Atomic scale study on growth and heteroepitaxy of ZnO monolayer on graphene

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Supplementary Note 1

Experimental methods

**Graphene sample preparation.** Graphene was synthesized by CVD on a 25-μm-thick copper foil (99.8% Alfa Aesar, 13382). First, 25-μm-thick copper foils were washed by HCl/H2O (1:10), rinsed by acetone and alcohol and dried by air ambient. The dried copper foil was inserted into a quartz tube and heated to 1,000 °C with flowing 2 sccm H2 at 10 mTorr. After annealing for 1 h, the gas mixture of 10 sccm CH4 and 2 sccm H2 at 100 mTorr was introduced for 25 min to synthesize graphene. Finally, fast cooling to room temperature with flowing 10 sccm CH4 and 2 sccm H2 was performed.

**Graphene transfer.** For Raman spectroscopy, XPS, field effect transistors, AFM, SEM and optical transmittance characterization, graphene was transferred to SiO2 substrates. The graphene was grown on both sides of the copper foils; Ar plasma was the applied to remove the graphene layer on the backside of the Cu foil. The transfer of the graphene films onto 300 nm SiO2 substrates was performed by the wet etching of the copper substrates. A PMMA solution was spin-coated on the surface of as-grown graphene on Cu foil at the speed of 4,000 rpm for 1 min and baked at 130°C for 10 min. Then the sample was placed into a solution of sodium persulphate (Na2S2O8, a concentration of 0.2 g in 1 ml of water) to etch the underlying copper foil and is then rinsed with deionized water for several times, and then transferred onto a 300 nm SiO2 substrates. After air drying, the PMMA was dissolved by acetone and the substrate was rinsed with isopropyl alcohol to yield a graphene film on the substrate.

**Graphene TEM grid preparation.** In the direct transfer, this support was provided by the target substrate, specifically the TEM grid’s carbon film. For TEM characterization, graphene was
transferred to Quantifoil holey carbon TEM grids (SPI supplies, 300 meshes, 2 μm hole size) using direct transfer method. To tightly attach the graphene and carbon, the TEM grid is placed on top of graphene on copper foil and a drop of IPA and air-dried. Finally, the sample was placed into a solution of sodium persulphate (Na2S2O8, a concentration of 0.2 g in 1 ml of water) to etch the underlying copper foil and is then rinsed with deionized water for several times.

**Atomic resolution TEM imaging and STEM-EELS spectra.** Transmission electron microscopy (TEM) analysis was performed by using an aberration-corrected TEM, Titan G2 Cube 60-300kV (FEI) installed at UNIST. To minimize beam exposure to the sample, images were collected at a low operating voltage of 80 kV with a minimal beam exposure approach. STEM HAADF images and EELS spectra were recorded with a monochromatic beam at 80kV with a probe size of 1.5 nm and an energy resolution of 0.2±0.05eV, as measured from the full-width-at-half-maximum of the zero-loss peak.

**Atomic layer deposition of ZnO.** ZnO growth on graphene was conducted in an automatic atomic layer deposition system (SVT associate ALD), using a low vacuum condition with 10 sccm of ultra-high pure Ar (99.999%) carrier gas in all deposition sequences. Diethylzinc (DEZ, Sigma Aldrich) and deionized water (> 18 MΩ) were prepared as precursors of seed layers in stainless cylinders, enclosed by a heater and thermocouple at room temperature and 30°C, respectively. For one cycle of ZnO monolayer growth, DEZ precursor was first injected into the growth chamber for 0.1 seconds (~ 80 mTorr). Then, the chamber was purged with Ar carrier gas (~ 1000 mTorr) for 30 seconds to remove residues and other impurities. Then, deionized water was injected for 0.5 s (~ 100 mTorr). Finally, the chamber was purged with the Ar gas (~ 1000 mTorr) to remove any remaining residues. The substrate temperature was maintained at 200°C.
during the deposition process. The set of ZnO samples presented in this report was grown by 10, 20, 100 and 200 ALD cycles.

**Characterization.** Raman spectra were acquired with a WiTech confocal Raman microscope (Helium Neon Laser 532 nm). X-ray Photoelectron Spectroscopy (XPS) analysis was performed using K-alpha system (Thermo Fisher Instruments Inc.). Contact angle was measured using Phoenix 300 (SEO Inc.). X-ray Diffraction (XRD) was measured using D8 Advance (Bruker Instruments Inc.). SEM images were taken using S-4800 (Hitachi Instruments Inc.). The UV-Vis-NIR was measured using Cary 5000 (Agilent Instruments Inc.). The Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) was analyzed using TOF-SIMS 5 (ION TOF Inc.). Electrical properties were measured in physical property measurement system (PPMS, Quantum Design) with controlling high vacuum and temperature variations.

**Image simulation.** Image simulations of AR-TEM Image were performed using MacTempasX with the experimental conditions. The simulated structure was constructed by Vesta and Matlab with an interlayer distance of 3.556 Å which was estimated from DFT Calculation (Supplementary Figure 7b). Brightness normalization and profiling were performed by Matlab.

**DFT calculation.** Density functional theory (DFT) calculation was performed with DMol³ module. Exchange and correlation interaction was described by the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional. Spin polarization was taken into account for all calculations. Core treatment was set to be all electrons relativistic with DNP 4.4 basis set. The convergence criteria for the geometry optimization were $2.0 \times 10^{-5}$ Ha for energy, 0.004 Ha/Å for force, and 0.005 Å for displacement, respectively. The self-consistent
field convergence was smaller than $1.0 \times 10^{-5}$ Ha. The long-range dispersion correction was taken into account with the semi-empirical DFT-D2 method suggested by Grimm$^5$.

**Supplementary Note 2**

**Field effect transistor measurement**

Graphene synthesized by CVD on a copper foil (see Methods) was transferred to a p-doped 500 μm Si substrate covered with a 300 nm of SiO$_2$ layer. The electrode patterns of source and drain were fabricated by photolithography with width 200 μm and length 5 μm, and then Au was directly deposited in a thermal deposition system in a high vacuum ($<10^{-7}$ Torr). The prepared device was installed to the PPMS and annealed in a high vacuum condition at 100 °C to remove residual dopants and impurities from the photolithography with air contamination. After 3 hours of annealing, $V_d$-$I_d$ characteristic depending on gate bias was measured at room temperature and we analyzed three samples, calculated the mobility of 1346, 1648 and 1490 cm$^2$/V·s, respectively (at $n = 10^{12}$). To compare the UV/Ozone treatment effect, the measured sample was immediately transferred from the PPMS to the UV/Ozone chamber, and then exposed UV/Ozone during 180 seconds. The treated sample was quickly moved back to the PPMS and measured the field effect behavior with the same condition of the untreated one. All transfer times including the UV/Ozone treatment were less than 4 min to avoid contaminating doping in air. The UV/Ozone-treated graphene devices showed 1281, 1424 and 1361 cm$^2$/V·s without notable Dirac voltage shift by air doping, indicated about 5, 14 and 10% decrease only compared to the pristine graphene conditions.
Supplementary Figure 1. Time-elapsed ARTEM images show the growth process of ZnO monolayer on graphene monolayer. The scale bar is 2 nm.
Supplementary Figure 2. (a) ARTEM image of the ZnO monolayer misoriented by 10° with respect to graphene substrate. (b) The Fourier transform of the image (a). The scale bar is 1 nm.
Supplementary Figure 3. (a) The atomic model of ZnO/Graphene rotated by 30°. (b) The diffractogram pattern obtained through the Fourier transform of the atomic model (a). (c) The atomic model of ZnO/Graphene rotated by 0°. The overlaid triangle shows unit moiré pattern. (d) The diffractogram pattern obtained through the Fourier transform of the atomic model (c).
Supplementary Figure 4. The optimized structure of hexagonal (a), oxygen-terminated (b) and zinc-terminated (c) triangular ZnO nanoclusters on graphene (See the Model Systems below for more information). The red and blue spheres represent oxygen and zinc atoms, respectively, and gray-stick honeycomb network represents graphene. (d) The adhesion energy between three types of ZnO nanoclusters and graphene vs the misorientation angle ($\theta$).
Supplementary Figure 5. The top view of atomic configuration of each lateral growth step of oxygen- and zinc-terminated zigzag edge models and armchair edge model, respectively. Note that each edge model consists of equal numbers of carbon, zinc, and oxygen atoms. The red, blue, burgundy, and navy spheres represent oxygen atoms, zinc atoms, oxygen adatom, and zinc adatom, respectively, and gray-stick honeycomb network represents graphene.
Supplementary Figure 6. (a) The top view of atomic configuration of each growth step of normal and parallel to the growth direction. The red, blue, burgundy, and navy spheres represent oxygen atoms, zinc atoms, oxygen adatom, and zinc adatom, respectively, and gray-stick honeycomb network represents graphene. (b) The formation energy of ZnO growth in normal and parallel to the growth direction at the oxygen terminated zigzag edges. The inset figure shows that the red arrow is normal to the growth direction and the black arrow is parallel to the growth direction.
Supplementary Figure 7. The top and side views of the optimized structure of periodic ZnO on graphene. (a) $4 \times 4$ supercell of hexagonal unit cell graphene is matched with a $3 \times 3$ supercell of ZnO monolayer, where the lattice mismatch is 0.59%. (b) The interlayer distance between ZnO monolayer and graphene is 3.556 Å. The red and blue spheres represent oxygen and zinc atoms, respectively, and gray-stick honeycomb network represents graphene.
Supplementary Note 3

Model System

For the ZnO nanocluster model, we modeled hexagonal nanocluster and oxygen-terminated and zinc-terminated triangular ZnO nanoclusters to investigate edge effect for adhesion strength. A 21.25 × 22.13 Å² rectangular graphene super-cell with 180 carbon atoms was used and 27 oxygen and zinc atoms were used for hexagonal ZnO nanocluster. 18 oxygen and 15 zinc atoms were used for oxygen-terminated triangular ZnO nanocluster. 15 oxygen and 18 zinc atoms were used for zinc-terminated triangular ZnO nanocluster. (Supplementary Figure 4). For lateral growth of ZnO model, a 21.25 × 19.58 Å² rectangular graphene super-cell with 160 carbon atoms was used for ZnO growth model to minimize lattice mismatch with zigzag and armchair edge of ZnO. All initial system has 160 carbon atoms and 12 oxygen and zinc atoms (Supplementary Figure 5). For ZnO growth of normal and parallel to the growth direction model, same size of graphene as lateral growth model was used for ZnO growth model to minimize lattice mismatch with zigzag of ZnO. Both normal to the growth and parallel to the growth direction initial systems have 160 carbon atoms and 26 oxygen and 27 zinc atoms (Supplementary Figure 6). The Brillouin-zone integration of 3×3×1 Monkhorst-Pack k-point grid was used. All growth model systems were constructed with 0° orientation angle between ZnO and graphene which is most stable configuration based on experimental and simulation results. A vacuum space consisting of a 20 Å normal to ZnO plane was used for all model system to avoid self-interactions. We modeled a periodic layer system with 4 × 4 supercell of hexagonal unit cell graphene and 3 × 3 supercell of ZnO monolayer. Lattice mismatch was about 0.59%. Geometry optimization was performed to find stable states (Supplementary Figure 7) with the Brillouin-zone integration of
$12 \times 12 \times 1$ Monkhorst-Pack k-point grid\textsuperscript{6}. Single layer ZnO on the graphene has graphene-like structure\textsuperscript{7} instead of wurtzite structure which is crystal structure of bulk ZnO.
Supplementary Figure 8. \((\alpha h v)^2\) versus photon energy of ZnO deposited on graphene by using ALD method. The extrapolation lines (dashed lines) indicate optical bandgaps \((E_g)\) of 4.03, 3.78 and 3.22 eV for (a) 10 cycle, (b) 20 cycle and (c) 200 cycles.
Supplementary Figure 9. Raman spectroscopy of UV/Ozone-treated CVD graphene on the SiO₂/Si substrate, 20 and 200 ZnO ALD cycles.
Supplementary Figure 10. X-ray diffraction patterns of 20 and 200 ZnO ALD cycles on UV/Ozone-treated CVD graphene on the SiO$_2$/Si substrate.
Supplementary Figure 11. XPS spectra of UV/Ozone-treated CVD graphene on the SiO₂/Si substrate with 20 and 200 ZnO ALD cycles. (a) Zn 2p and (b) O 1s.
Supplementary Figure 12. Comparison of EEL spectra of a ZnO monolayer and ZnO multilayer. (a) Atomic resolution TEM image of ZnO on graphene. (b) STEM HAADF image of ZnO on graphene. (c) EEL spectrum obtained from the red circle in (b) of show oxygen K-edge and zinc L-edge of the ZnO monolayer on graphene. The inset figure shows the carbon K-edge from graphene. (d) EEL spectrum obtained from the blue circle in (b) of oxygen K-edge and zinc L-edge of the multilayer ZnO on graphene. Scale bars indicate 5 nm.
Supplementary Figure 13. Scanning electron microscope images of UV/Ozone-treated CVD graphene on SiO₂/Si substrate. (a) SEM image of UV/Ozone-treated graphene on a SiO₂/Si substrate after 20 ALD cycles of ZnO deposition. (b) SEM image of UV/Ozone oxidized graphene on a SiO₂/Si substrate after 200 ALD cycles of ZnO deposition. The scale bar is 200 nm.
Supplementary Note 4

Raman spectroscopy, X-ray diffraction, XPS, STEM HAADF imaging, EELS core loss spectra and SEM measurement

ZnO nanostructures well grow on SiO₂/Si or Al₂O₃ substrates. However, the lattice mismatch between ZnO and SiO₂ is larger than that between ZnO and graphene, and the SiO₂ used here is amorphous having many defect sites. Therefore, these defect sites and the large lattice mismatch destabilize the energy of the ZnO-SiO₂ interface. The calculated results also show that the destabilization energy of the ZnO-graphene binding is 4.55 eV/nm², while that for ZnO-SiO₂ is 5.35 eV/nm², indicating that ZnO has a more stable bond with graphene than it does with amorphous SiO₂. However, ZnO growth has some issue with graphene. Graphene is a strongly hydrophobic material, which limits its applications in metal oxide deposition and may contaminate the nanoelectromechanical systems. We performed UV/Ozone treatment for 180 seconds in order to induce the wettability transition in graphene from hydrophobic to hydrophilic. However, UV/Ozone treatment can usually induce lattice damaging in graphene. To minimize surface defects graphene sheet, we controlled UV/Ozone treatment time. Our UV/Ozone treatment did not deteriorate a graphene structure for electrical properties notably. Supplementary Figure 9 shows Raman spectra of 20 and 200 ZnO ALD cycles on UV/Ozone-treated graphene on SiO₂/Si substrate. In the Raman spectra of the 200 cycles ZnO on graphene, distinct ZnO peaks were observed near 1131 cm⁻¹ and 1526 cm⁻¹, respectively. A negligible difference in I_D/I_G between the 20 cycles ZnO and 200 cycles ZnO is clearly observed. X-ray diffraction (XRD) of the 20 and 200 ZnO ALD cycles on UV/Ozone-treated graphene prepared on SiO₂/Si substrates are shown in Supplementary Figure 10. In the X-ray diffraction patterns for the 200 cycles ALD grown ZnO on UV/Ozone-treated graphene sample revealed a [10\{\bar{1}10\},
[0002], and [10\bar{1}1] reflections. Supplementary Figure 11 shows the Zn 2p3/2, 2p1/2 and O 1s XPS spectra for the 20 and 200 ZnO ALD cycles on UV/Ozone-treated graphene on SiO2/Si substrates. The binding energies were calibrated by taking the C 1s peak (284.6 eV).

Supplementary Figure 12 shows comparison of EEL spectra of a ZnO monolayer and a ZnO multilayer. Supplementary Figure 12a shows atomic resolution TEM image of ZnO on graphene. We then switched to the STEM mode and acquired quickly an HAADF image and simultaneously EEL spectra. STEM HAADF images show the contrast difference between ZnO monolayer, multilayer and graphene. The corresponding oxygen K-edge and zinc L-edge spectra are presented in Supplementary Figure 12c, d. The inset figure in (c) shows signal for the carbon K-edge from ZnO monolayer on graphene.

Supplementary Figure 13 shows scanning electron micrograph (SEM) of 20 and 200 ZnO ALD cycles on UV/Ozone-treated graphene on SiO2/Si substrate. In the SEM image of the 200 cycles ZnO on graphene clearly shows uniform and high-quality growth thin film. The ALD technique is capable of growing uniform and high-quality thin films on a large-area graphene.
Supplementary Figure 14. TOF-SIMS mapping images and depth profiles of UV/Ozone oxidized CVD graphene on SiO₂/Si substrate, 20 (a & d), 100 (b & e) and 200 (c & f) ZnO ALD cycles.
Supplementary Note 5

Compositional analysis of ZnO deposited on graphene by TOF-SIMS measurement

The compositional analysis of ZnO monolayer have been studied using Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). Supplementary Figure 14 shows TOF-SIMS elemental mapping and depth profile data of UV/Ozone-treated graphene on SiO$_2$/Si substrate, 20, 100 and 200 ZnO by using ALD cycles. TOF-SIMS mapping were analyzed in the area of 300 $\mu$m by 300 $\mu$m (Supplementary Figure 14a-c). These TOF-SIMS mapping results show yellow color for ZnO growth areas. ZnO coverages on graphene were improved as the ALD cycles increased (Supplementary Figure 14a-c). TOF-SIMS depth profiles were analyzed in the area of 70 $\mu$m by 70 $\mu$m (Supplementary Figure 14d-f). Depth profile spectra of 20 cycle ZnO monolayer nanoclusters disappear as soon as etched of Cs ion after few seconds (Supplementary Figure 14d). In case of 100 cycles of ZnO has uniform growth on graphene substrate (Supplementary Figure 14e). Supplementary Figure 14f shows 200 cycles of ZnO thin film. The ALD technique is capable of growing uniform and high-quality thin films on a large-area graphene substrate.
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