Silver catalyzed ultrathin silicon nanowires grown by low-temperature chemical-vapor-deposition

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In this work we demonstrate the synthesis of monocrystalline silicon nanowire using silver particles as catalysts at temperatures of less than 500 °C by means of ultrahigh vacuum chemical vapor deposition. The nanowires were grown epitaxially on silicon substrates and had diameters of about 10 nm. We furthermore show that the silver remnants can be wet chemically removed with potassium ferricyanide and sodium thiosulfate. © 2010 American Institute of Physics. [doi:10.1063/1.3393601]

I. INTRODUCTION

The standard technique for silicon nanowire (SiNW) growth is chemical vapor deposition (CVD) of silicon precursors using gold as catalyst via the vapor-liquid-solid (VLS) mechanism.1–6 Liquid metal-semiconductor alloy droplets form at the surface above the eutectic temperature. Silicon precursor molecules, e.g., monosilane (SiH₄), predominantly crack at the droplet surface and silicon gets incorporated into the droplets. At the liquid-solid interface between the eventually supersaturated droplet and the substrate a wire forms due to silicon precipitation. The nanowire synthesis using gold is very robust; gold, however, exhibits unfavorable properties to electronic industry. Therefore, a lot of effort was put into identifying substitute catalysts.3,7–9 Surprisingly little attention was paid to silver as alternative for SiNW synthesis although silver exhibits—compared to gold—distinct advantages regarding chemical treatment and electronic properties. Surfacial silver can be removed effectively (shown below), which is particularly important as metal contaminations are problematic for semiconductor processing. Gold creates two impurity energy levels within the metal: a donor level 0.26 eV above the valence band (VB) and an acceptor level 0.29 eV above the valence band (VB), schematically depicted in Fig. 1(a). Deep level energy traps in silicon strongly influence the minority carrier lifetime. In a simplified model, energy levels become more detrimental the closer they are to the band gap middle.10 Therefore, the two recombination centers created by silver—a donor level 0.26 eV above the VB and an acceptor level 0.29 eV below the CB—are much less effective.11 Naturally the carrier lifetime is inversely proportional to the trap density, i.e., the Ag concentration, in silicon. In order to minimize silver contamination one should decrease the growth temperature as both the diffusivity and the equilibrium solubility of silver in silicon increase with temperature.12 In Fig. 1(b) the binary phase diagram of silver and silicon is depicted.13 In accordance with this, growth of silicon whiskers with large diameters above the eutectic temperature of 836 °C via the VLS mechanism was shown.1,2,4,14 Also synthesis of thick amorphous silicon whiskers well below the eutectic temperature was demonstrated by Tatsumi et al.15 In this respect, the Ag–Si phase diagram [see Fig. 1(b)] is similar to the binary phase diagrams of aluminum-silicon or gold-germanium;16 and for aluminum catalyzed SiNWs8 as well as for gold catalyzed germanium nanowires17 growth below the eutectic temperature via a supersaturated solid-solution was shown.

In the following we present the fabrication of ultrathin SiNWs grown below 500 °C with silver particles. First, the preferred growth direction of silver catalyzed wires is analyzed. Afterwards, the wet chemical removal of the surfacial catalyst is examined via x-ray photoelectron spectroscopy (XPS) and high resolution transmission electron microscopy (HRTEM). In addition the crystallinity of the SiNWs and their epitaxial alignment with the substrate is studied.

II. EXPERIMENTAL PROCEDURES

Low p-doped silicon substrates were cleaned by standard two-step Radio Corporation of America (RCA) cleaning.18 Subsequently the wafers were dipped in diluted hydrofluoric acid to obtain silicon oxide free and hydrogen terminated silicon surfaces. The substrates were then immediately transferred to the noncommercial ultrahigh vacuum (UHV) system having a base pressure better than 5×10⁻¹⁰ mbar. Less than a monolayer silver was evaporated (Alfa-Aesar; purity: 99.9%) onto the heated silicon substrate (300 °C). Elevating the substrate temperature increases the surface mobility of silver atoms, so that instead of a silver film, silver nanopar-

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particles readily form. By this approach, an additional high temperature annealing step to break up the metal film can be avoided. The wafers with the silver particles were transferred into the cold-wall UHV-CVD process chamber, wherein nanowire synthesis was carried out by a conventional thermal CVD process. The silicon wafer temperature was checked with a pyrometer (LumaSense Technologies; spectral response: 900 nm). The error of the given substrate temperature is—conservatively estimated—less than ± 30 K.

High resolution XPS scans of the Ag 3d and Si 2p lines were performed after silver particle deposition, after SiNW growth, and after silver removal (non–monochromatic Al source; step size: 0.1 eV; exposure time: 5 s per measurement point; pass energy: 50 eV). To eliminate surface charging effects, spectra were calibrated to the Si 2p line (99.0 eV for p-type Si). Position and intensity of XPS peaks were determined by fitting a Voigt function with Shirley background.

For silver removal, first the wafer with the silver catalyzed SiNWs was dipped in diluted hydrofluoric acid (1%) for one minute, in order to get rid of potential silica layers covering the catalyst surface. Afterwards, the wafer was placed for 5 min in a mixture of 2.1 g potassium ferricyanide and 4.91 g sodium thiosulfate dissolved in 200 ml purified water. Subsequently the sample was rinsed for 1 min in purified water and transferred into the UHV system for XPS analysis.

III. RESULTS AND DISCUSSION

Figure 2(a) shows a top view scanning electron microscopy (SEM) micrograph of SiNWs grown on a silicon (100) wafer at 490 °C for 10 min at a monosilane partial pressure of 0.2 Torr. SEM micrographs were taken with a JEOL JSM 6701F microscope. The mean diameter of the SiNW in this experiment was 10.2 nm with a standard deviation of 2 nm. The growth directions of the nanowires can be deduced by relating the observed growth directions in the top view electron micrograph [Fig. 2(a)] to the stereographic projections of a (100) surface. Transparent grids and colored arrows sketch the projections of the associated directions in Fig. 2(a). As can be seen therein, one third of the possible (211) orientations coincide with the (111) directions. These contributions are disentangled by assuming that all (211) directions are equally probable, the (211) and (111) counts are corrected accordingly. The directions of roughly 300 wires were evaluated. For about 15% of SiNWs distinct growth directions could not be assigned due to their undefined geometry, which is indicative for a high defect density among these wires. Figure 2(b) shows a number density histogram of the different nanowire directions as a function of their diameter. The histogram indicates that the (110) directions are slightly favored at diameters of about 10 nm. A preferential (110) growth direction is often observed considering SiNWs in this diameter range. In order to attain a higher yield of perpendicular SiNWs, growth was carried out on a Si (110) substrate [see Fig. 2(c)] as described before, using 0.1 Torr of silane at 500 °C for 20 min. The 45° tilted view SEM micrograph in Fig. 2(c) suggests synthesis of a fair percentage of perpendicular NWs.

The applied temperatures never exceeded 500 °C, which is more than 300 K below the eutectic temperature. The binary phase diagram for bulk materials does not apply for nanosized objects; the calculated lowering of the silver-silicon eutectic temperature was 45 K for particles with a diameter of 10 nm. This indicates that the catalyst particle was solid throughout the process and the growth scheme should therefore be vapor-solid-solid instead of VLS. In this regime the silicon equilibrium concentration is less than 1% as depicted in Fig. 1(b). This is about one order of magnitude smaller than the concentration in Au–Si catalyst droplets. A low silicon concentration is essential for growth of axial heterostructure nanowires with abrupt interfaces—particularly for tunneling field effect transistors—since the transition between two sections is sharper when the solubility in the catalyst is lower.

As mentioned above, a major obstacle for implementing bottom up SiNWs in electronic devices is the ubiquitous metal contamination of the catalyst. In particular, the complete removal of gold in a one step wet etching process has turned out to be challenging. Yet grown SiNWs need to be free of catalyst remnants in order to use them as building blocks in devices. In contrast to gold, residual silver can be removed from the surface and the SiNW more easily due to a lower chemical stability of silver. One well-known cleaning recipe is based on a solution containing potassium ferricyanide and sodium thiosulfate. In order to verify the effectiveness of the removal procedure, we performed UHV XPS measurements. XPS spectra were taken (a) after depositing silver nanoparticles onto a (100) p-type silicon wafer, (b) after SiNW growth, and (c) after wet chemical Ag removal. The high resolution XPS spectra corresponding to the three different processing steps are shown in the lower half of Figs. 3(a)–3(c) along with respective SEM micrographs above. The peaks for silicon (Si 2p) and for silver (Ag 3d5/2 at 368.3 eV and Ag 3d3/2 at 374 eV) are investigated in the respective binding energy intervals. The XPS spectra of the Ag nanoparticles on the Si wafer [see Fig. 3(a)] as well as of the grown Si nanowires [see Fig. 3(b)] clearly indicate the presence of both Si and Ag. The ratio between the XPS intensities of Si 2p and Ag 3d5/2 decreases from 1.2 (after silver deposition) to 2.0 (after the CVD process), see Fig. 3(b). This rise in intensity reflects the relative increase in silicon surface area due to the growth of the SiNWs. The
SEM micrograph in Fig. 3(b) furthermore depicts the presence of silver catalyst particles on the SiNWs tips.

For the wet-chemical removal of silver (for details see experimental section), the sample was taken out of the UHV environment. The final XPS scan in Fig. 3(c) proofs the successful silver removal. In addition to the crystalline silicon 2p peak at 99 eV, also a peak at 102.2 eV—indicative for fractional oxidation of silicon—can be seen in Fig. 3(c). This oxidation originates from the silver removal in aqueous solution.

In addition to XPS measurements, also HRTEM cross sectional micrographs were taken with a JEOL JEM 4010 microscope to prove the efficiency of the silver removal process. Figure 4(a) shows a [211] oriented SiNW (zone axis is [011]) homoepitaxially grown at 480 °C for 5 min at 0.1 Torr monosilane partial pressure on a (100) silicon substrate. After growth the silver catalyst was removed as conducted above. In contrast to gold removal studies, no residual silver could be observed in any TEM micrograph. The HRTEM micrograph in Fig. 4(b) displays a silver catalyzed [110] oriented SiNW grown at 490 °C on a (110) Si surface for 30 min. Note that in this case disilane with a partial pressure of $3 \times 10^{-3}$ Torr was used as precursor. One can also see in Fig. 4(b) that the Ag catalyst detached from the nanowire tip, presumably during TEM sample preparation. The fast Fourier transform (FFT) of the wire and parts of the substrate [see Fig. 4(c)] suggests that the wire grew epitaxially and as a single crystal, though, about half of the nanowires from the same process show defects, such as stacking faults and/or twins. In Fig. 4(d) a HRTEM micrograph ([110] zone axis; (110) Si substrate) shows a straight SiNW with [112] growth direction exhibiting as the only defect a (111) twin boundary extending along the whole growth axis. This a well known defect phenomenon for (211) SiNWs.

**IV. CONCLUSION**

In summary we have introduced ultrathin silver catalyzed SiNWs as promising candidate for application in electronic industry. The preferred growth orientations of the SiNWs were identified as (110). Wires were found to be epitaxial though some exhibited planar defects. Successful post-growth Ag catalyst removal was verified using XPS.

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