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Citation: Applied Physics Letters **76**, 562 (2000); doi: 10.1063/1.125852
View online: http://dx.doi.org/10.1063/1.125852
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/76/5?ver=pdfcov
Published by the AIP Publishing

Chemical vapor deposition of Si nanowires nucleated by $TiSi_2$ islands on Si

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(Received 23 August 1999; accepted for publication 6 December 1999)

Silicon ''nanowires'' can be formed by chemical vapor deposition of Si onto Si substrates on which nanometer-scale, Ti-containing islands have been grown. At the growth temperatures used, the Ti-containing islands remain solid and anchored to the substrate, while the Si nanowires grow out from the islands, which remain at their bases. The nanowire growth mechanism, therefore, differs from the usual vapor-liquid-solid process and provides a potential route for the formation of oriented Si nanostructures or semiconductor-metal-semiconductor structures compatible with Si integrated circuits. © *2000 American Institute of Physics.* [S0003-6951(00)02305-6]

With the constantly decreasing feature sizes of integrated-circuit devices, the need for increasingly fine, lithographically defined patterning is limiting further advances of the technology. Consequently, a growing amount of effort is being devoted to self-assembly techniques to form switching elements without fine-scale lithography.[1] The self-assembled switching elements may be integrated on top of a Si integrated circuit so that they can be driven by conventional Si electronics in the underlying substrate. To address the switching elements, interconnections or wires, preferably also formed by self-assembly, are needed. The self-assembled wires connecting the conventional electronics to the self-assembled switching elements should be anchored at locations defined by the underlying circuitry and should be composed of materials compatible with Si integrated-circuit processing.

Recent reports have shown that catalytic decomposition of a Si-containing gas by a metal, such as Au or Fe, can form long ''nanowires.'' [2,3] These studies were based on the earlier work of Wagner and Ellis,[4,5] who developed a technique frequently called the vapor-liquid-solid (VLS) mechanism. A liquid alloy droplet containing the metal and Si is located at the tip of the wire and moves along with the growing end of the wire. The wires may either be formed in the gas phase or anchored at one end on a substrate.[6,7] However, Au and Fe migrate into Si rapidly and create deep levels, which can degrade devices, such as addressing circuitry and other portions of the system formed by conventional Si integrated-circuit technology.

Titanium and $TiSi_2$ are compatible with integrated-circuit technology and are frequently used in Si circuits to reduce resistance of silicon and polycrystalline-silicon conducting regions. Although Ti forms deep levels in Si, its solubility and diffusion coefficient in Si are low,[8,9] and the deep levels are not at midgap. With suitable handling, Ti is generally accepted in integrated-circuit facilities. This report demonstrates the formation of nanowires nucleated by Ti-containing islands. The formation mechanism will be shown to differ from the VLS mechanism generally reported.

Ti-containing islands were formed by chemical vapor deposition (CVD) on 150-mm diameter, Si(001), and Si(111) substrates in a commercially available, lamp-heated, single-wafer reactor using $TiCl_4$ in argon as the precursor for the Ti (Ref. 10) and a H_2 ambient. The partial pressure of $TiCl_4$ was 0.06 Pa (4.5×10^{-4} Torr), and the total reactor pressure was 670 pa (5 Torr). Although the Ti deposition process is selective,[11,12] unpatterned wafers were used in this demonstration. In most cases, only $TiCl_4$ was introduced from the gas phase, with the Si being supplied from the Si substrate. In a few cases, a Si-containing gas (SiH_4 or SiH_2Cl_2) was added during the deposition of the Ti to minimize consumption of the Si substrate during $TiSi_2$ formation. At the low deposition temperatures of 640–670 °C used, the islands are likely to be Ti-rich compared to $TiSi_2$. After deposition, the islands were sometimes annealed at a higher temperature (~920 °C) to reduce their density. On unpatterned wafers, the island density after annealing is determined primarily by the amount of Ti initially deposited, and the island size is determined by the annealing temperature.[10] The island composition after annealing at 920 °C is assumed to be stoichiometric $TiSi_2$.

After Ti deposition and possible annealing, the temperature was set to the silicon deposition temperature (generally 640 or 670 °C), and the islands were exposed to a Si-containing gas. SiH_4 and SiH_2Cl_2 were used in different experiments, with SiH_2Cl_2 having the potential advantage of allowing selective Si deposition. After removing the substrate from the reactor, the surface was examined by scanning electron microscopy and/or atomic-force microscopy. The location of the Ti within the wire was measured by field-emission Auger analysis.

Figure 1(a) shows a sparse array of $TiSi_2$ islands formed on a Si(001) substrate by Ti deposition at 640 °C, followed by annealing at 920 °C for 30 min; Fig. 1(b) shows corresponding islands formed on a Si(111) substrate. After exposing similar substrates with annealed $TiSi_2$ islands to a partial pressure of 70 Pa (0.54 Torr) of SiH_2Cl_2 in a 2.7 kPa (20 Torr) hydrogen ambient at 640 °C, Si nanowires extended from the $TiSi_2$ islands, as shown in Fig. 2(a) for Si(001) and in Figs. 2(b) and 2(c) for Si(111). The Si nanowires nucleated at the $TiSi_2$ islands, rather than on the bare Si. Most of the wires are curved, suggesting that they contain defects.

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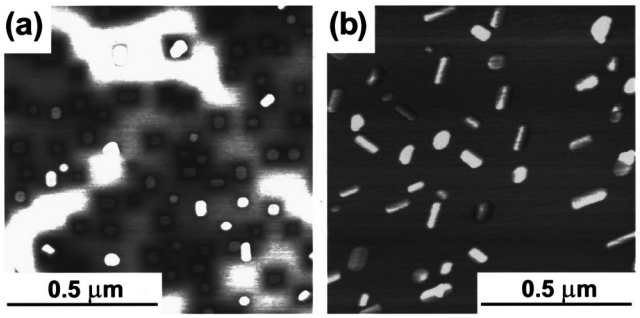

FIG. 1. Atomic-force micrographs of $TiSi_2$ islands formed by chemical vapor deposition at 640 °C and annealed at 920 °C on (a) Si(001) and (b) Si(111). (Image size: 1 μm; z scale: 10 nm.)

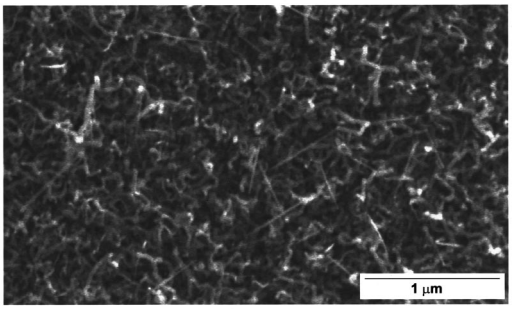

FIG. 3. Scanning-electron micrograph of long, dense Si nanowires nucleated on Ti-containing islands grown at 670 °C on Si(001) and not annealed. The Si wires were grown at 670 °C for 395 s using SiH_4.

Some wires branch along their length. Less than 1 nm of Si would be grown on bare Si under these conditions.

Figure 3 shows a Si(001) substrate with a dense array of nucleating islands deposited at 670 °C and subsequently exposed to a partial pressure of 5 Pa (0.038 Torr) SiH_4 at a total pressure of 2.7 kPa (20 Torr) at 670 °C for an extended time of 395 s. [The Ti-containing islands were not annealed before Si wire growth in this case and were much denser than those shown in Fig. 1(a).] A dense array of curved wires and a few exceedingly straight wires were formed. The straight wires are likely to be free of defects. From the scanning electron micrographs, the median wire diameter appears to be ~25 nm. One of the straight wires is 1.3 μm long and ~22 nm in diameter, corresponding to an aspect ratio of 60:1.

To determine the composition of the nanowires, field emission Auger measurements were performed. After mild sputter cleaning (equivalent to removing about 2 nm of SiO_2) to reduce the amount of C and O on the sample surface, a clear Ti Auger signal was seen for Si wires on a Si(111) substrate. Two wires were examined in detail with both spot analysis and line scans. On a Y-shaped, branched wire the base of the Y is very likely the end attached to the substrate, with the two branches of the Y possibly arising from coalescence of wires forming from two adjacent nucleation sites on the same $TiSi_2$ island during growth. As shown in Fig. 4, a strong Ti Auger signal was observed at the base of the Y. No Ti was detected at the growing end of the branch examined. These observations, together with the fact that $TiSi_2$ and Si are essentially insoluble in each other,[8,9] lead to the conclusion that the wire is pure Si, with no appreciable Ti at the tip to catalyze the decomposition of the Si-containing gas. A straight wire was examined at both ends, and a line scan was taken. Ti was observed at the darker end of the wire (assumed to be the base), and not at the brighter end (assumed to be the free end), confirming that the Ti remains at the base of the wire for Si(111). The Auger signal from wires on the Si(001) substrate was weaker, but the measurements again suggest that Ti remains at the base of the wire.

Because Ti remains at the base of the wire, Ti-catalyzed decomposition of the Si-containing gas probably occurs, with wire growth by extrusion from the base region. This behavior differs from wire formation by Au and Fe catalysis of the Si decomposition reaction, where the growth occurs at the tip by the VLS process.[4,5] In the VLS process, the metal reacts with Si from a vapor source to form a low-melting-temperature liquid droplet. This droplet then dissolves additional Si from the vapor source. When the solubility of Si in the liquid droplet reaches saturation, Si precipitates from the

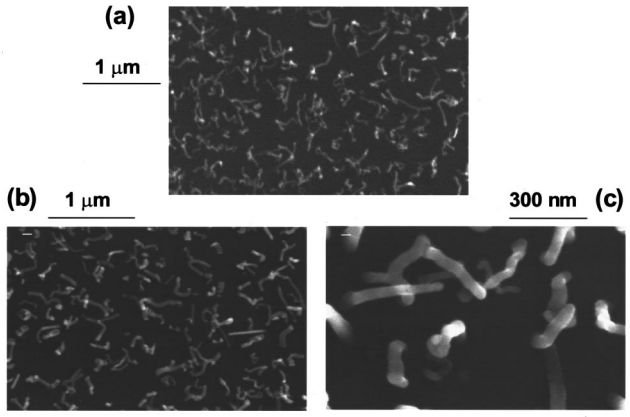

FIG. 2. Scanning-electron micrographs of Si nanowires nucleated on annealed $TiSi_2$ islands on (a) Si(001) and (b) and (c) Si(111). The Si wires were grown at 640 °C for (a) 160 s and (b) and (c) 40 s using SiH_2Cl_2.

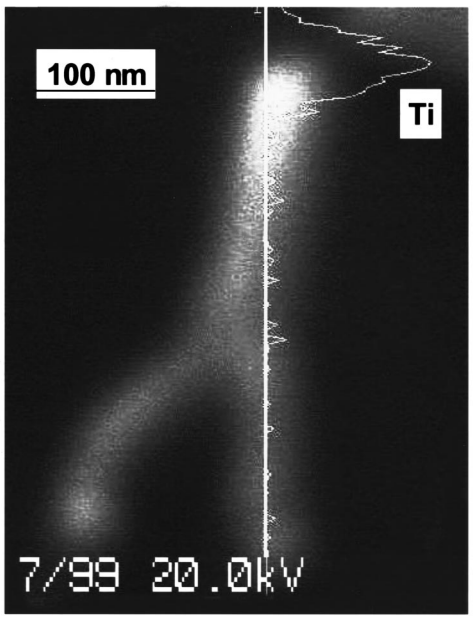

FIG. 4. Ti signal from Auger measurement (white line) superposed on scanning electron micrograph of Y-shaped Si wire on Si(111), showing Ti at the wire base, but not at the tip.

liquid, leading to the growth of a thin Si wire, with the liquid moving along with the tip of the wire. In the present case of Ti and Si, the lowest temperature for a liquid eutectic to form is ~1300 °C, far above the 640–670 °C deposition temperature of the Si. The enhanced, rapid decomposition of the silicon containing gas (SiH_4 or SiH_2Cl_2) presumably arises from a catalytic effect of the small Ti-containing islands. The decomposed Si immediately attaches to the Ti-containing surface. The added Si probably first satisfies any Si deficiency in the Ti-containing island to form stoichiometric $TiSi_2$. Additional incoming Si then diffuses to the surrounding Si, leading to the growth of the nanowire. Nucleation of Si on the Ti-containing islands is consistent with the small $Ti/TiSi_2$ interfacial energy.[13,14]

If the decomposition reaction occurs at the base of the wire, and Si grows on the surrounding Si with its normal rate, the Ti-containing island is likely to eventually become completely surrounded by the Si growing on the adjacent Si. At that time, the Si-containing gas will no longer be able to reach the Ti-containing island. The accelerated reaction will cease, and the wire length will no longer increase rapidly. The length of the wire will, therefore, be limited by the relative reaction rates on $TiSi_2$ and on Si. This ratio is likely to be greater at lower temperatures and to decrease as the temperature increases, consistent with the observed limited wire growth and thicker wires formed at the higher Si deposition temperature of 920 °C. On the other hand, if deposited Si atoms weakly bound to the surrounding Si surface diffuse to the wire, growth may continue for an extended period of time.

In summary, we have observed accelerated decomposition of Si-containing gases at Ti-containing islands on a Si surface to form Si nanowires anchored at one end to the substrate. The Ti appears to remain at the base of the growing wire. These wires are also likely to nucleate on Ti-containing regions formed by conventional techniques on a Si integrated circuit, allowing interconnection of conventional circuitry with self-assembled elements.

The authors would like to thank M. Juanitas and G. Girolami for assistance with the measurements, Hewlett-Packard's ULSI Laboratory for use of deposition equipment, and Dr. N. Shamma for CVD $TiSi_2$ process information.

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