Vapor–Liquid–Solid Growth of Small- and Uniform-Diameter Silicon Nanowires at Low Temperature from Si_2H_6

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Received November 12, 2007; accepted December 7, 2007; published online January 11, 2008

We report 350 °C as a critical growth temperature for overcoming the aggregation of gold (Au) in the synthesis of high-density silicon nanowires (SiNWs) with controlled diameters in a vapor–liquid–solid (VLS) mechanism by the low-temperature decomposition of Si_2H_6. Low-temperature growth is considered essential for preserving the initial distribution of Au droplets (8 ± 5 nm) during SiNW nucleation with small (12 nm) and uniform (± 5 nm) diameters. Au–Si eutectics increase in size with aggregation at high temperatures, resulting in SiNWs with large and random diameters. The crystal quality, defect formation, and morphology of the wires, grown in the (111) direction, are size dependent.

DOI: 10.1143/APEX.1.014003

Silicon nanowires (SiNWs) are promising materials for future nanoelectronic and photonic device applications.[1,2] SiNWs may also be key components in chemical and biomedical sensors.[3,4] The proposed applications have been motivating new research and development of growth technologies for realizing the synthesis of controlled-diameter SiNWs via a vapor–liquid–solid (VLS) mechanism.[5,6]

Gold (Au) has been commonly used to mediate SiNW growth because the eutectic temperature of bulk Au–Si is lower than those of other catalyst systems. However, the aggregation of Au at elevated temperatures is a major problem when realizing controlled-diameter SiNWs by a VLS technique.[7] SiNWs with uniform-diameters have been synthesized using well-defined Au nanocolloids from SiH_4 and $SiCl_4$.[8,9] However, high-density SiNWs with fixed diameters cannot be grown from densely packed Au nanocolloids due to aggregation at high growth temperatures. It is also difficult to achieve the uniform dispersion of Au colloids on the substrate. Furthermore, the low-temperature plasma decomposition of SiH_4 has also been performed to grow small-diameter SiNWs.[10] By this technique, a radio frequency plasma also enhances the uncatalytical decomposition of the source gas and there is a risk of plasma damage to the SiNWs. Such growth techniques did not yield high-density SiNWs with controlled diameters.

Low-temperature growth is a prerequisite for growing high-density SiNWs with uniform-diameters from dense Au droplets. We have been performing the low-temperature decomposition of Si_2H_6 to grow SiNWs at low temperatures.[11] The synthesis of SiNWs from Si_2H_6 has been reported, but growth temperatures could not be reduced below 500 °C, resulting in wires with random diameters (30–135 nm) due to the agglomeration of Au.[12] Whereas the diameter of a single wire does not seem to be fixed. Hence, a further reduction in growth temperature is essential for growing controlled-diameter SiNWs.

In this study, we show that 350 °C is the critical growth temperature required to overcome the aggregation of Au for growing high-density SiNWs with small and uniform diameters from densely packed Au droplets. We perform the low-temperature decomposition of Si_2H_6 in a low-pressure chemical vapor deposition (LPCVD) system to achieve such low-temperature growth. We also demonstrate that the structural properties of the SiNWs, such as crystal quality and defect formation, depend on the size of Au–Si eutectic droplets and hence the diameter of the wires.

High-density Au droplets were prepared on H-terminated Si(111) substrates at room temperature (RT) by e-beam evaporation to grow SiNWs. The resistivity of the substrates was 1–1.2 Ω·cm. The equivalent thickness of the Au film evaluated using a quartz crystal monitor was 0.5 nm. SiNW growth was carried out in an LPCVD chamber by typically exposing the substrates covered by Au droplets at a Si_2H_6 flow rate of 1 sccm and a H_2 flow rate of 49 sccm at a pressure of 3 Torr after heating to 350 °C. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were performed to characterize the wires.

Figure 1 shows SEM images of the Au droplets prepared at RT by e-beam evaporation and those obtained after annealing at 350 and 400 °C without exposing to the source gas. The average size distribution of the Au droplets was found to be 8 ± 5 nm [Fig. 1(a)]. This distribution almost remains the same (10 ± 5 nm) after the formation of Au–Si eutectic droplets by annealing at 350 °C [Fig. 1(b)], where droplets become spherical. We suggest that these molten Au–Si eutectics were formed by consuming Si from the underlying substrate.[13,14] However, the size distribution of the Au–Si eutectic alloys was adversely affected by annealing at 400 °C, where random and large eutectic islands were formed [Fig. 1(c)]. The coarsening of Au at higher annealing temperatures has also been reported,[7,12] but we observed that this coarsening effect only occurs above 350 °C. These observations suggest that the aggregation of Au can be suppressed in low-temperature growth.

Figure 2(a) shows the SEM image of a SiNW with a diameter of 8 nm, which indicates that wires grow via VLS mechanism. Figures 2(b)–2(d) show the SEM images of the SiNWs grown at 350, 375, and 400 °C, respectively. In all these cases, the SiNWs were grown by exposing Au droplets covering the Si(111) substrate to a mixture with a Si_2H_6 flow rate of 1 sccm and a H_2 flow rate of 49 sccm for 30 min at 3 Torr. Figure 2(b) shows the high-density SiNWs grown at

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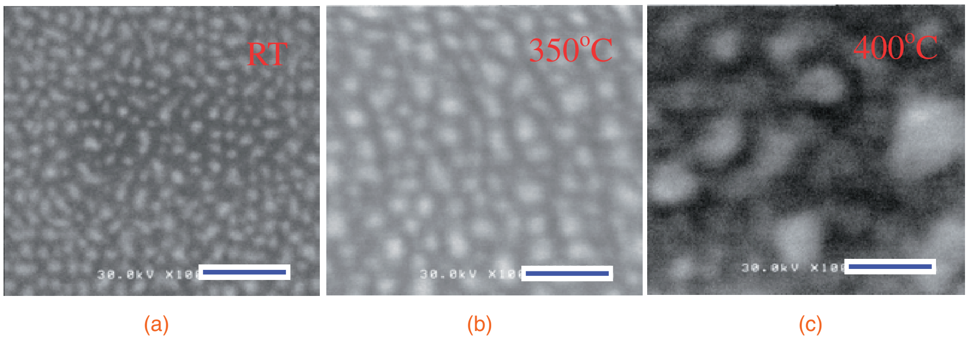

Fig. 1. SEM images of (a) Au droplets deposited on Si substrate at room temperature by e-beam evaporation, (b) Au–Si eutectics formed after annealing at 350 °C, and (c) Au–Si eutectics formed after annealing at 400 °C. Scale bar in (a)–(c) is 30 nm.

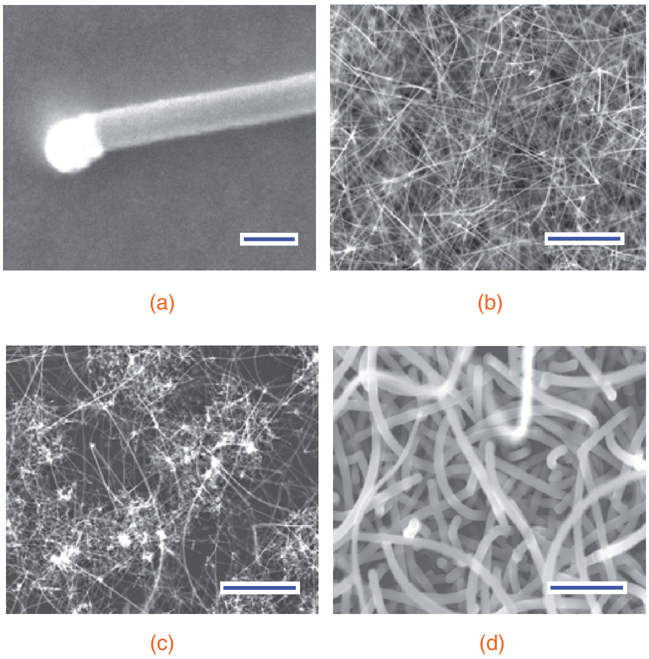

Fig. 2. SEM images of (a) SiNW showing VLS growth, (b) high-density SiNWs grown on Si(111) at 350 °C, (c) SiNWs grown at 375 °C, and (d) SiNWs grown at 400 °C. Scale bar in (a) is 10 nm and in (b)–(d) is 2 μm.

350 °C. The wires were found to be straight and have small and uniform-diameters (12 ± 5 nm). The diameters of the wires were observed to be consistent with the sizes of the Au droplets prepared at RT. Some very long wires showed bending. The effect of the Au aggregation at 375 °C can be observed in Fig. 2(c), where the SiNWs grow in 5 × 5 μm patches by leaving micron-sized empty spaces around them resulting in a relatively large size distribution (8–40 nm). However, at 400 °C, the SiNWs grow in small spheres widely separated from one another with very random and large diameters (350 ± 50 nm) due to the aggregation of Au [Fig. 2(d)]. We observed that 350 °C is a critical temperature above which the aggregation of Au adversely affects the diameter distribution of the VLS grown SiNWs.

Figure 3 shows the size distributions of the Au droplets prepared at RT and SiNWs grown at 350 °C. The heights of the lines represent the occurrences of the Au droplets and SiNWs determined on the basis of SEM results shown in Figs. 1(a) and 2(b). The counts and sizes of the Au droplets can be correlated to those of the SiNWs grown at low temperatures. The size distribution of the SiNWs grown at high temperatures cannot be correlated to that of the Au droplets prepared at RT.

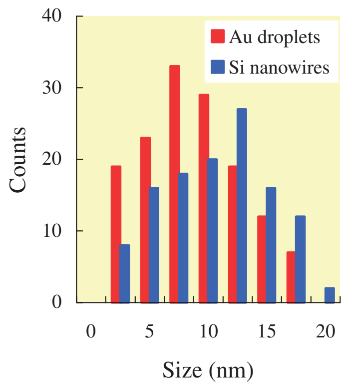

Fig. 3. Size distributions of Au droplets (8 ± 5 nm) and SiNWs (12 ± 5 nm) prepared at 350 °C.

High-resolution TEM analysis revealed that the structural properties of the SiNWs are size dependent. Figures 4(a) and 4(b) show TEM images of the SiNW grown at 350 °C with a diameter of about 8 nm. We observed that the SiNWs with small-diameters, grown in (111) as a preferential direction, are straight and have clean side walls [Fig. 4(a)]. Figure 4(b) shows that the wires have a single-crystal defect-free core covered with a very thin surface oxide layer. A high crystal quality ensures better physical properties for small-diameter wires.

However, different types of defect were observed in the SiNWs with increasing diameters grown at 375 °C. A twin boundary appears in the SiNWs with a diameter of about 18 nm in the form of a slightly visible line without affecting the lattice orientation, as shown in Fig. 5(a) in red. Meanwhile, the SiNWs with a diameter of 20 nm become bicrystalline and contain a single (111) twin boundary. Figure 5(b) shows the high-resolution TEM image of the bicrystalline SiNWs grown in the (111) direction when viewed down the [110] plane. Bi crystal orientation has been

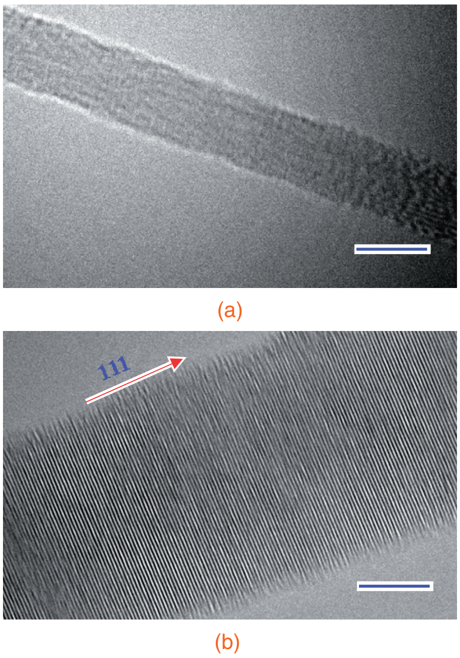

Fig. 4. (a) Low-resolution TEM image of SiNW with diameter of 8 nm. Scale bar is 10 nm. (b) High-resolution TEM image of same wire grown in (111) direction. Scale bar is 2 nm.

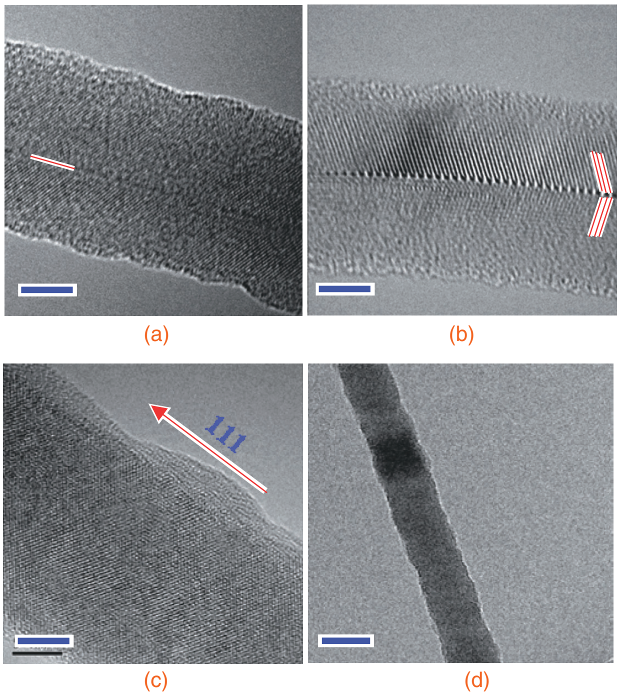

Fig. 5. High-resolution TEM images showing twin defects in SiNWs with diameters of (a) 18, (b) 20, and (c) 24 nm, (d) low-resolution TEM image indicating zig-zag appearance of wires. Scale bar in (a)–(c) is 5 nm and in (d) is 20 nm.

indicated with red lines. Periodic twins were formed in the SiNWs with diameters above 20 nm, transforming the side walls of the wires to have a zig-zag morphology [Figs. 5(c) and 5(d)]. These structural defects were observed in the SiNWs with diameters larger than 17 nm.

In conclusion, we have investigated the effect of substrate temperature by the VLS growth of SiNWs from a Au catalyst. We have demonstrated that 350 °C is the critical temperature required to preserve the initial size distribution of high-density Au droplets during Au–Si eutectic alloy formation for growing SiNWs with small and uniform diameters. Such a low temperature has been achieved by the low-temperature decomposition of Si_2H_6. High growth temperatures, such as 400 °C, form large and random eutectic droplets by aggregation, which results in the large and random diameters of Si wires. We have shown that the crystal quality of the wires is size dependent. TEM analysis has revealed that, in contrast to the large wires, SiNWs with small diameters are defect-free and have high-quality single-crystal cores. Low-temperature-grown SiNWs with small diameters are attractive for SiNW-based electronic and photonic device applications because defect-free wires ensure good physical properties.

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