Fabrication and Characterization of Free-Standing Silicon Nanowires Based on Ultrasono-Method

Sung-Gi Lee, Donghee Sihn, Sungyong Um, Bomin Cho, Sungryong Kim, and Honglae Sohn†

Abstract
Silicon nanowires were detached and obtained from silicon nanowire arrays on silicon substrate using a ultrasono-method. Silicon nanowire arrays on silicon substrate were prepared with an electroless metal assisted etching of p-type silicon. The etching solution was an aqueous HF solution containing silver nitrate. SEM observation shows that well-aligned nanowire arrays perpendicular to the surface of the silicon substrate were produced. After sonication of silicon nanowire array, an individual silicon nanowire was confirmed by FESEM. Optical characteristics of SiNWs were measured by FT-IR spectroscopy. The surface of SiNWs are terminated with hydrogen.

Key words: Silicon Nanowires, Metal-assisted Etching, Electroless Metal Deposition

1. Introduction
The development of preparation of silicon nanomaterials are very interesting for various applications in the fields of photonics, opto- and photo-electronics, photovoltaics[1-4], field-effect transistors[5-7], optical band pass filters, chemical and biological sensors, and drug delivery materials[8-30]. Silicon is an abundant and bio-compatible material. Since silicon has an advantage over other elements such as high production yields and low production/processing costs, the silicon-based materials have been highly favored in industrial development. Due to an indirect band gap of bulk silicon, it does not emit visible light. However, low dimensional nanostructured-silicon materials such as quantum dots, nanocrystals, nanowires, and porous silicon emit visible light. This may be accounted for a direct band gap and quantum confinement effect.

Due to the importance of silicon as a semiconducting material, silicon nanowires have attracted tremendous research interest due to their possible applications in microelectronic industry. Many preparation techniques for the silicon nanowires have been developed in recent years. The fabrication of silicon nanowires can be achieved through various synthetic techniques such as metal catalyzed growth called “vapor-liquid-solid growth[31], chemical vapor deposition, physical vapor deposition[32], or electron beam evaporation[33-36]. These techniques often require hazardous reaction conditions such as high temperature, complex equipment, and so on. Disadvantage of these methods are very expensive and the slow growth of silicon nanowire.

To overcome these issues, an electroless metal deposition on a silicon substrate in ionic metal HF solution might be an alternative. Deposition of metals such as Pt, Au, Pd, Cu, and Ni on silicon wafers in HF solution have been extensively studied[41]. This technique has advantages such as low cost, low operating temperature, and simplicity[37-40]. They are widely used in the microelectronic industries for preparing electrodes, patterning circuit boards, and ohmic contacts.

Electroless metal deposition has been extended to the fabrication of various nanostructures including silicon nanowires[42-43]. This method allows the rapid fabrication of high-quality silicon nanowire array on the silicon substrate. The length of silicon nanowire could be effectively controlled through tuning the etching time. The morphologies of silicon nanowires can be affected by many factors such as the type, doping level, and orientation of the silicon wafer, concentration of H₂O₂ in the
etchant, etching temperature, and etching time. Since these silicon nanowires are attached on a silicon substrate, they need to detach from the silicon substrate to prepare silicon nanowire composite materials for some applications.

Here the fabrication of free-standing silicon nanowires using ultrasonic method is reported after simple chemical etching of silicon wafers in an aqueous HF solution containing silver nanoparticles at room temperature.

2. Experimental Section

2.1. Preparation of Silicon Nanowires

Si(100) wafers (p-type, boron-doped, 500 mm thick), was used in this work. HF (49%), H$_2$O$_2$ (30%), H$_2$SO$_4$ (98%), and AgNO$_3$ (>99.9%) were purchased from Sigma-Aldrich. Silicon wafers were cut into 10 mm$^2$ pieces, which were washed in deionized water, acetone, and ethanol at room temperature to entirely remove contaminated organics from the silicon surface. The wafer pieces were then cleaned in oxidant solution containing H$_2$SO$_4$ and H$_2$O$_2$ (4:1) in a volume ratio 4:1 for 10 min under room temperature to form a thin oxide layer and then in a solution of NH$_4$OH/H$_2$O$_2$/H$_2$O (1:1:5) for 1 h each. After each cleaning step, the wafer pieces were rinsed with excess deionized water. The cleaned silicon wafer pieces were then immersed in 5% HF aqueous solution for 3 min under room temperature and the fresh Si surfaces were H-terminated. The silicon wafers were immediately placed into a Ag coating solution containing 4.8 M HF and 0.04 M AgNO$_3$, which were slowly stirred for 1 min under atmosphere ambient. Ag particles were coated on silicon by immersing silicon pieces in that solution. After a uniform layer of Ag nanoparticles (AgNPs) coating, the silicon substrate was washed with water to remove the extra Ag$^+$ ions and then immersed in oxidizing HF etching solution composed of 4.8 M HF and 30% H$_2$O$_2$ (10:1 v/v) in a reaction vessel. After 1 h etching in the dark under room temperature, the wafers were washed repeatedly with water and then were immersed in dilute HNO$_3$ (1:1 v/v) to dissolve the Ag catalyst. The sample was rinsed with deionized water and dried at room temperature. The wafers were washed with 5% HF again to remove the oxide layer and then cleaned with water and dried under N$_2$ flow. For the isolation of silicon nanowires, the prepared silicon nanowire array films were placed in 100 mL of toluene in a Schlenk flask under argon atmosphere, and then made into particles by ultrasonic fracture in toluene solution for 5 min. After the removal of all removable liquid under a reduced pressure, silicon nanowires were stored in nitrogen atmosphere prior to use.

2.2. Instrumentation and Data Acquisition

FT-IR instrument in the diffuse reflectance mode (Spectra-Tech diffuse reflectance attachment), with diffuse reflectance absorption spectra are reported in absorbance units. Morphologies of silicon nanowires and silicon nanowire array were observed with a cold field emission scanning electron microscope (FE-SEM, S-4800, Hitachi).

3. Results and Discussion

Silver particles were produced on the surface of silicon wafer using conventional electroless metal deposition techniques. The surface of wafer was in deep black, and its back sides in gray. Fig. 1 showed a FE-SEM image of Ag-nanoparticle film deposited onto a p-type silicon wafer in HF/AgNO$_3$ solution for 1 min. The silver nanoparticles were evenly coated on the surface of silicon wafer. The deposited silver nanoparticles exhibit interconnected networks. Ag-covered silicon wafer was immersed in HF/H$_2$O$_2$ solution at room temperature. Ag-coated silicon wafer was etched in HF/H$_2$O$_2$ solution for 30 min. The etching of a silicon wafer proceeds very rapidly when silicon substrates covered with Ag-

![Fig. 1. SEM image of Ag-nanoparticle film deposited onto a p-type silicon surface.](image-url)
nanoparticle films are immersed. The color of as-synthesized sample was black indicating its excellent antireflection capability. A high-quality, oriented, and hydrogen-terminated silicon nanowire array were produced on silicon substrates under optimized etching conditions.

Fig. 2 shows the surface FE-SEM image of silicon substrate after 10 min etching. Metal assisted-etching based on the metal-seed-induced excessive local oxidation and dissolution of silicon substrates is a localized micro-electrochemical redox reaction process in which both anodic and cathodic process simultaneously occurs at the silicon surface and involves the spontaneous oxidation of silicon atoms and the reduction of metal ions to metallic particles in the absence of an external source of electric current.

Fig. 3 shows the cross-sectional FE-SEM image of silicon substrate after 10 min etching. Silicon nanowire begin to form on a silicon substrate. In the beginning stage, the shapes of silicon nanowires are very rough and uneven. Image of silicon substrate is similar to the porous silicon. The depth of etching layer on silicon substrate is about 2 microns.

Fig. 4 showed the cross-sectional SEM image of the as-synthesized silicon nanowire array after 30 min etching in etchant. They showed a large-area aligned silicon nanowire array perpendicular to the silicon surface and the interface between silicon nanowires and the silicon substrate. The length of silicon nanowires are about 5 microns. The length of silicon nanowires gradually increased with the increase of an etching time as the silver nanoparticles sink down into the bulk silicon.

Fig. 5 showed the surface SEM image of the as-synthesized silicon nanowire array after 30 min etching in etchant. They showed about 200 nm thickness silicon nanowires on the silicon substrate. Fig. 6 showed the FT-IR spectrum of prepared silicon nanowire array. Silicon nanowires exhibit a characteristic absorption peak at 2100 cm$^{-1}$ for the $\nu$(Si–H) stretching vibration. This result indicated that the surfaces of silicon nanowires are covered with hydrogen atoms.

The silicon nanowires were detached from the silicon substrate using ultra-sono method to create free-standing silicon nanowires. The free-standing silicon nanowires shown in Fig. 3 revealed that these silicon nanostructures have two main shapes such as wires and rods. Most of the silicon nanostructures are rods, typically couple of micron wide. The silicon nanostructures
Fabrication and Characterization of Free-Standing Silicon Nanowires Based on Ultrasono-Method

4. Conclusion

Freestanding silicon nanowires were successfully prepared by an electoless chemical etching of silicon wafer in etchant solution of HF and H$_2$O$_2$ for 30 min, after the deposition of the Ag-nanoparticle films using EMD. The etching of silicon wafer proceeds very rapidly. After 30 min of etching, the silicon nanowire arrays formed perpendicular to the silicon surface. The length of the silicon nanowires is about few microns. The length of silicon nanowires gradually increased with the increase of an etching time. FT-IR spectrum showed a characteristic stretching and bending vibration peaks at 2100 cm$^{-1}$, indicating that the surface of silicon nanowires are terminated with hydrogen. The freestanding silicon nanowires were prepared using ultrasone method. The main structures of silicon nanowires are wires and rods. The thicknesses of rods and wire are typically 150-250 nm and 10-20 nm, respectively.

Acknowledgment

This research was financially supported by the Ministry of Education (MOE) and National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation (2012H1B8A2026282).

References


