The impacts of surface conditions on the vapor-liquid-solid growth of germanium nanowires on Si (100) substrate

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The impacts of surface conditions on the growth of Ge nanowires on a Si (100) substrate are discussed in detail. On SiO_2-terminated Si substrates, high-density Ge nanowires can be easily grown. However, on H-terminated Si substrates, growing Ge nanowires is more complex. The silicon migration and the formation of a native SiO_2 overlayer on a catalyst surface retard the growth of Ge nanowires. After removing this overlayer in the HF solution, high-density and well-ordered Ge nanowires are grown. Ge nanowires cross vertically and form two sets of parallel nanowires. It is found that nanowires grew along ⟨110⟩ directions. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2968201]

One-dimensional semiconductor nanostructures have attracted much attention because of their potential applications in the design of nanoelectronic, photonic, and sensing devices.[1] Due to their high mobility of electrons and holes, Ge nanowires show their potential application in high-speed field-effect transistors.[2–4] Moreover, Ge nanowires are potentially useful for high-speed quantum computing because of long decoherence time due to the predominance of spin-zero[5,6] nuclei and the advantage of a large excitonic Bohr radius in Ge (24.3 nm), allowing for quantum confinement to be observed in relatively large structures[7,8] and at high temperatures. In order to realize these applications, controllable and high-quality nanowire growth is important. Much attention has been focused on the growth of Ge nanowires.[9–12] However, only few papers discuss the impacts of surface conditions on the vapor-liquid-solid synthesis of Ge nanowires. In this letter, we will discuss them in detail.

Au catalyst layers with thicknesses of 0.1 and 1 nm were evaporated by electron beam evaporation at room temperature on two kinds of substrates: SiO_2-terminated (a few nanometers of native SiO_2 layer or 170 nm thermal oxidized SiO_2) and H-terminated (the wafers were dipped in 1.5% HF solution for 1 min and were immediately loaded in the chamber for electron beam evaporation) silicon (100) substrates. In order to satisfy the rules of minimum surface energy, the evaporated Au shows different topographies at different substrate surface conditions, as shown in Figs. 1(a)–1(d). On the SiO_2-terminated substrate, because the condensing Au adatoms are more strongly bound to each other than to the substrate,[13] these atoms encounter other atoms, nucleate, and agglomerate to form stable islands with diameters of 2–10 nm [Figs. 1(a) and 1(b)]. The thicker Au layer will induce the formation of bigger Au dots. On the other hand, on the H-terminated Si substrate, the Au catalyst prefers to deposit in the Stranski–Krastanov mode to form Au small islands with a wetting layer, as shown in Figs. 1(c) and 1(d).

All Ge nanowires were grown at 300 °C for 20 min by a low-pressure chemical vapor deposition method with 10% GeH_4 precursors (in an atmosphere of hydrogen) in a total pressure of 5 Torr. On a SiO_2-terminated Si substrate, without any pretreatment to the catalysts, high-density Ge nanowires with diameters of 5–20 nm were grown on Au catalysts with thicknesses of 1 nm (Fig. 2) and 0.1 nm. Both high-resolution transmission electron microscopy and x-ray diffraction results reveal high-quality single-crystalline Ge nanowires with a cubic diamond structure as we discussed before.[14] It was found that the thickness of the SiO_2 layer, either a few nanometers of native layer or a thicker thermal oxidized SiO_2, has no influence on the growth of Ge nanowires.

However, very few Ge nanowires were grown on the H-terminated Si substrate under the same growth conditions (Fig. 3). Even after high temperature preannealing (650 °C in vacuumed condition) to dewet the Au wetting layer, it had no great influence on the growth of Ge nanowires.

When observing the topography of Au catalysts evaporated on the H-terminated substrate by a scanning electron microscope (SEM), we noticed that the contrast between the

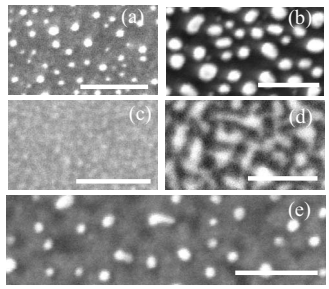

FIG. 1. SEM images of Au catalysts evaporated on SiO_2-terminated silicon substrates with a thickness of (a) 0.1 nm and (b) 1 nm. Au catalysts evaporated on H-terminated silicon substrates with a thickness of (c) 0.1 nm and (d) 1 nm. (e) SEM image of 1-nm-thick Au evaporated on H-terminated silicon after HF treatment for 2 min. The scale bars in the figures are 30 nm.

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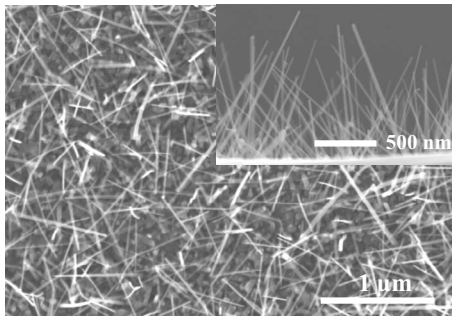

FIG. 2. Top-view SEM image of high-density Ge nanowires grown on 1-nm-thick Au catalysts evaporated on SiO_2-terminated silicon substrates. The inset shows their cross-section image.

Au metal and the Si substrate at the edge area is smaller and the brightness of the Au metal in the SEM image is weaker compared with that evaporated on the SiO_2 substrate. It seems that Au catalysts are covered by some insulator layers. So maybe the formation of a very thin silicon oxide overlayer due to the gold catalyzed migration of silicon through the gold film[15–18] retards the growth of Ge nanowires.

In order to verify this hypothesis, Au catalysts evaporated on H-terminated substrates were dipped into a 1.5% HF solution for 2 min and then were immediately loaded into a growth chamber to grow Ge nanowires. On 1-nm-thick Au catalyst substrates, high-density and well-ordered Ge nanowires were grown, as shown in Fig. 4(a). Obviously, it has a great improvement for Ge nanowire growth by removing this overlayer, and it confirms that the SiO_2 overlayer formed on the catalyst surface prevents the growth of Ge nanowires. Figure 1(e) shows the SEM image of 1-nm-thick Au catalysts after HF treatment. Clear Au dots can be found after removing the SiO_2 overlayer. In the case of 0.1-nm-thick Au catalysts, even after HF treatment, no nanowire was grown. We did not find any Au dots after HF treatment in the SEM image since they are still in the wetting layer stage. So there are no nucleation centers for Ge atoms to grow in the axial direction. The GeH_4 will get more chances to be decomposed and deposited to form a film since the AuSi eutectic alloy exists on the whole surface.

Compared with the random-directed Ge nanowires grown on the SiO_2-terminated substrate, as shown in Fig. 2, Ge nanowires grown on the H-terminated Si (100) substrate show a more ordered structure. Almost all Ge nanowires cross vertically and form two sets of parallel nanowires. It should be pointed out that each set of Ge nanowires has around 45° angle with a [110] cleavage direction as labeled in Fig. 4(a). Until now, only two growth directions, [110] and

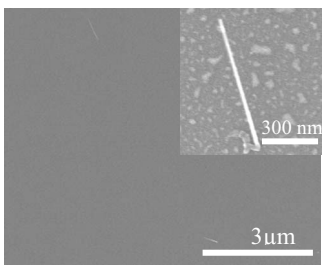

FIG. 3. Top-view SEM image of Ge nanowires grown on H-terminated silicon substrates. Inset shows the enlarged image of one wire, and it exhibits the same diameter as that grown on SiO_2-terminated substrates.

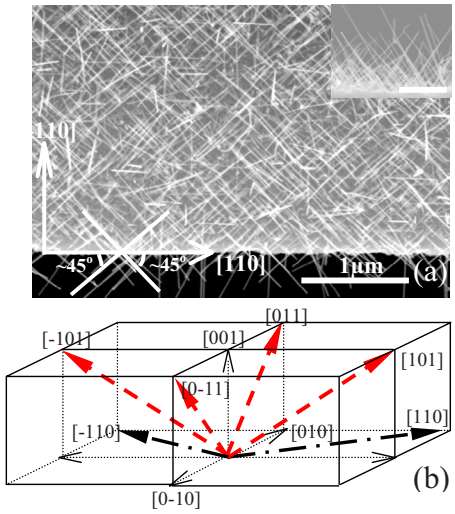

FIG. 4. (Color online) (a) Top-view SEM image of high-density and well-ordered Ge nanowires grown on 1-nm-thick Au catalysts evaporated on H-terminated silicon (100) after being dipped into the HF solution to remove the SiO_2 overlayer. The bottom edge is the [110] cleavage direction. The inset shows its side-view SEM image, and the scale bar is 500 nm. (b) Three-dimensional schematic of the Ge nanowire growth direction on a Si (100) wafer. Four dashed arrows directed to [101], [011], [−101], and [0−11] are the Ge nanowire growth directions.

[111], were found for Ge nanowires grown on silicon substrates.[2,3,5,10–12] Based on this fact and our experiment results, we believe that Ge nanowires are grown orderly along [101], [011], [−101], and [0−11] directions as the four dashed arrows shown in Fig. 4(b), in which these four growth directions are crossed vertically and have a 45° degree with [110] and [−110] cleavage directions. It agrees well with the experiment results as shown in Fig. 4(a). The two dashed-dotted arrows in Fig. 4(b) are [110] and [−110] cleavage directions for (100) wafer as labeled in Fig. 4(a).

During the growth of Ge nanowires on Au catalysts evaporated on the H-terminated Si substrate after HF treatment, GeH_4 will decompose in the AuSi eutectic alloy located at the interface between the single-crystalline Si surface and Au layer, and then the supersaturation Ge atom will separate out to grow in the axial direction. This ordered structure at the interface can induce the Ge nanowires to grow along only ⟨110⟩ directions. This capability to control the nanowire growth direction would be very important in engineering the transport characteristics for electrons and holes separately to get the best switching performance of a complementary logic circuit configuration.[19] Also it is quite attractive for future large-scale nanowire integration.

In the case of Au catalysts evaporated on the SiO_2-terminated substrate, maybe the strong bond between Si and O atom retards the migration of silicon to the surface and the formation of the SiO_2 overlayer. Therefore Ge nanowires can be grown without HF treatment.

In conclusion, high-density Ge nanowires can be easily grown on SiO_2-terminated Si (100) substrates. However, the SiO_2 overlayer formed on the surface of Au catalysts evaporated on the H-terminated Si substrate prevents the growth of Ge nanowires. After removing this SiO_2 overlayer by HF solution, high-density and well-ordered Ge nanowires can be obtained. Moreover, nanowires can be grown orderly along [101], [011], [−101], and [0−11] directions.

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