

Supporting Information

Growth and Analysis of the Tetragonal (ST12) Germanium Nanowires

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Experimental method:

Synthesis of ST12-Ge nanowires. Anhydrous toluene 99.8 % was purchased from Sigma-Aldrich Co. and diphenylgermane (DPG) 95 % was purchased from Fluorochem. All chemicals were stored and used in a nitrogen glovebox ($O_2 < 0.1$ ppm, $H_2O < 0.5$ ppm).

ST12-Ge nanowire synthesis was carried out in a 5 mL stainless steel reaction cell from High-Pressure Equipment Company. Prior to synthesis, the reaction cell and connectors were dried under vacuum at 125 °C for 12 hr. Reactions were performed at temperatures between 290 to 440 °C on Si (100) with dimensions of 0.5 cm × 1.5 cm. The native oxide was not removed from the surface of the Si substrates prior reaction. The reaction temperature was monitored by a thermocouple connected to the reaction vessel and the pressure was monitored via a pressure gauge, connected to one end of the reaction cell. In a typical reaction, 3 ml of a toluene/DPG solution was added to a 5 ml reaction cell which was heated to the desired temperature in a tube furnace for 60 min. The DPG concentration was varied between 40 and 60 mM. The filling volume of the reactant solution, *i.e.* filling fraction, was 60 % of the total reactor's volume (5 ml). The reaction cell was cooled to room temperature after the reaction and disassembled to access the growth substrate. Growth substrates were washed with dry toluene and dried under N_2 for further characterisation.

Characterisation. The as-grown samples were imaged using an FEI Quanta FEG 650 scanning electron microscope (SEM) operated at 15 kV. High-resolution transmission electron microscopy (HRTEM) and high resolution scanning transmission electron microscopy (HRSTEM) imaging were performed on a JEOL 2100 electron microscope operated at 200 kV, an FEI Titan electron microscope (operating at 300 kV) and a Titan Themis double-corrected and monochromated transmission electron microscope at 300 kV. High-angle annular-dark-

field scanning-transmission-electron-microscopy (HAADF-STEM) was performed on the FEI Titan electron microscope operated at 300 kV. X-ray Photoelectron Spectroscopy (XPS) spectra were acquired on an Oxford Applied Research Escabase XPS system, equipped with a CLASS VM 100-mm-mean-radius hemispherical electron-energy-analyser with a five-channel detector arrangement in an analysis chamber with a base pressure of 10×10^{-10} mbar. Raman experiments were carried out in a Horiba Yuvon micro-Raman spectrometer equipped with 1800 lines/mm grating and a Peltier cooled charge-coupled device (CCD) camera. An Ar ion laser of wavelength 488 nm was used to excite the sample and a $100 \times$ objective lens was used to focus the sample as well as collect the data in backscattering geometry. The crystal structure of the product was confirmed by X-ray diffraction (XRD) using a Philips X'pert Pro MPD, equipped with a Panalytical Empyrean Cu X-ray tube and a Philips X'celerator detector. Texture characterization of the Ge wires were performed with a Brucker D8 Discover diffractometer equipped with a Co micro-source, a 2D Vantec-500 detector and a 300 μ m collimator. The Bragg-Brentano angle 2θ was set to 38.8° to probe the (112) orientation plane with the Co K- α wavelength. The sample holder was rotated in plane of an angle φ varying between 0° and 359° through successive 20° steps while a 5° rotation out of plane was performed. Fourier-transform infrared spectroscopy (FTIR) spectra were recorded on an infrared spectrometer (IR 660, Varian) over a wavenumber range between 400 to 4000 cm^{-1} . EDX mapping was performed on a Titan Themis double-corrected and monochromated transmission electron microscope at 300 kV with a Bruker Super X detector. Software used for imaging and EDS mapping was FEI Velox. Photoluminescence (PL) data were obtained using a Ti:Sa pulsed laser as the excitation source, tuned to a wavelength of 700 nm and an 80 MHz repetition rate, a 300 fs pulse width and a mean power of 0.2 W. The laser spot was focused on a 9 μ m spot, providing a pump power density of 200 kW/cm^2 . Samples were cooled to 10 K using a Helium cryostat. PL was detected using liquid nitrogen chilled InAs detector with a

sensitivity range from 0.9 μm to 3 μm (~ 0.41 - 1.338 eV). For dc-Ge nanowires high sensitivity InGaAs detector is used with a sensitivity range from 1.25 μm to 1.7 μm .

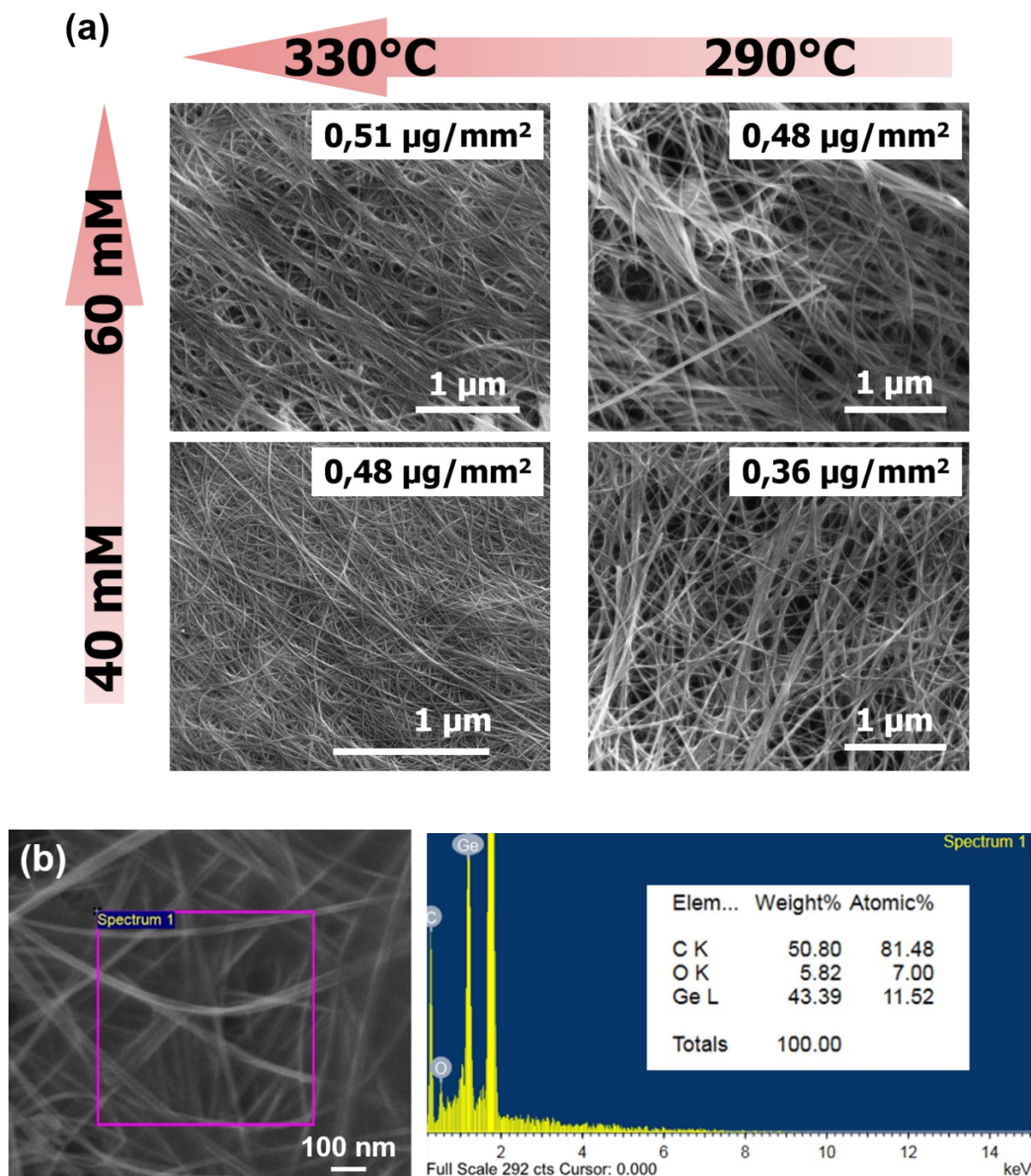


Figure S1. (a) SEM images of ST12-Ge nanowires obtained as a function of reaction temperature and precursor (DPG) concentration. Corresponding yield of every reaction

condition is given on top-right of SEM images. (b) EDX analysis from a nanowire sample grown at 330 °C.

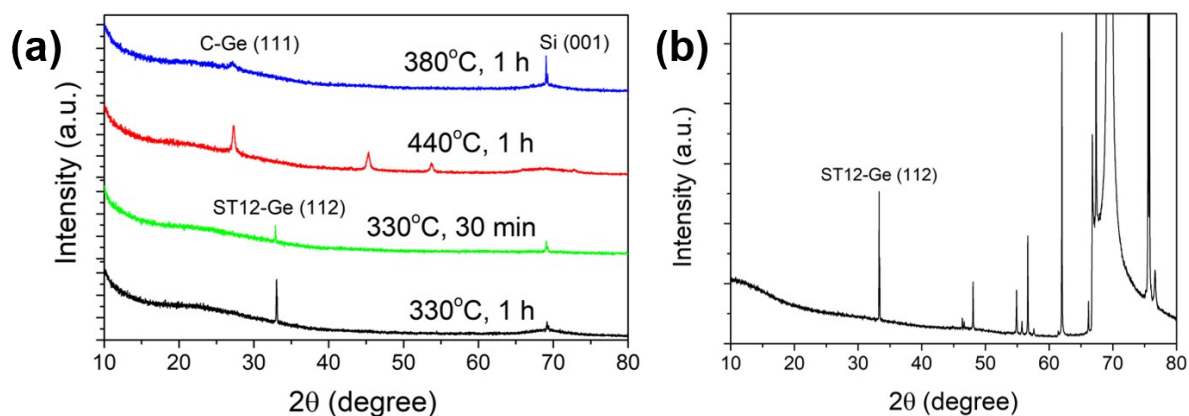


Figure S2. (a) XRD pattern of the dc-Ge and ST-Ge nanowires grown at different growth condition (with 60 mM DPG concentration). (b) XRD pattern of ST12 Ge nanowires (330 °C, 1 hr) grown on Ti substrates.

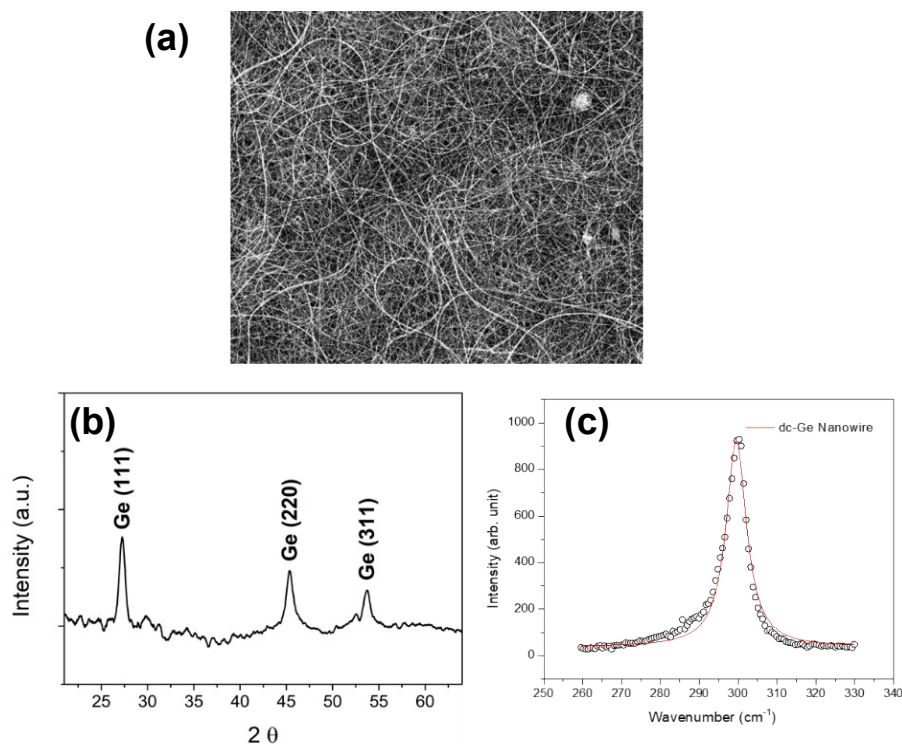


Figure S3. (a) SEM micrographs of dc-Ge nanowires grown at a temperature of 440 °C from a 60 mM DPG/toluene solution and a filling volume of 60 % of the total reactor's volume. (b) XRD pattern of a nanowire sample showing the formation of dc-Ge crystal structure. (c) Raman spectra from dc-Ge nanowire grown at 440 °C.

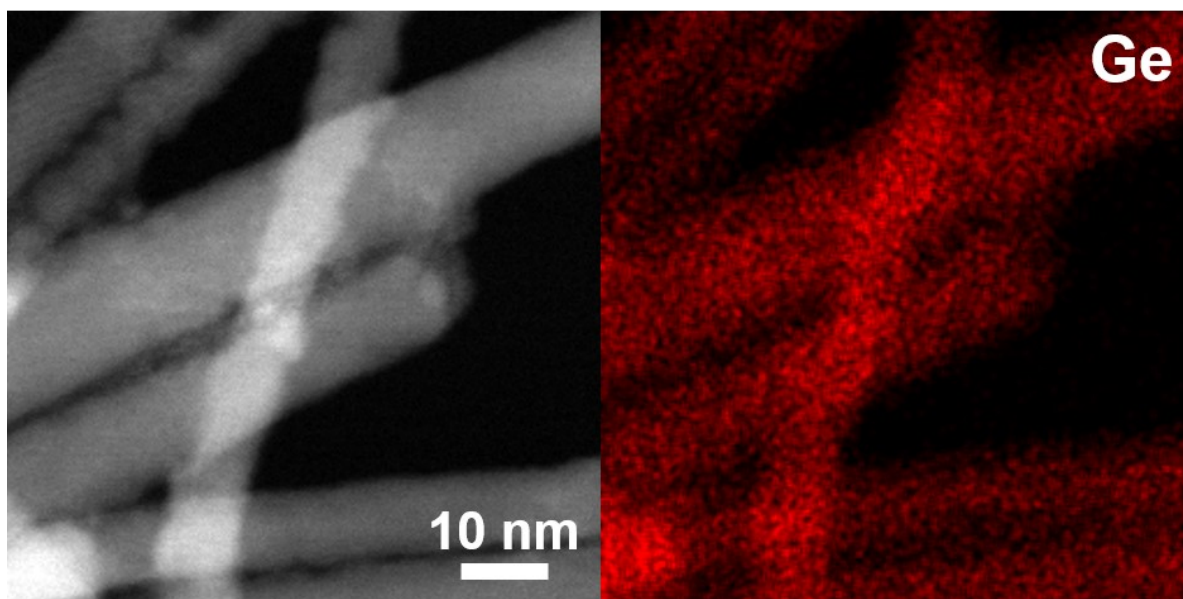


Figure S4. EDX spectrum recorded from the body of several ST12-Ge nanowires showing the sole presence of Ge in the nanowire bulk.

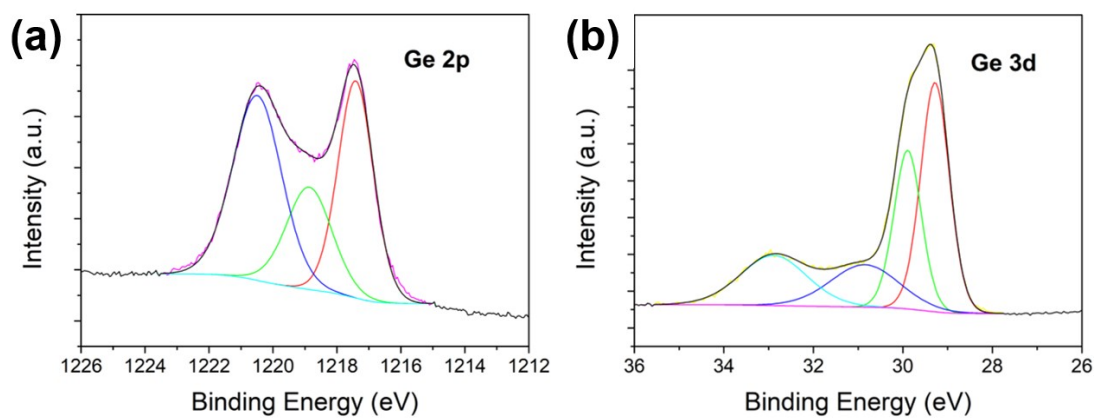
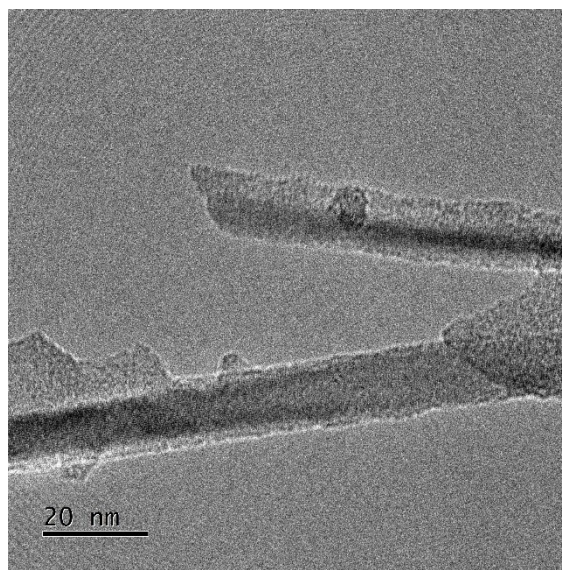
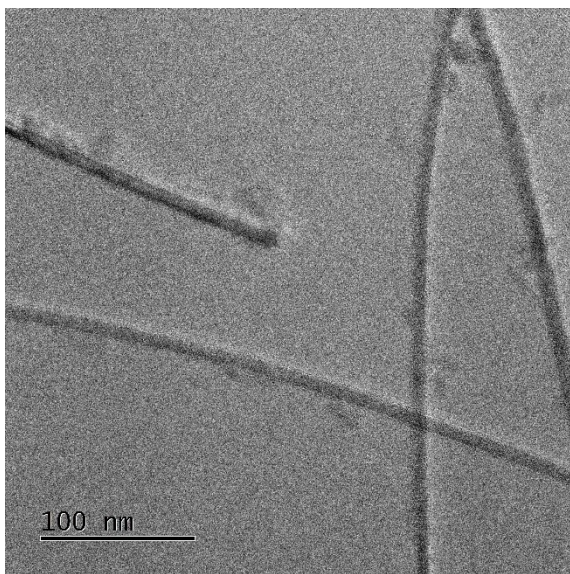


Figure S5. XPS spectra from ST12-Ge nanowires of the (a) Ge 2p and (b) Ge 3d regions. Oxidation peaks appeared on the sample exposed to air for a year.



(a)

Figure S6. (a), (b) TEM images of ST12-Ge nanowires where the discontinuous and uneven amorphous carbonaceous coating can be observed along the length of the nanowires.

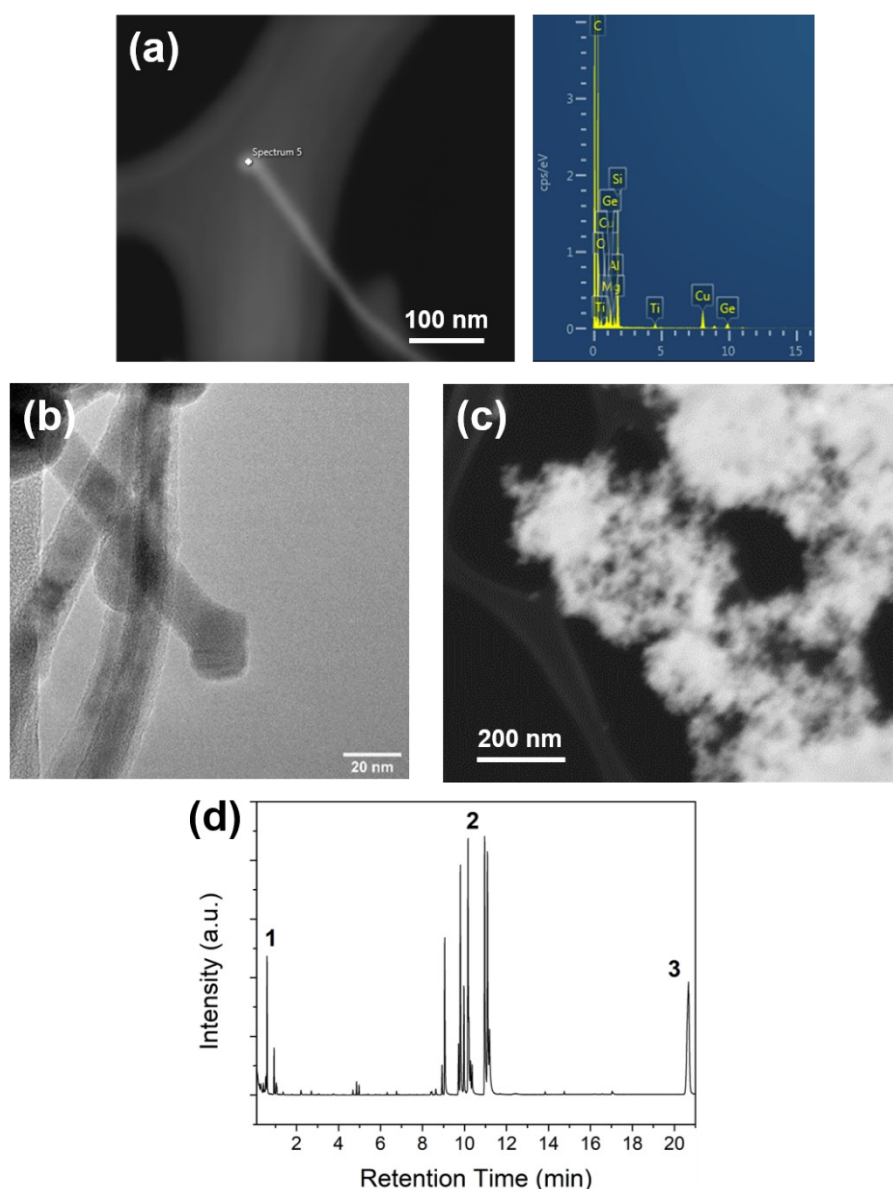


Figure S7. (a) EDX point analysis of the Ge nanowire tip showing only the presence of Ge (Si and Ti peaks are from the STEM detector). (b) A representative TEM image of a nanowire with Ge seed at the tip. (c) Growth of small spherical clusters of Ge nanoparticles at 330 °C with short growth time (10 mins). (d) Gas-chromatography spectrum from the analysis of the residual liquid present in the reactor after the reaction. The spectrum presents three zones such as: (1) Toluene-like structures and derivatives (*i.e.* ethylcyclohexane, ethylbenzene and *o*-xylene), (2) diphenylmethane and derivatives (*i.e.* 2,3'-dimethyl-1,1'-biphenyl, bybenzyl or 1-methyl(4-phenylmethyl)benzene) and (3) tetraphenylgermane (TPG).

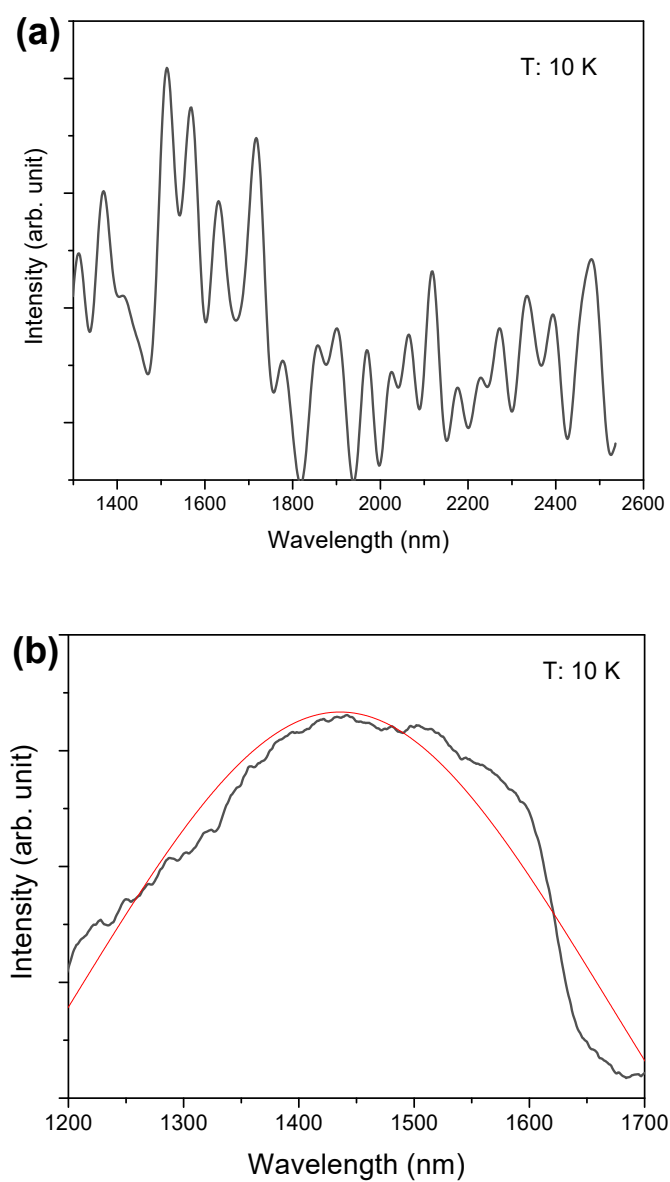


Figure S8. (a) PL spectrum from dc-Ge nanowires grown at 440 °C with InGaAs detector showing no emission. (b) Broad PL emission was observed from dc-Ge nanowire with high sensitive InAs detector.