Vertically Oriented Germanium Nanowires Grown from Gold Colloids on Silicon Substrates and Subsequent Gold Removal

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ABSTRACT

A linker-free method to deposit citrate-stabilized Au colloids onto hydrogen-terminated Si by acidifying the Au colloid solution with HF or HCl is presented. This method prevents oxide formation and provides a model system for studying orientation control of nanowires by epitaxy. Conditions are reported that result in vertically oriented Ge nanowires of uniform diameter and length on Si(111). We then present a method to remove Au catalysts from the nanowires with aqueous triiodide and HCl.

Vertically oriented semiconductor nanowires of controlled diameter and length are desired for many applications, including use as active elements for 3-D electronics.[1,2] Germanium nanowires (GeNWs) in particular are interesting due to their low growth temperatures of less than 400 °C.[3−6] To control the orientation of growing nanowires, many groups have used epitaxy from crystalline substrates.[7−23] Because GeNWs larger than 20 nm in diameter grow preferentially along the Ge⟨111⟩ crystal direction,[23] vertical orientation can in principle be achieved by choosing an appropriate crystalline substrate to match the Ge⟨111⟩ orientation. For instance, we have previously studied GeNW heteroepitaxy on Si(111) substrates using vapor-deposited gold films as catalysts.[23] While some degree of orientation control was achieved, the heterogeneity in catalyst particle size and high particle density that results from vapor-deposited gold films made it difficult to discover conditions that gave predominantly vertical GeNW growth. A system with homogenously sized gold catalyst particles on bare silicon substrates is needed to effectively study orientation control by epitaxy. In this letter, we present a method to deposit homogenously sized gold catalysts from aqueous solutions onto oxide-free silicon that results in GeNW heteroepitaxy. We then present GeNW growth conditions that give predominantly vertically oriented nanowires of uniform diameter and length on Si(111) substrates. Because,

for many applications, removal of the gold catalyst after growth is desired, we have investigated and present here a method to remove the gold catalyst after growth while preventing substantial etching of the GeNWs.

The narrow size distribution of commercially available gold colloids offers a convenient way to control nanowire diameters.[24] However, as received from the vendor, citrate-stabilized gold colloids do not adhere to silicon substrates (Figure 1a). For that reason, a positively charged polyelectrolyte layer on the substrate is often used as a linker to attract and bind the negatively charged gold colloids.[24−26] Another method reported in the literature is simply to dry the gold colloid solution on the silicon substrate.[14] We have found, however, that these deposition methods prevent GeNW heteroepitaxy on silicon substrates. We hypothesize that the lack of epitaxial growth from such samples is due to a thin oxide film on the silicon substrate formed by either the water-based polyelectrolyte or the gold colloid solution. High-temperature methods above 400 °C that promote nanowire epitaxy from gold colloids deposited in these ways are, however, known. For instance, several groups have used gaseous HCl (or $SiCl_4$ in H_2 producing HCl) at high temperatures to remove oxide during silicon nanowire growth on silicon substrates.[10,13,19] Kamins et al. have annealed colloid-coated silicon substrates in hydrogen at 650 °C prior to growth to promote epitaxy of GeNWs on silicon substrates.[14] The high temperatures needed for these methods are undesirable, however, because GeNW growth is otherwise achievable at low temperatures. A method was therefore

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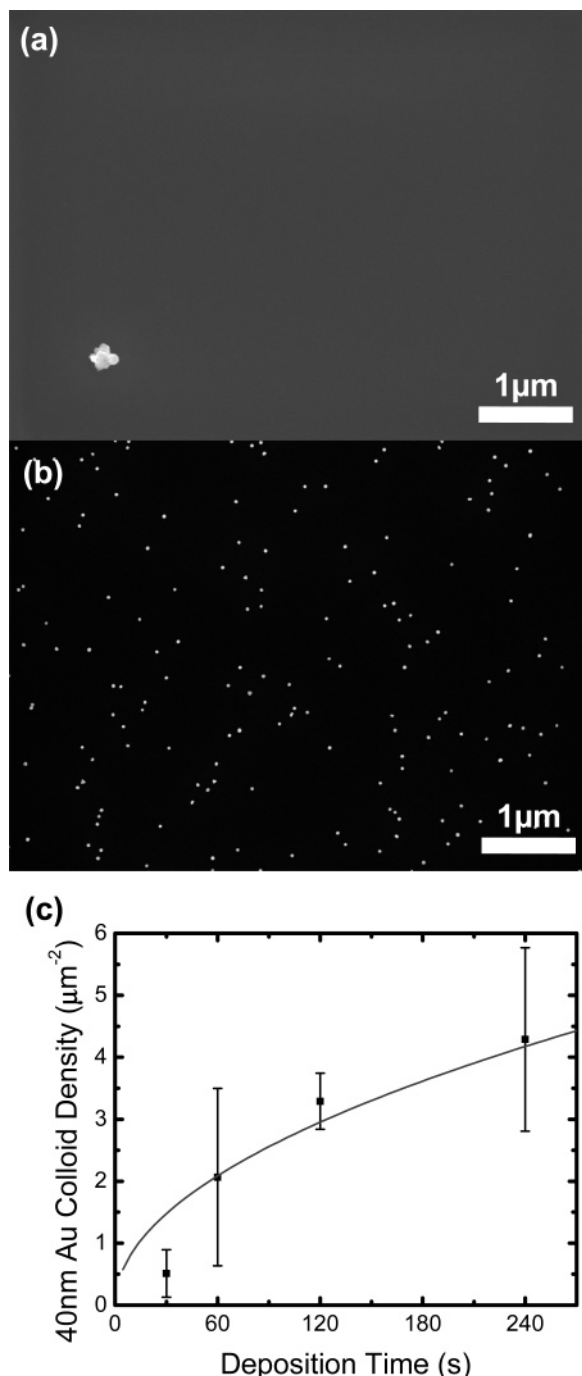† Department of Chemistry.
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Figure 1. SEM micrographs showing gold colloid deposition from 2 min exposure of (a) hydrogen-terminated Si(111) to as-received 40 nm gold colloid solution, (b) hydrogen-terminated Si(111) to 40 nm gold colloid solution containing 0.1M HF, (c) plot of 40 nm gold colloid density vs deposition time on Si(111) substrates. The solid line is a guide to the eye based on the square root time dependence of gold colloid deposition density that has been previously observed for a related system.[25]

sought either to prevent oxide formation on the silicon substrate during gold colloid deposition or to remove any oxide after gold colloid deposition using a room-temperature chemical etch.

While investigating methods to deposit gold colloids onto silicon substrates that would avoid silicon oxide formation, we added 1% HF, a common silicon oxide etchant, to a solution of 40 nm gold colloids to give a concentration of

0.1 M HF.[27] We found that exposure of a hydrogen-terminated silicon substrate to this solution resulted in gold colloid deposition without the need for a polyelectrolyte linker. An SEM micrograph of this result on Si(111) is shown in Figure 1b. Si(111) substrates were pretreated with 1M HF for 5 min to remove native oxide and form the hydrogen-terminated surface[28] prior to exposure to the gold colloid solution containing 0.1M HF. The resulting gold colloid density on Si(111) after 2 min was 3.3 ± 0.5 colloids/μm^2, and no agglomeration of the gold colloids was visible (Figure 1b). Figure 1c shows that the density of gold colloids on the surface increased with time. Deposition was also observed on Si(100) and Si(110) substrates. Similarly, while 5 and 10 nm gold colloids do not deposit on hydrogen-terminated silicon surfaces from as-received gold colloid solutions,[29] the addition of HF to the gold colloid solutions resulted in colloid deposition.[30]

To determine the reason for gold colloid deposition, we investigated the possible effect of pH. The pH of the gold colloid solution prior to the addition of HF was 6.5, as measured using a pH meter. The addition of HF at 0.1 M lowered the pH to approximately 2, as measured using pH paper. To test if the lowered pH may be the reason for gold colloid deposition, HCl was added at 0.01 M to the as-received gold colloid solution to lower the pH to 2. Exposure of Si(111) to this gold colloid solution for 2 min resulted in deposition similar to that obtained by adding HF.[30]

The gold colloids used in this study are citrate stabilized. At neutral pH, negatively charged citrate ions coat the gold colloids, providing Coulombic repulsion to prevent agglomeration. This negative charge may also prevent deposition onto bare silicon, which is expected to have a negatively charged surface in water at neutral pH.[31] On the other hand, at pH 2, the citrate ions should be converted to neutral citric acid because the pK_a for the first ionization of citric acid is 3.1.[32] The colloids do in fact appear to be neutralized, as evidenced by their slow agglomeration over a day, with the normally red gold colloid solution turning purple. It is therefore important to acidify the colloid solution immediately prior to use.

Exposure of a thermally oxidized silicon surface [5000 Å SiO$_2$ on Si(100)] to either HF- or HCl-acidified gold colloid solutions for 2 min resulted in no gold colloid deposition.[30] The lack of gold colloid deposition onto silicon oxide from acidified colloid solutions may be due to the notoriously poor adhesion of gold to silicon oxide.[33] This selectivity for colloid deposition on silicon versus silicon oxide may provide a way to pattern gold colloids by selective deposition onto exposed silicon windows etched in an overlying silicon oxide mask.

GeNWs were found to grow epitaxially on silicon substrates from gold colloids deposited using acidified gold colloid solutions. Figure 2 shows results for nanowire growth on hydrogen-terminated Si(111) from 40 nm gold colloids deposited by the HF-addition method described above. GeNWs were grown in a lamp-heated, cold-wall CVD reactor immediately after colloid deposition to prevent oxidation of the silicon substrate from air. The pressure of the reactor chamber was controlled using an automatic
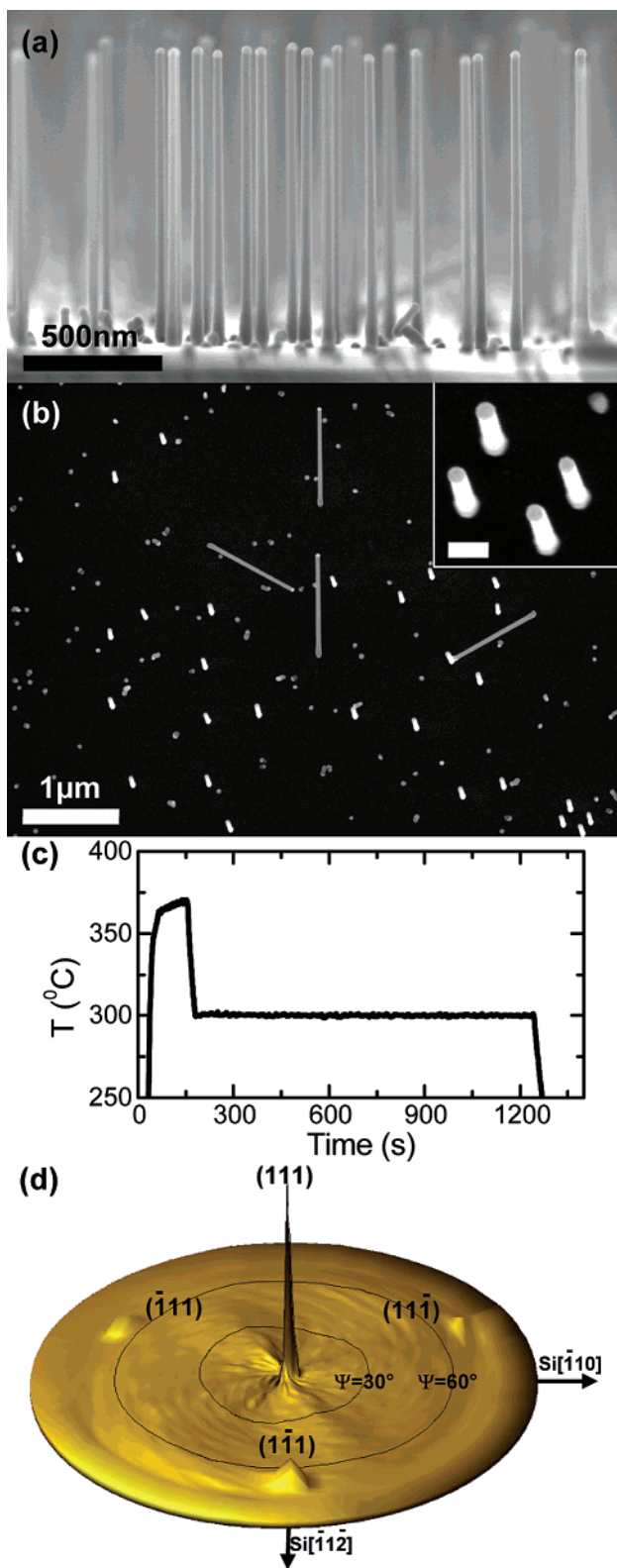
(a)

500nm

(b)

1µm

(c)

(d)

(111)

(ī11)   (11ī)

Si[ī10]

Ψ=30°   Ψ=60°

(1ī1)

Si[īī2]

Figure 2. (a) Cross-section SEM of GeNWs grown epitaxially on Si(111) from 40 nm gold colloids deposited using the HF-addition method showing predominantly vertically oriented GeNW of uniform diameter and length, (b) plan-view SEM of the sample in Figure 2a showing the other three ⟨111⟩ growth directions and (2b inset) magnified view of vertical GeNWs (scale bar is 100 nm), (c) two-step temperature profile used to grow GeNWs in Figure 2a,b, (d) XRD pole figure of Ge{111} diffraction from the sample shown in Figure 2a,b.

pressure controller and was set to 30 Torr. The source gas used was 10% germane diluted in hydrogen, and a secondary source of hydrogen was used to further dilute the source gas for a final germane partial pressure of 0.44 Torr. A two-step temperature profile was used, shown in Figure 2c, to initiate nanowire growth at a high temperature near 375 °C for 2 min and then continue growth at a reduced temperature of 300 °C for 18 min to suppress uncatalyzed sidewall deposition.[23,34,35]

To confirm epitaxy, XRD analysis of the sample was performed. An XRD pole figure measuring diffraction intensity from Ge{111} planes is shown Figure 2d. The peak showing diffraction from Ge(111) planes normal to the Si(111) substrate (at $\psi = 0°$) and the three peaks corresponding to the other Ge{111} planes (at $\psi = 70.5°$) match the pole pattern of the Si(111) substrate (provided in the Supporting Information), thus confirming the heteroepitaxial relationship between the nanowires and the substrate.

The cross-section SEM image in Figure 2a shows that these sample preparation and growth conditions result in predominantly vertically oriented GeNWs on Si(111) substrates. Vertically oriented GeNWs appear as bright spots in the plan-view SEM images, allowing the fraction of vertical wires to be determined (Figure 2b and inset). From analysis over an area of 460 μm^2 (429 nanowires), we find that 94% of nanowires grew in the vertical [111] direction. Six percent of the nanowires grew in the other nonvertical ⟨111⟩ directions, which appear at 120° from each other in the plan-view SEM in Figure 2b. No other growth directions were observed. We suspect that the high fraction of vertical wires is a result of the clean silicon surface and the use of an initial growth temperature above the Au−Ge eutectic of 360 °C. If a lower initial growth temperature is used or the substrate becomes slightly oxidized, a reduction in the fraction of vertical wires is observed.

It can also be seen in the cross-section SEM image in Figure 2a that all nanowires are the same length, indicating that they started growing at the same time. We have found that, to achieve uniform GeNW lengths, it is necessary to lower the growth temperature below the minimum temperature needed to initiate nanowire growth after a short initiation step above this minimum temperature (∼320 °C for 40 nm gold particles). The lower temperature prevents progressive initiation of nanowires, resulting in varying nanowire lengths while still allowing nanowires that have already initiated to continue growing. A drawback, however, to reducing the growth temperature to prevent progressive initiation of GeNW growth is that the yield decreases.[36] The overall yield of nanowire growth was approximately 28% for the samples shown in Figure 2a,b as compared to 72% for samples where the temperature is kept at 375 °C for 20 min. Increasing the initiation temperature above 375 °C can improve the yield, but uncatalyzed germanium deposition increases dramatically above these temperatures. An important future goal is to find ways to achieve 100% initiation in a short period of time without uncatalyzed deposition.

Another observation from Figure 2a is that there is a small section at the bottom of the nanowires that has a diameter
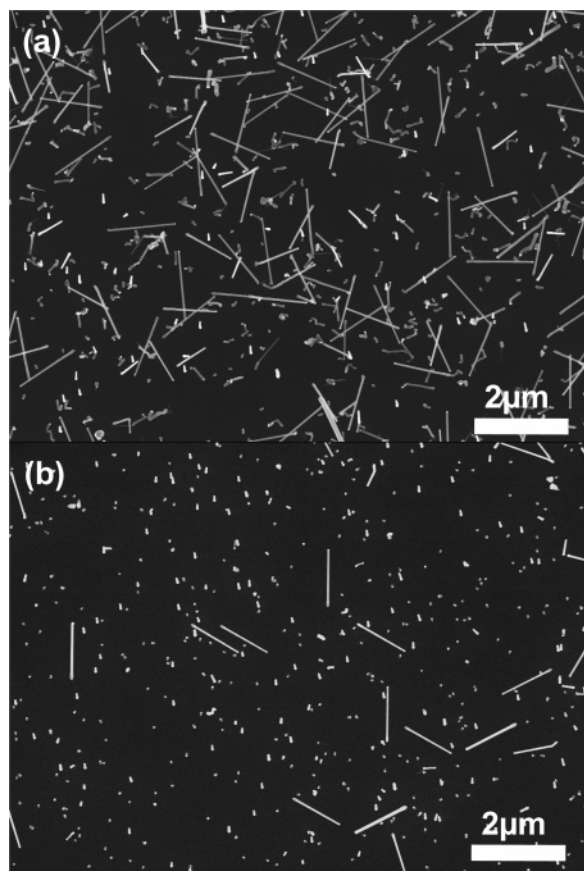
Figure 3. SEM micrographs showing (a) poor GeNW epitaxy on Si(111) from gold colloids deposited using the ATPES technique and (b) the resulting improvement of epitaxy by treating the same samples with 1M HF for 3 s after colloid deposition and immediately prior to nanowire growth.

wider than the rest of the nanowire. This "base" is formed during the initiation step and may result from either sidewall deposition or a larger Au−Ge liquid volume of the catalyst at the higher temperature. The narrower section of the nanowires is formed during the lower temperature growth step, and its nontapered shape indicates a low rate of uncatalyzed germanium deposition on the nanowire sidewalls.

An alternate approach to achieving nanowire epitaxy on silicon substrates from gold colloids is to deposit gold colloids using other methods and then remove any oxide that may have formed during sample preparation. An obvious choice is to use aqueous HF to remove silicon oxide after gold colloid deposition. We indeed found that epitaxy was achieved with the use of an HF-last treatment on samples for which the gold colloids were deposited using the polyelectrolyte 3-aminopropyltriethoxysilane (APTES) as the linker, as shown in Figure 3.[37] Figure 3a shows the low degree of epitaxy (24%) of GeNWs grown from gold colloids deposited onto APTES-treated Si(111), while Figure 3b shows the high degree of epitaxy (94%) when the sample is exposed to 1M HF for 3 s immediately prior to placement in the reactor.[38] The fraction of vertically oriented GeNWs for the sample treated with HF is 82%. While using an HF-last treatment improves the degree of epitaxy significantly

when the gold colloids are deposited using an APTES binding layer, this method is less effective in achieving epitaxy and vertically oriented GeNWs than depositing gold colloids from HF-acidified gold colloid solutions. It is therefore concluded that the HF-addition method for depositing gold colloids is preferred.

While the HF-addition method is preferred for depositing gold colloids, an HF-last treatment can be useful to recover epitaxy if samples have been oxidized in air after gold colloid deposition. It was found that if samples prepared using the HF-addition method are left in air for 60 min prior to nanowire growth, the degree of epitaxy is reduced to 63%. Treatment with 1M HF for 3 s largely recovers the degree of epitaxy to 98%, although again the fraction of vertical nanowires drops to 81%.[30]

On the basis of our findings, to obtain the greatest fraction of vertical nanowires, it is important to remove any native oxide on the substrate prior to gold colloid deposition, prevent oxide formation during gold colloid deposition by using the HF-addition gold colloid deposition method, immediately place samples into the reactor for GeNW growth, and use an initial GeNW growth temperature above the Au−Ge eutectic.

Removal of the gold catalyst after growth is needed for many applications. We therefore investigated two gold etches commonly used in microelectronics: aqua regia (an aqueous solution of HNO_3 and HCl) and a commercial triiodide etch, Transene TFA (an aqueous solution of I_2 and KI). We found that, while both solutions removed the gold from the tips of the nanowires, as determined by SEM and TEM, they also significantly etched the GeNWs, aqua regia more aggressively than the triiodide etch. Figure 4a shows a bright-field TEM image of an unetched GeNW with the gold catalyst clearly visible at the tip, while parts b and d of Figure 4 show a bright-field TEM image and an SEM image of GeNWs after a 20 s gold etch using Transene TFA. The GeNWs are significantly narrower than unetched wires and have very rough sidewalls. Previous work in our group has shown that treating GeNWs with aqueous HCl creates a chlorine passivation that inhibits oxidation of the germanium in air.[39] We speculated that the passivation might also protect the GeNWs from dissolving in the triiodide etch. Indeed, we found that adding HCl to the triiodide etch solution resulted in minimal nanowire etching with much smoother sidewalls while still removing the gold catalysts from the tips of the nanowires, as shown in the bright-field TEM and SEM image in parts c and e of Figure 4, respectively. By analyzing bright-field TEM images such as Figure 4c, it was determined that the GeNW sidewalls are etched approximately 4 nm. Also, as shown in Figure 4c, the gold etch results in a small tapered section at the tip of the GeNW. Bright-field TEM images of magnified portions of the nanowire surfaces shown in Figure 4a−c are provided in the Supporting Information. The procedure for removing the gold catalyst using the HCl-containing aqueous triiodide solution is described below.

Gold colloids were deposited onto Si(111) substrates using the HF-addition method as described above, with an extended
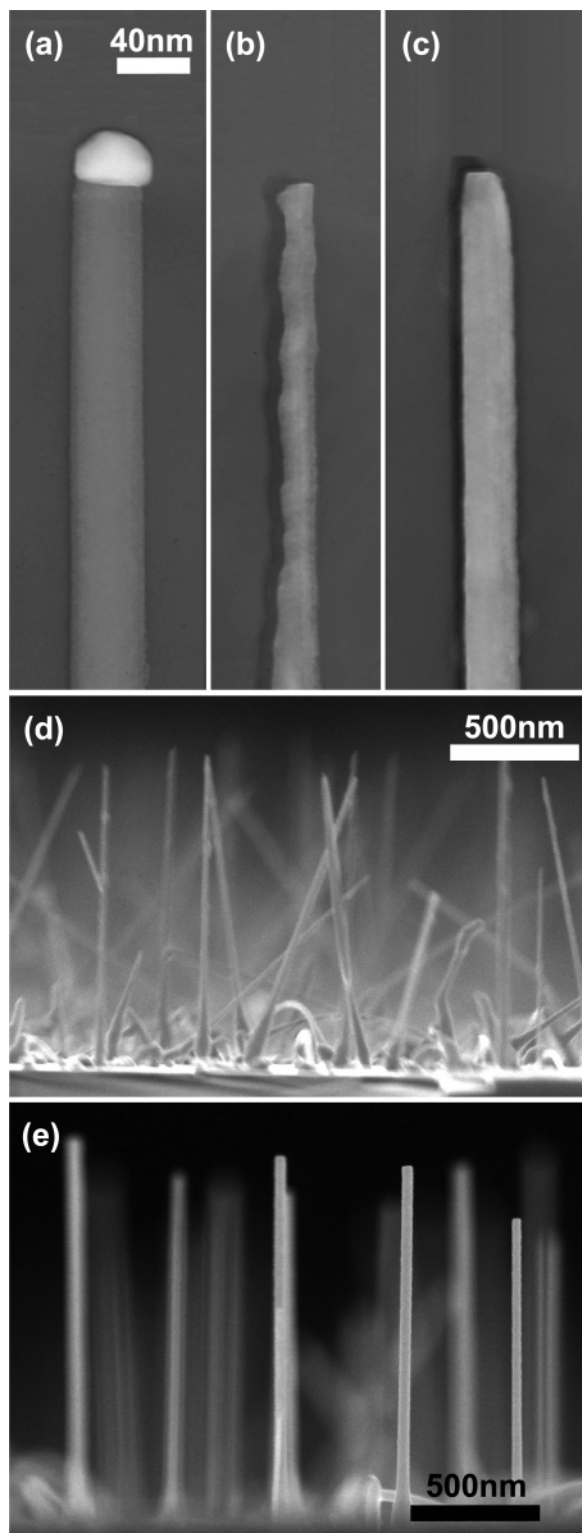
Figure 4. (a) Bright-field TEM image of a nanowire prior to etching showing the gold catalyst at the tip, (b) bright-field TEM image showing damage by treatment with an aqueous triiodide solution, (c) bright-field TEM image showing removal of gold with minimal etching of the nanowire using an aqueous triiodide solution containing HCl, (d) SEM image showing damage to GeNWs by treatment with an aqueous triiodide solution, and (e) SEM image showing the removal of the gold catalyst from the GeNW tip without damaging the wires using an aqueous triiodide solution containing HCl.

deposition time of 5 min. The resulting density of colloids observed by SEM was 5.7 colloids per μm^2 (approximately 1.1×10^{15} gold atoms per cm^2). GeNWs were grown from the gold colloids as described above. To remove the gold from the tips of germanium nanowires, the sample was immersed into an HCl-containing etch solution (9 parts by volume Transene TFA to 1 part by volume 36% HCl) for 20 s. The gold removal solution was rinsed from the sample surface with 1M HCl, and the wet sample surface was then dried in the vapor of boiling isopropyl alcohol for 10 s. The isopropyl alcohol vapor drying step appears to reduce capillary damage to the nanowires.

The etching and rinsing solutions were collected and analyzed for gold by inductively coupled plasma optical emission spectroscopy (ICP-OES). The measured amount of gold corresponded to $1.5 \pm 0.1 \times 10^{15}$ Au atoms/cm^2, in reasonable agreement with the estimated gold coverage determined above from the SEM images. The gold coverage measured by ICP-OES for another GeNW sample that was destructively etched (all nanowires were dissolved) using the triiodide solution without HCl for 300 s was $1.4 \pm 0.3 \times 10^{15}$ Au atoms/cm^2, in agreement with the values obtained by the nondestructive etch and from the SEM images. To confirm the removal of the gold by the nondestructive etch, the sample from which the gold had been removed was then etched by the destructive method and the etching and rinsing solutions were analyzed by ICP-OES. The measured amount of gold was below the detection limit of the ICP-OES instrument (3×10^{14} Au atoms/cm^2), confirming the removal of most of the gold.

In conclusion, we have successfully grown vertically oriented GeNWs of uniform length and diameter on silicon substrates from gold colloids and then removed the gold catalysts. To achieve GeNW epitaxy on silicon substrates from gold colloids, the silicon surface must be oxide free. We have discovered a linker-free method to deposit citrate-stabilized gold colloids onto hydrogen-terminated silicon substrates by acidifying the gold colloid solution with HF or HCl, which prevents oxide formation and allows for epitaxial growth of GeNWs. It was also found that nanowire epitaxy can be achieved, although of lesser quality, from samples prepared using other gold colloid deposition methods that normally give randomly oriented nanowire growth by using an aqueous HF treatment to remove any oxide formed during the preparation. A two-step temperature profile was used to achieve vertically oriented GeNWs of uniform length. More investigation is needed to improve the yield of nanowire growth. Finally, adding HCl to a triiodide etch allowed the removal of gold catalysts from the GeNW tips after growth while preventing significant etching of the nanowires.

Supporting Information Available: SEM images showing 5 and 10 nm gold colloid deposition on Si(111) substrates resulting from treatment with HF acidified colloid solutions, SEM image of 40 nm gold colloid deposition on Si(111) resulting from treatment with HCl-acidified colloid solution, SEM image showing no gold colloid deposition on SiO_2 substrate from treatment with HCl-acidified 40 nm gold colloid solution, SEM images showing the reduction of the degree of GeNW epitaxy by exposure of sample to air for 60 min prior to GeNW growth and the subsequent improvement of epitaxy by treatment with 1M HF prior to GeNW growth, and bright-field TEM images of the nanowire surfaces prior to etching, after etching with an aqueous triiodide etch, and after etching with an HCl-containing aqueous triiodide etch. This material is available free of charge via the Internet at http://pubs.acs.org.

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NL070595X