C bond. The resulting carbon radical on the molecule then abstracts a hydrogen atom from the neighboring dimer, which creates a new dangling bond site where an additional styrene molecule can attach to continue the chain reaction. Styrene molecules (99%, Sigma Aldrich) were leaked into the UHV chamber at doses of 15−30 L. Figure 2a shows a surface similar to that shown in Figure 1c after exposure to styrene, which results in the growth of many styrene chains. They grow along dimer rows until they encounter a defect, a step edge, or a Bi nanowire. When such an obstacle is encountered, the chain usually reverses direction by abstracting a hydrogen atom from the same dimer and continuing backward to form a double chain along the other side of the dimer row.

At intersections with a Bi nanowire, a styrene double chain is commonly observed. An example of such an intersection is shown in the high resolution STM image of Figure 2b. The Bi nanowire runs from the top left to the bottom right of the image, and a double styrene chain intersects it perpendicularly. Individual molecules within the styrene double chain are resolved, and two protrusions are seen at the intersection with the Bi nanowire, one for each row of molecules in the double chain. These protrusions can be possibly attributed to a change in geometry of the styrene molecules at the edge of the Bi nanowire, where there exists a shallow dimer-width trench parallel to the nanowire. In other words, the phenyl ring of the styrene molecule at the end of the chain has more space available to it and is no longer restricted to stack parallel to the other molecules in the chain. Thus, it may rotate perpendicular to the other rings to form a T-shaped conformation, which has been shown to be energetically favorable in the absence of other steric hindrance.[28] The protrusions may also result from charge transfer between the styrene chain and the Bi nanowire, which is also likely to be influenced by the geometry of the styrene molecules.[29]

In conclusion, we have demonstrated compatible inorganic and organic surface chemistry on the Si(100) surface that enables fabrication of orthogonal, hybrid one-dimensional nanostructures. This self-assembly process creates intersecting Bi nanowires and styrene molecular chains over the entire sample surface in a massively parallel fashion. While Bi and styrene were the focus of this study, this general procedure can likely be extended to many other inorganic and organic systems that are known to undergo one-dimensional self-assembly on the Si(100) surface.[30−32]

Supporting Information Available: Full experimental details for Bi nanowires, H-passivation, and styrene chain growth. STM images showing effects of Bi nanowire anneal, hydrogen dose, and registry of styrene molecules with respect to Bi atoms. This material is available free of charge via the Internet at http://pubs.acs.org.

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