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Authors	Raha, Sreyan;Srivastava, Divya;Biswas, Subhajit;Garcia-Gil, Adrià;Karttunen, Antii J.;Holmes, Justin D.;Singha, Achintya
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Supplementary Material
Probing lattice dynamics in ST12 phase germanium nanowire by Raman spectroscopy

Sreyan Raha,[1] Divya Srivastava,[2] Subhajit Biswas,[3] Adrià Garcia-Gil,[3]
Antti J. Karttunen,[2] Justin D Holmes,[3] and Achintya Singha[1,*]

[1] *Department of Physics, Bose Institute, 93/1 Acharya Prafulla Chandra road, Kolkata 700009, India*
[2] *Department of Chemistry and Materials Science, Aalto University, P.O. Box 16100, FI-00076, Aalto, Finland*
[3] *School of Chemistry & Advanced Materials and Bioengineering Research (AMBER) Centre, University College Cork, Cork, T12 YN60, Ireland*

* achintya@jcbose.ac.in

I. METHODS

1. Nanowire synthesis

ST12-Ge NW synthesis was carried out in a 5 mL stainless steel reaction cell. Prior to synthesis, the reaction cell and connectors were dried under vacuum at 125°C for 12 hr. Reactions were performed at temperatures of 330°C on Si (100) substrates of 0.5×1.5 cm^2 dimension. In a typical reaction, 3 ml of a toluene (99.8%, Sigma-Aldrich Co)/DPG (95%,Fluorochem) solution of 60 mM concentration was added to the 5 ml reaction cell and the cell was heated to 330^{o}C in a tube furnace for 60 min. The filling volume of the reactant solution was fixed at 60 % of the total reactor's volume (5 ml). The reaction cell was cooled to room temperature and the samples were washed with dry toluene and dried under N_2 flow for further characterization. The novel batch procedure performed at mild temperature (330°C) and under in-situ generated pressure for the growth of ST12-Ge NW merely requires low boiling point solvents (toluene) and commercially-available precursor (DPG). The closed cell NW growth in supercritical toluene atmosphere provides ideal conditions for fast precursor decomposition and in-situ carbonaceous polymer formation, which is crucial for the self-seeded growth of the ST12-Ge NWs.

2. Characterization

The as-grown samples were imaged using a FEI Quanta FEG 650 scanning electron microscope (SEM) operated at 15 kV. Transmission Electron Microscopy (TEM) and High Resolution TEM (HRTEM) imaging were performed on a JEOL 2100 electron microscope operated at 200 kV and on a Titan Themis double-corrected and monochromated TEM at 300 kV. 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.The Raman measurement was carried out using a microRaman spectrometer (LABRAM HR Jovin Yvon) equipped with 1800 lines/mm grating and a peltier cooled charge-coupled device (CCD) detector. Raman data was taken in backscattering geometry while illuminated by Ar^+ laser of wavelength 488 nm with extremely low power (20 µW) to avoid the laser induced heating. The temperature dependent Raman spectra are measured from 80 K to 300 K using a Linkam (THM 600) temperature control stage.

3. Computational methods

Periodic density functional theory (DFT) calculations has been carried out for ST12-Ge and dc-Ge with the PBE0 hybrid density functional theory method (DFT-PBE0)[1, 2]. Triple-zeta-valence+ polarization (TZVP) level basis sets are used for germanium [3, 4]. All calculations have been performed using the CRYSTAL17 program package[5]. The reciprocal space is sampled with the Monkhorst-Pack-type k-point $8 \times 8 \times 8$ grid [6]for both ST12-Ge and dc-Ge. The crystal structures of both studied Ge phases are fully optimized (the atomic positions and lattice parameters) within the constraints imposed by the space group symmetry. Default DFT integration grids, optimization convergence thresholds and tight tolerance factors of 8, 8, 8, 8, 16 for the evaluation of the Coulomb and exchange integrals (TOLINTEG) are employed in all calculations. The vibrational frequencies at the Γ-point are calculated within the harmonic approximation by evaluating the second derivatives of the potential energy with respect to atomic positions as implemented in CRYSTAL code [7, 8]. Raman intensities are calculated using the Coupled Perturbed Kohn-Sham method implemented in CRYSTAL [9].

II. XPS OF ST12-GE NW

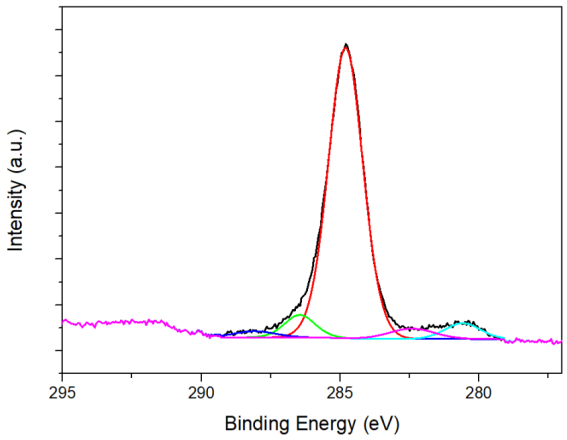


FIG. S1. C-C(red), C-O(green), C-O(blue) and C-Ge(magenta) bonds were present in the C1s spectrum for the tetragonal Ge. The peak at 283.9 eV was present in the XPS C1S spectrum of ST12-Ge and can be assigned to a strong interaction (covalent bonding) between carbon and the surface of the ST12-Ge nanowire as Ge-C. Germanium oxide formation was also found in the XPS due to air exposure of the samples when stored in an ambient atmosphere.

III. CALCULATED RAMAN SPECTRUM OF DC-GE

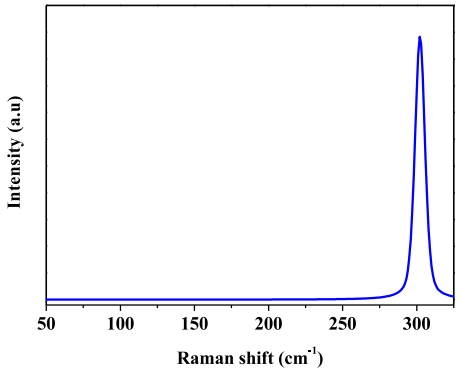


FIG. S2. Calculated Raman spectrum of diamnond cubic Germanium

IV. TEMPERATURE DEPENDENT RAMAN STUDY OF BULK DC-GE

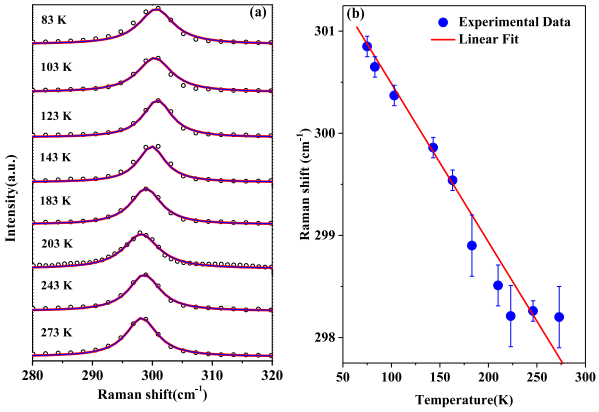


FIG. S3. (a) Raman spectra of dc-Ge bulk at various temperatures. The spectra are fitted with Lorentzian functions. (b) Temperature vs Raman peak position shows linear behaviour with slope (β)=-0.02103 $cm^{-1}K^{-1}$. Using equation (2), the calculated isobaric Grüneisen parameter (γ_p) for dc-Ge bulk is 11.92.

V. TEMPERATURE DEPENDENT RAMAN STUDY OF DC-GE NW

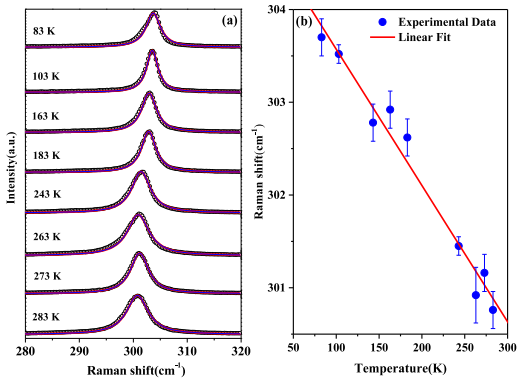


FIG. S4. (a) Raman spectra of dc-Ge NW at various temperatures. The spectra are fitted with Lorentzian functions. (b) Temperature vs Raman peak position show linear behaviour with slope (β)=-0.0147 $cm^{-1}K^{-1}$. Using equation (2), the calculated isobaric Grüneisen parameter (γ_p) for dc-Ge NW is 8.25.

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