Epitaxially Integrating Ferromagnetic $Fe_{1.3}Ge$ Nanowire Arrays on Few-Layer Graphene

Hana Yoon,[†] Taejoon Kang,[†] Jung Min Lee,[‡] Si-in Kim,[†] Kwanyong Seo,[†] Jaemyung Kim,[§] Won Il Park,[‡] and Bongsoo Kim[†,*]

[†]*Department of Chemistry, KAIST, Daejeon 305-701,* [‡]*Department of Materials Science Engineering, Hanyang University, Seoul 133-791, and* [§]*CRD Energy Lab, Samsung SDI, Gyeonggi-do, Korea*

Supporting information:

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*To whom correspondence should be addressed.

Professor Bongsoo Kim (E-mail: bongsoo@kaist.ac.kr, FAX: +82-42-350-2810)

1. Identification of graphene

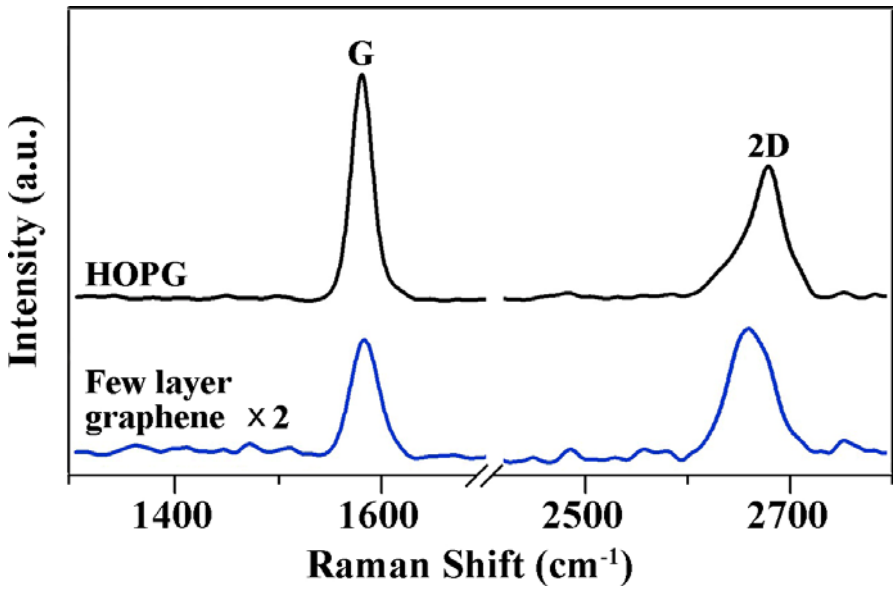

Figure S1. Raman spectra of HOPG and graphene/SiO_2/Si substrates.

Figure S1 shows the Raman spectra of HOPG and graphene/SiO_2/Si substrates. Raman spectra were collected from a micro-Raman system based on Olympus BX41 microscope. The 633 nm radiation of a He-Ne laser (Melles Griot) was used as an excitation source and the laser was focused through a ×100 objective (NA = 0.7, Mitutoyo). The signals were recorded with a thermodynamically cooled electron multiplying charge coupled device (EMCCD, Andor) mounted on the spectrometer with a 1200 groove/mm grating. The collection time was 100 s.

The major features in the Raman spectra of HOPG and graphene are the G and D bands and the second order of the D band (2D band). The G band at ~1580 cm^{-1} is due to E_{2g} vibration mode, corresponding to in-plane carbon atom stretching vibrations.[S1] This band becomes more intense with increasing layer numbers due to more carbon atoms contributing to this vibration mode. The D and 2D bands at ~1350 cm^{-1} and 2700 cm^{-1}, respectively, are induced by two-phonon mode.[S1] The D band requires detects for its activation, therefore, it is absent for perfect crystalline samples.[S2,S3] The 2D band, on the contrary, always exists even if its first order is absent and shows a significant change as the

number of layers is decreased.[S1] In Figure S1, the well-isolated G and 2D bands are presented and D band is absent in both spectra, attesting to the high crystalline quality of samples. For a graphene/SiO_2/Si substrate, the G band is decreased and 2D band is blue-shifted comparing to Raman bands of HOPG. This confirmed that the graphene is only few layers (3-5).[S2-S4,12]

Furthermore, the size of graphene flakes may vary from about a few hundred nanometers to several micrometers similar to the grain sizes of employed Ni film[S5,12] because it has been assumed that the size of graphene flakes can be influenced by an underlying Ni grain size.[S6]

2. TEM analysis of $Fe_{1.3}Ge$ NWs on graphene

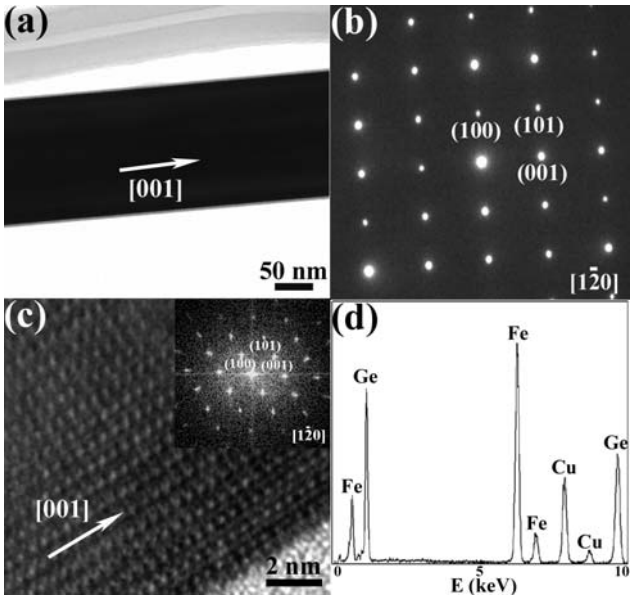

Figure S2. (a) TEM image and (b) SAED pattern of a $Fe_{1.3}Ge$ NW grown on a graphene. The SAED pattern is indexed to a hexagonal $Fe_{1.3}Ge$ down the $[1\bar{2}0]$ zone axis. (c) HRTEM image of a $Fe_{1.3}Ge$ NW and its FFT (inset in panel (c)). The growth direction of the $Fe_{1.3}Ge$ NW is parallel to the [001] direction. (d) TEM-EDS spectrum of a $Fe_{1.3}Ge$ NW reveals that Fe and Ge are the only elements present

in the NW in an average atomic ratio of 56 : 44.

Figures S2a and S2b show TEM image and a selected area electron diffraction (SAED) pattern, respectively, obtained from a NW grown on graphene. The NW shows a regular SAED spot pattern, reflecting the single-crystalline nature with the spots matching well to the hexagonal $Fe_{1.3}Ge$ structure. Figure S2c shows a HRTEM image of a $Fe_{1.3}Ge$ NW, a two-dimensional FFT (inset in panel S2c) of which could be indexed to the hexagonal $Fe_{1.3}Ge$ structure, indicating a [001] NW growth direction. EDS data (Figure S2d) obtained from the NW exhibits that only Fe and Ge are present in the NW in an average atomic ratio of 56 : 44.

3. $Fe_{1.3}Ge$ NWs grown on a graphene/SiO_2/Si substrate

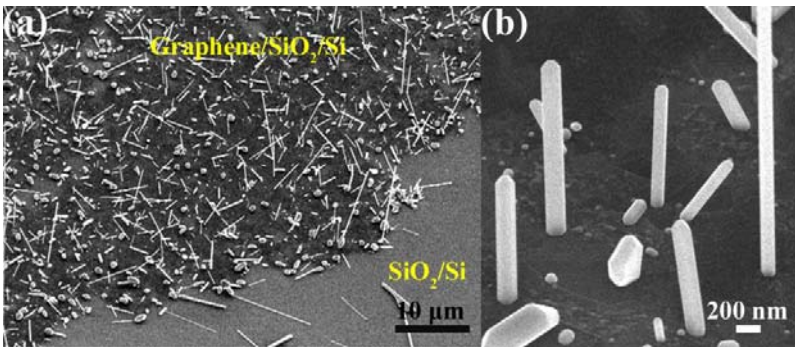

Figure S3. (a) Tilted view SEM image of freestanding $Fe_{1.3}Ge$ NWs grown on a graphene/SiO_2/Si substrate. (b) A magnified SEM image of vertical NWs and inclined NWs grown on the graphene/SiO_2/Si substrate.

4. $Fe_{1.3}Ge$ NWs grown on a *c*-cut sapphire substrate and a SiO_2/Si substrate

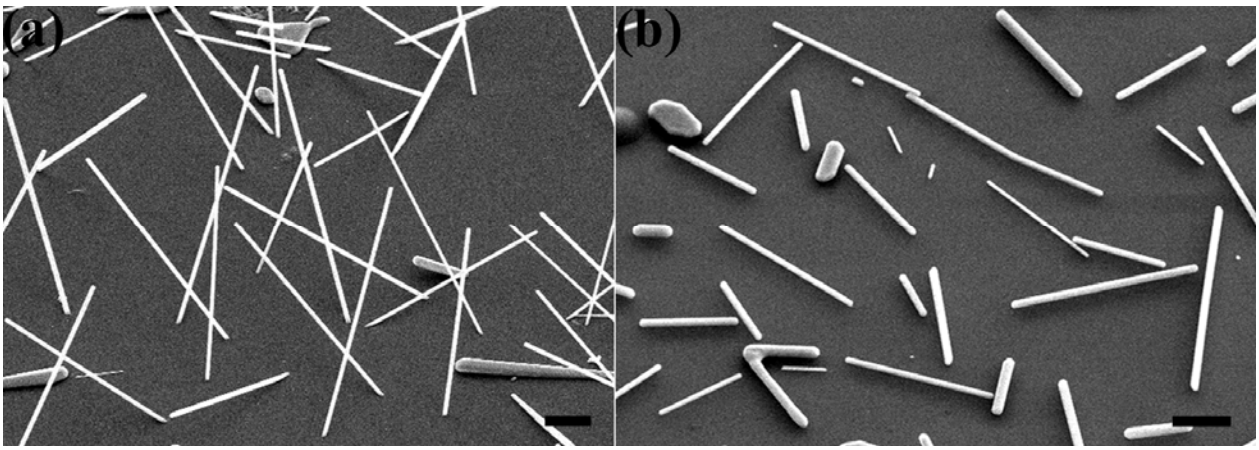

Figure S4. Tilted SEM images of as-grown $Fe_{1.3}Ge$ NWs grown on (a) a *c*-cut sapphire substrate and (b) a SiO_2/Si substrate (scale bars: 2μm).

Inclined and horizontal NWs were synthesized on the sapphire substrate and the SiO_2/Si substrate not covered by graphene as shown in Figure S4.

5. $Fe_{1.3}Ge$ NWs grown on an HOPG substrate

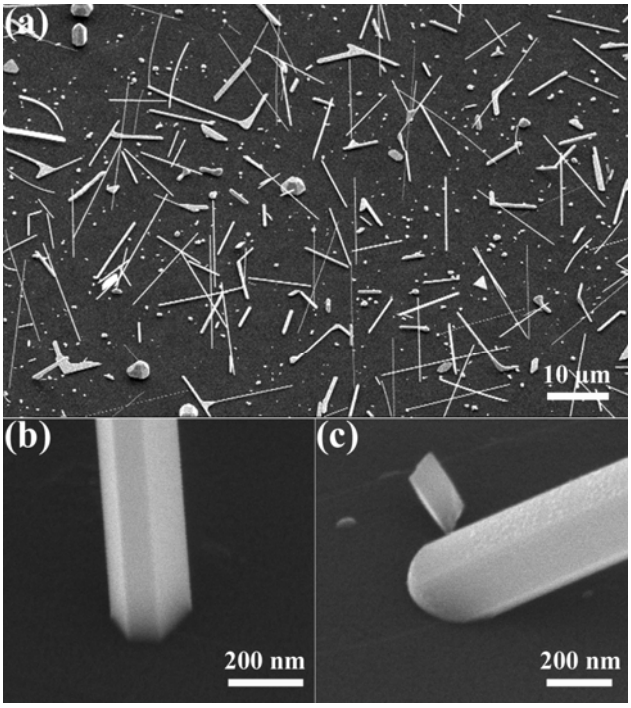

Figure S5. (a) Tilted SEM image of as-grown $Fe_{1.3}Ge$ NWs on an HOPG substrate. Enlarged SEM images of (b) a vertical NW and (c) an inclined NW on the HOPG substrate.

6. Additional FE data

Insets in Figure 3 show Fowler-Nordheim (F−N) plots obtained from the *J-E* results of $Fe_{1.3}Ge$ NWs on graphene/ITO and HOPG, respectively. The F−N relationship can be expressed by the following equation:

$$J = (A\beta^2E^2/\Phi)\exp(-B\Phi^{3/2}/\beta E)$$

where J is the local current density, $E = V/d$ is the applied field, V is the applied voltage, d is the distance between the anode and cathode, I is the current, Φ is the work function, and A and B are constants, corresponding to 1.56×10^{-10} ($AV^{-2}eV$) and 6.83×10^{3} ($eV^{-3/2}V\mu m^{-1}$), respectively.[16-18,29-32] The field enhancement factor, β, reflects the degree of FE enhancement due to the NWs. The β value is related to the geometry, crystal structure, and the density of emitting points of the NWs. β can be

calculated from the slope of the F−N plot if the work function of the emitter is known. Because the work function of $Fe_{1.3}Ge$ has not been reported to date, we calculated the approximate work function of $Fe_{1.3}Ge$ by applying the following equation suggested by Freeouf[S7,S8]

$$\Phi_{(MxGey)} = [\Phi_{(M)}{}^{x}\ \Phi_{(Ge)}{}^{y}]^{1/(x+y)}$$

where $\Phi_{(MxGey)}$ is the work function of a metal germanide M_xGe_y, $\Phi_{(M)}$ is the work function of a metal, and $\Phi_{(Ge)}$ is the Ge work function. The $\Phi_{(Fe)}$ value of Fe and $\Phi_{(Ge)}$ value of Ge were previously reported to be 4.7 eV[S9] and 4.8 eV,[S10] respectively. Using these values, the approximate $\Phi_{(Fe1.3Ge)}$ value of the $Fe_{1.3}Ge$ was obtained as ~ 4.74 eV. Employing the slopes obtained from the $\ln(I/V^2)-1/V$ plots (insets in Figure 3) and the $\Phi_{(Fe1.3Ge)}$ value, β values of the NWs grown on the graphene and the HOPG are calculated to be ~ 4650 and ~ 7300, respectively.

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