Stress-driven formation of Si nanowires

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We present an alternate mechanism for the growth of Si nanowires directly from a silicon substrate, without the use of a metal catalyst, silicon vapor or chemical vapor deposition (CVD) gasses. Since the silicon wires grow directly from the silicon substrate, they do not need to be manipulated or aligned for subsequent applications. Wires in the 20–50 nm diameter range with lengths over 80 μm can be easily grown by this technique. The critical parameters in the growth of these nanowires are the surface treatment and the carrier gas used. A model is proposed involving stress-driven wire growth, which is enhanced by surface Si atom diffusion due to the presence of hydrogen gas. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1925756]

There is a great deal of interest in one-dimensional (1D) structures, including carbon nanotubes and semiconductor nanowires, due to their unique physical properties and potential applications.[1–3] A number of applications have been investigated for such 1D structures, including nanoscale devices,[4,5] devices on flexible substrates,[6] conductive plastics,[7] and sensor applications.[8] There has also been a significant effort focused on Si nanowire synthesis, especially for electronic applications, such as field effect transistors.[4] There are several growth mechanisms which have been reported in the literature, including the well known vapor-liquid-solid (VLS) growth,[1,9–11] solution-liquid-solid growth,[2] the solid-liquid-solid growth,[12] as well as other methods.[13,14] Among these, the most common method of Si nanowire growth is by VLS, in which a catalyst liquid metal droplet acts as a site for vapor-phase adsorption of Si atoms, and subsequent Si nanowire growth[9] from the liquid metal/semiconductor interface. In this case, a metal catalyst and a source of silicon vapor is required, which is generally obtained by high-temperature heating of Si or SiO powder,[15] by chemical vapor deposition techniques using gases such as silane,[16] or by laser ablation.[1,17,18] Successful VLS-type silicon nanowire growth at a high temperature has also been reported by the use of oxygen as a growth catalyst[18] and silicon vapor obtained from high-temperature decomposition of SiO powders.

In this letter, we report on a growth mechanism for silicon nanowires which does not require the presence of any silicon-based vapor, or is any metal catalyst used. In fact, a high density of silicon nanowires, as long as 85 μm, can be produced by this method, using only a silicon substrate at moderate temperatures. Since the wires produced by this method can grow directly from the silicon substrate, use no metal catalyst, and can be produced at moderate temperatures in localized regions, they may be easily incorporated into micro electro mechanical system-type chemical sensors or other sensor designs.

Silicon substrates ([111] and [100]) were cleaned in acetone and methanol while alternate samples were also dipped in dilute hydrofluoric acid (HF). After the cleaning procedure, the substrates were placed in an alumina boat and inserted into a quartz tube inside a tube furnace. The quartz tube was evacuated to a base pressure of 25 mTorr, and the furnace was heated to temperatures between 700 °C and 1150 °C. During the heat up cycle, the evacuated quartz tube was flushed several times with argon (Ar) gas in order to minimize the oxygen content. Once at temperature, the wire growth was initiated by the flow of a set ratio of Ar and hydrogen (H_2) gases over the sample.

An example of the Si nanowires produced by this growth process is shown in Fig. 1. As can be seen, a high density of silicon wires has been produced, originating directly from the silicon substrate. The wire diameter has been measured to be in the 20 to 30 nm range.

High-resolution electron microscopy performed on the wires showed that the wires were partially crystalline, as determined from the diffraction image, which showed both amorphous diffraction rings as well as crystalline diffraction spots. The wires were also examined in scanning electron microscopy and their energy dispersive x-ray spectra were recorded. Results indicated that they consisted of silicon with a small amount of oxygen. The oxygen was most likely incorporated on the surface of the nanowires, similar to the oxide sheathing of silicon nanowires that has been previously reported in the literature.[19]

In order to examine the effect of initial surface conditions, two different growths were performed. One type of growth involved a sample with a native oxide layer, and one was stripped of this oxide using a dilute HF solution. Results for the oxide-stripped substrate showed no wire growth under any conditions, but the sample with the native oxide exhibited dense and long Si nanowire growth. From the

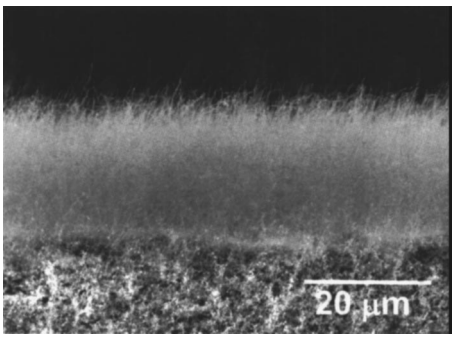

FIG. 1. Si nanowires produced using a Si(111) substrates which had a native oxide present prior to the growth.. The growth was performed at 1050 °C for 1 h using a 36 sccm Ar to 4 sccm H_2 gas ratio.

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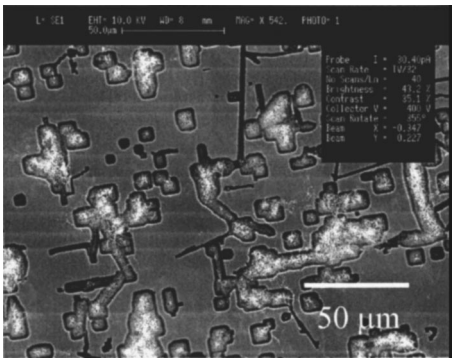

FIG. 2. Si wafer annealed at 1100 °C in a vacuum, under Ar/H_2 gas flow. Note the extended cracks and the presence of silicon nanowires (white regions) only within these regions, while the smooth silicon areas contain no wires.

above results, it was determined that the presence of an oxide layer was critical to the nanowire growth.

A series of temperatures, ranging from 700 °C to 1200 °C, have also been investigated in order to further characterize this nanowire growth process. Results indicated neither nanowire growth at 700 °C, nor did the surface exhibit a stress crack pattern that was seen at the higher temperatures (shown in Fig. 2). The lowest temperature at which nanowire growth began was near 950 °C and interestingly, this was also the temperature where the initiation of stress cracks occurred. The highest density of silicon wires was attained in the temperature range from 1000 °C to 1100 °C. By 1100 °C, the stress crack pattern expanded significantly, and the wires nucleated only in these regions, as shown in Fig. 2. Above 1100 °C, no wire growth was seen, the stress cracks disappeared, and oxidation of the substrate became much more pronounced. Similar wire growth could also be achieved under resistive heating of the substrate, where only localized heating occurred. This result suggests that the wires can also be grown directly onto an existing device without subjecting the whole structure to heating effects.

If the growth was performed under optimal conditions but without any carrier gas or with Ar gas only, no wire growth was noted. This result clearly rules out the possibility that the growth was occurring by Si evaporation from the substrate, but more importantly, it also established the role of hydrogen gas in this growth process. In fact, the addition of only a small amount of H_2 gas resulted in Si nanowire growth, and a higher H_2 to Ar ratio led to a denser growth of nanowires; an increase of annealing time at the same H_2/Ar ratio led to a significant increase of the nanowire length. For example, a 1 h growth using Si(111), under a 36 sccm Ar/4 sccm H_2, resulted in an average nanowire length of 40 μm, while under the same conditions, a 2 h growth resulted in nanowires which were in excess of 90 μm. In the case of Si(100), the nanowire lengths were about one-half of those seen in Si(111). Interestingly, the density of stress cracks was also lower for the Si(100) surface.

Since no source of Si vapor exists and the temperature is not high enough for evaporation of the silicon substrate,[20] our growth process is significantly different from the VLS (Ref. 9) process or the oxide-assisted growth process[19] reported in the literature. In order to understand the possible mechanism for our wire formation, let us first examine several interesting results previously reported in the literature.

The formation of "hillocks" has been reported when a Pb alloy thin film, confined under an SiO_2 layer, underwent warming up from liquid nitrogen to room temperature.[21] It was found that the growth of these hillocks occurred due to the presence of a compressive biaxial stress from to the thermal mismatch between the Pb and the SiO_2, and the driving force for the hillock growth was a lateral stress gradient in the thin Pb film. Under these conditions, a flux of material was transported to low stress regions of the film, resulting in the growth of a hillock out of the plane of the film. A related phenomenon is the formation of Sn whiskers from a compressively stressed Sn thin film,[22] in which the whisker growth was attributed to a lateral stress gradient where the Sn film was under biaxial compressive stress.

In view of these results, let us now examine the growth of the silicon wires. As already mentioned, the wire growth occurred only if an oxide layer was present, and only after a crack pattern formed at the higher temperatures, with the wire growth initiating within the cracked regions (shown in Fig. 2). These conditions appear similar to those reported for the growth of the hillocks and whiskers discussed above. In our case, the thermal expansion coefficient of SiO_2 is roughly an order of magnitude smaller than that of Si, which results in significant tensile stress in the SiO_2 film and a compressive stress in the underlying Si interfacial region, with increasing temperature. As the tensile stress in the thin SiO_2 layer increases with heating, cracks begin to form, thereby relaxing the compressive stress in these local regions. This leads to a stress gradient, in which Si atom transport occurs from the compressed regions to the stress-free cracks, leading to the accumulation of Si in these regions and the nucleation of whiskers or Si wires out of the surface of the cracks.

However, the presence of the stress gradient alone cannot explain the growth rate of our wires, since no noticeable wire growth occurs with Ar gas flow under otherwise identical conditions. A high density of long wires can only be seen when hydrogen gas is added, which suggests that hydrogen gas must also be playing a role in this process. In order to understand this, it is useful to examine the work of Bratu and Hofer,[23] who reported a very surprising increase in the sticking coefficient of hydrogen on a Si(111) surface with increasing temperature. This increase was as large as three orders of magnitude for the temperature range between 580 K and 1050 K, and it was even higher in regions of defects or cracks on the surface. This enhanced reaction of hydrogen with the silicon surface then allows a much greater surface silicon atom diffusion, as reported by Kuribayashi *et al.*[24]

Thus, it is suggested that the role of hydrogen in this case is to enhance surface diffusion kinetics of the silicon atoms at the nucleated whiskers, allowing a much more efficient Si mass transport along the Si atom concentration gradient, leading to wires of very high aspect ratios. Thus, the driving force for the wire nucleation (Si atom accumulation) is a stress gradient, while the growth of the wires is driven by a concentration gradient, in which the diffusion kinetics are significantly enhanced by the presence of hydrogen (see Fig. 3).

In summary, an alternate Si nanowire growth process is described, which does not require a metal catalyst, or any silicon vapor source. A growth mechanism is proposed which involves a stress-driven nanowire formation, aided by the presence of hydrogen gas, which enhances the kinetics in the

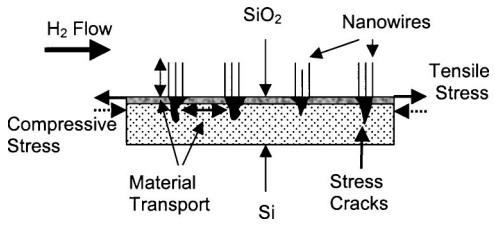

FIG. 3. Model for the growth of Si nanowires: The SiO_2 layer experiences large tensile stress, while the underlying Si region undergoes biaxial compressive stress due to difference in thermal expansion. The tensile stress in the oxide layer leads to stress cracks, which relieve the stress locally. This stress gradient results in mass transport to and the accumulation of Si atoms at or near the cracks, where material starts to build up, initiating the growth of the nanowires. The addition of hydrogen allows much enhanced surface diffusion along the concentration gradient, leading to the growth of long nanowires with a large aspect ratio.

wire growth process. The stress gradient occurs due to the different thermal expansion coefficients of silicon and SiO_2, resulting in a tensile stress in the oxide layer and a compressive stress in the silicon upon heating. As the stresses become large at higher temperatures, crack formation is initiated, relieving the compressive stress locally, resulting in a silicon atom flux to these crack regions and accumulation of material, leading to silicon wire growth. These results indicate that a similar wire growth mechanism may be possible in other layered systems, where a biaxial compressive stress can be introduced thermally or by other means.

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