Electronic Supplementary Material (ESI) for Nanoscale.
This journal is © The Royal Society of Chemistry 2018

Supporting Information for

Enhanced Nucleation of Germanium on Graphene via Dipole Engineering

Jinkyoung Yoo[1], Towfiq Ahmed[2], Renjie Chen[3], Aiping Chen[1], Yeon Hoo Kim[4], Ki Chang Kwon[4], Chan Woong Park[5], Hee Seong Kang[6], Ho Won Jang[4], Young Joon Hong[5], Woo Seok Yang[7], Chul-Ho Lee[6]*

[1]Center for Integrated Nanotechnologies, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

[2]T-4, Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

[3]Department of Electrical and Computer Engineering, University of California San Diego, LA Jolla, CA 92093, USA.

[4]Department of Materials Science and Engineering, Seoul National University, Seoul 08826, Republic of Korea.

[5]Department of Nanotechnology and Advanced Materials Engineering, Sejong University, Seoul 05006, Republic of Korea.

[6]KU–KIST Graduate School of Converging Science and Technology, Korea University, Seoul 02841, Republic of Korea.

[7]Electronic Material and Device Research Center, Korea Electronics Technology Institute, Seongnam, Gyeonggi-do 13509, Republic of Korea

Chemical vapor deposition of Ge on graphene and graphene/h-BN stack Germanium (Ge) was grown by low-pressure chemical vapor deposition (CVD) in a cold-wall reactor. The precursor was germane (GeH_4) diluted in H_2 with a concentration of 30%). The substrate temperature and the partial pressure of GeH_4 were 500°C and 5 mTorr, respectively. Before the Ge growth, the graphene and graphene/*h*-BN stack were transferred on 150 nm-thick SiO_2/Si substrates with PMMA supporting layer. After the graphene and graphene/*h*-BN transfer, the PMMA layer was removed by acetone for >6 hours. The prepared substrates containing graphene and graphene/*h*-BN stack were loaded into the CVD reactor through a load-lock chamber. After the base pressure of the CVD reactor reached to $1x10^{-6}$ Torr, substrate was heated up to 650°C and kept at 650°C for 10 min with hydrogen flow. Then, the substrate was cooled down to growth temperature (500°C), and the CVD growth was conducted.

Preparation of polarized regions on bismuth ferrite (BFO) 400 nm-thick polycrystalline BFO thin film on Nb:$SrTiO_3$ (Nb:STO) substrate was purchased from MTI corporation. 50 nm-thick Au layers were deposited on the Nb:STO substrate and the BFO thin film for bottom and top electrodes by *e*-beam evaporation, respectively. For the top electrode shadow mask (hole center-to-center spacing of 100 μm) was used to form Au dot arrays on the BFO thin film. To induce polarization of the BFO electrical bias

ranging from –75 to 75 V was applied through the top and bottom electrodes. After the polarization Au was removed by potassium iodide (KI)-based Au etchant (TFA) produced by Transene Inc.. The Au etching rate was ~0.3 nm/sec at room temperature. Subsequently, the BFO thin film sample was rinsed with deionized water, and dried at 100°C.

Density Functional Theory (DFT) Calculations All calculations in this report are performed using the plane-wave pseudo-potential code VASP[1-3] unver the generatlized gradient approximation of Perdew, Burke, and Ernzerhof (PBE).[4] For atomic core-levels, we have used projected augmented wave (PAW) potentials[5,6] treating the $2s2p$ of C, N, and B as the explicit valence electrons. For all calculations, the total energy during electronic relaxation is converged to 10^{-6} eV while the force/atom during ionic relaxation is converted to 0.01 eV/ Å. A maximum energy cutoff of 400 eV is used for plane-wave basis set.

In the calculations, the bulk Ge has cubic unit cell with diamond like structure (lattice constant a = 5.658 Å). For the combined Ge/graphene/h-BN system, we have taken a supercell with P1 symmetry. The lattice constants of this triclinic supercell are constants a =12.669 Å, b = 13.275 Å , c = 30.6 Å , $\alpha = \beta = 90^{o}$, and $\gamma = 88.85^{o}$. There are in total 30 N, 30 B, 60 C, and 56 Ge atoms in this supercell.

We have relaxed our heterostructure using van der Waals (vdW) interaction. To keep the calculation expense reasonable, we have only considered two Ge planes. Figure 1 shows the supercell structure for the DFT calculations.

To incorporate the vdW interaction, we have used optB86b-vdW functional where the exchange functionals were optimized for the correlation part.[7] Therefore, the LDA correlation part present in the PBE functional is removed by using the parameter AGGAC=0.000 in the input file in order to avoid double-counting.

For ionic relaxation of Ge/graphene/h-BN system, we have used the Γ point to sample the Brillouin zone, while for all other calculations, e.g., SCF, and charge density, we used 5×5×1 k-points in the Brillouin zone, while the dipole moment calculations were performed using 25×25×1 k-points. The dipole center was set at the center of the unit cell. Out of the plane (z-direction) dipole moment is calculated using:

$$\mu_z = \int_{cell} (z - \vec{R}_{center})\rho(\vec{r})d^3\vec{r},$$

where $\vec{R}_{center} = \{0.5a, 0.5b, 0.5c\}$.

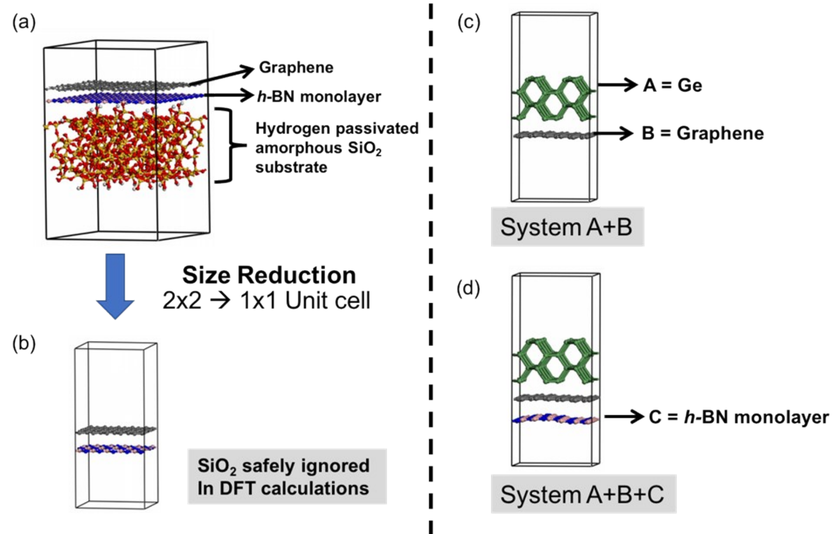

Figure S1. Structure in (a) shows a supercell of the substrate which includes layers of amorphous SiO_2, *h*-BN monolayer, and graphene. For computational simplicity, the 2×2 supercell is reduced into 1×1 unit cell, which only contains graphene and *h*-BN while the underlying SiO_2 ignored. Bilayered Ge is on top of graphene substrate (c) and graphene/*h*-BN bilayer substrate (d).

We defined cohesive energy for system A+B as,

$$\Delta E = E_A + E_B - E_{A+B},$$

while, for system A+B+C it is defines as,

$$\Delta E = E_A + E_{B+C} - E_{A+B+C},$$

As shown in Fig. 1, we denoted A=Ge, B=graphene, and C=*h*-BN.
Our DFT calculated charge-density-difference ($\Delta\rho$) is defined as,

$$\Delta\rho = \rho_{A+B} - \rho_A - \rho_B.$$

$\Delta\rho$ implies excess electrons ($\Delta\rho > 0$) and lack-of-electrons or holes ($\Delta\rho < 0$) after the vdW heterostructure is formed through DFT relaxation process.

Selective area electron diffraction patterns (SAEDs) of Ge layers grown on graphene/h-BN stacks

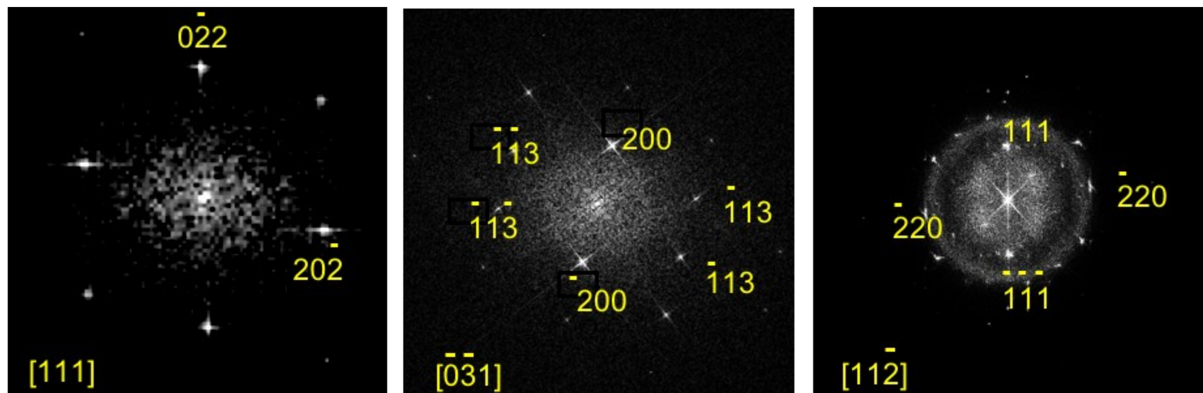

Figure S2. The SAEDs of Ge thin films grown on graphene/*h*-BN stacks

References:

1. Kresse, G.; Furthmüller, J. *Phys. Rev. B* 1996, **54**, 11169.
2. Kresse, G.; Hafner, J. *Phys. Rev. B* **1993**, 47, 558.
3. Kresse, G.; Furthmller, J. *Compt. Mater. Sci.* **1996**, 6, 15.
4. Perdew, J. P.; Burker, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, 77, 3865.
5. Vanderbilt, D. *Phys. Rev. B* **1990**, 41, 7892.
6. Kresse, G.; Hafner, J. *J. Phys.: Condens. Matter.* **1994**, 6, 8245.
7. Klimeš, J.; Bowler, D. R.; Michaelides, A. *Phys. Rev. B* **2011**, 83, 195131.