Supplementary Material (ESI) for Chemical Communications

Growth of germanium nanowires using liquid $GeCl_4$ precursor: The critical role of Si impurity

Hyun Jae Song,[a] Seok Min Yoon,[a] Hyun-Joon Shin,[b] Hyunseob Lim,[a] Chibeom Park[a] and Hee Cheul Choi*[a]

[a] Department of Chemistry and Graduate Institute of Advanced Materials Science, Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-Gu, Pohang, 790-784, Korea. E-mail: choihc@postech.edu
[b] Department of Physics and Pohang Accelerator Laboratory, Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-Gu, Pohang, 790-784, Korea.

Electronic Supplementary Information

Materials

Germanium tetrachloride ($GeCl_4$, 99.9999%, Alfa Aesar), silicon tetrachloride (SiCl4, 99.998%, Aldrich) and Gold(III) chloride trihydrate ($HAuCl_4.3H_2O$, 99.9+%, Aldrich) were used as purchased without further purification.

Growth of Germanium Nanowires

For the VLS growth utilizing liquid precursors, we slightly modified a chemical vapor deposition (CVD) system that was conventionally used for the growth of carbon nanotubes. Glass bottles containing neat liquid $GeCl_4$ and $SiCl_4$ precursors were connected as a branch through which Ar carrier gas is bubbled (Scheme 1). Hence, the total amount of $GeCl_4$ was precisely controlled by modulating the flow rate of Ar carrier gas. As for the catalyst, Au nanoparticles (NPs) were directly formed on silicon or germanium wafer substrates via spontaneous electroless deposition process.[S1] In brief, a Si wafer substrate cleaned with HF solution was soaked into 1 mM $HAuCl_4$ aqueous solution for 5 min. In the case of Ge substrate, a small piece of water-cleaned Ge wafer was soaked into 1mM $HAuCl_4$ solution for a few seconds. Both samples were thoroughly rinsed with deionized water and hexane, then dried under N_2 stream. Note that the main driving forces for the formation of Au NPs on Si and Ge substrates are the spontaneous reduction of Au(III) ions by surface hydrides (Si-H_x) and by energetically favorable electrochemical reduction potential of Ge^0, respectively.

For the growth of Ge NWs, a substrate coated with highly dense Au NPs was placed at the center of 1 inch quartz tube. After the quartz tube was fully flushed, the temperature of the furnace was increased with H_2 and Ar gas flowing at the rates of 15 sccm (square cubic centimeter per minute) and 87 sccm, respectively. When the furnace temperature was reached to 750 ^oC, $SiCl_4$ vapors (5 sccm of Ar, Ar^{Si}) and $GeCl_4$ vapors (2 sccm of Ar, Ar^{Ge}) were introduced simultaneously for 20 min by turning 4-way valves (Scheme 1).

Characterizations

The morphologies, crystallographic information, elemental compositions were obtained by scanning electron microscopy (SEM, JSM-7401F, JEOL), energy dispersed spectrometer (EDS) equipped Cs-corrected high resolution transmission electron microscopy (HR-TEM, JEM-2100F, JEOL), X-ray diffractometer (XRD, M18XHF22, Mac Science), atomic force microscope (AFM, NanoscopeIII, Digital

Instrument) and Ar-ion laser (514.5 nm) lined Raman spectroscope (Renishaw). X-ray photoelectron spectroscopy study was also performed at 650 and 179 eV of photon energies of linear polarized soft X-ray. (8A1 U7-Undulator beamline, Pohang Accelerator Laboratory).

Electrical measurement

Germanium NW field effect transistors (FETs) were fabricated using a conventional e-beam lithography technique. A SiO_2/Si substrate (100 nm of SiO_2 on a highly doped (B) silicon) on which Ge NWs were dispersed was coated with EL9 (Microchem) and PMMA (950K 5%, Microchem) for easy lift-off process. 30 nm of Cr and 80 nm of Au metals were thermally evaporated as a sticky layer and a passivation layer, respectively. Before deposition of metal electrodes, the oxide layer on the Ge NW was briefly etched for 30 s in 5 % HCl aqueous solution. All the electrical signal measurements were conducted using a semiconductor analyzer (SCS4200, Keithley).

Au Nanoparticles for the growth of Ge NWs

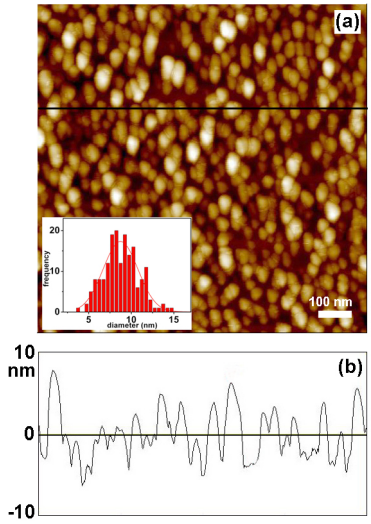

Figure S1 (a) AFM image of as-formed Au NPs on a silicon substrate by electroless deposition method. (b) Cross-sectional height profile along the black line in (a). Inset of (a) shows the size distribution of Au NPs and its Gaussian curve.

Further information of the verification of Ge bonding states.

The deeper sampling depth at high photon energy than at low photon energy was confirmed by comparing the intensity ratios of reduced and oxidized forms of Ge 3d peaks (Ge^0/Ge^{x+} ~ 0.12 at 179 eV, Ge^0/Ge^{x+} ~ 2.8 at 650 eV). Consequently, we were able to get meaningful elemental information of Ge NWs at and underneath the oxide overlayers when samples were irradiated with both low and high photon energy sources.

Raman Spectrum of Ge NWs

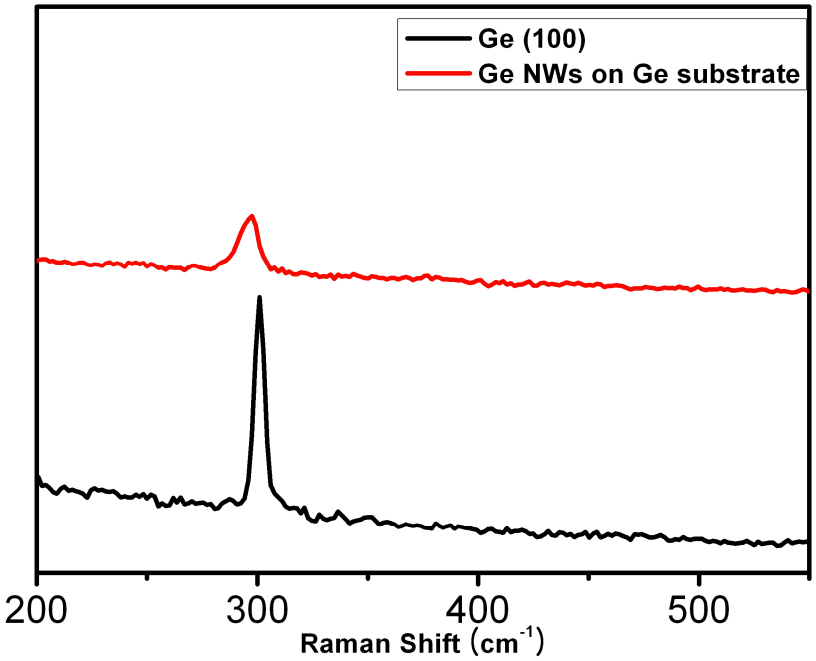

Figure S2 Raman spectrum of Ge NWs grown on Ge(100) substrate (red). Only Ge-Ge band was observed at 300 cm^{-1} from Ge NWs, which is similar to the band of pure Ge(100) (black).

S1 L. A. Portor, H. C. Choi, A. E. Ribbe and J. M. Buriak, *Nano Lett.*, 2002, **2**, 1067.