Atomic mechanism of strong interactions at the graphene/sapphire interface

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For atomically thin two-dimensional materials, interfacial effects may dominate the entire response of devices, because most of the atoms are in the interface/surface. Graphene/sapphire has great application in electronic devices and semiconductor thin-film growth, but the nature of this interface is largely unknown. Here we find that the sapphire surface has a strong interaction with some of the carbon atoms in graphene to form a C-O-Al configuration, indicating that the interface interaction is no longer a simple van der Waals interaction. In addition, the structural relaxation of sapphire near the interface is significantly suppressed and very different from that of a bare sapphire surface. Such an interfacial C-O-Al bond is formed during graphene growth at high temperature. Our study provides valuable insights into understanding the electronic structures of graphene on sapphire and remote control of epitaxy growth of thin films by using a graphene–sapphire substrate.
he interface is the device. At the interface of crystal materials, the broken translation symmetry usually strongly alters the optical, electric, and magnetic properties, resulting in many interesting phenomena such as interface-induced superconductivity, two-dimensional (2D) electron gas, and magnetoelectric coupling. In particular, the interface effects are much more pronounced or dominant in atomically thin 2D materials (e.g., graphene (Gr)), because most of the atoms are part of the interface when supported on a substrate. For instance, in a field-effect transistor system, strong hybridization (orbital overlap) between 2D materials and contact metals can eliminate the van der Waals (vdW) gap, which results in a reduction of the tunnel barrier for carriers. Such an effect is also observed in 2D/2D heterostructures, e.g., the topological current is detected in the Gr/BN superlattice and the reconstruction at the Gr/BN interface provides a periodic scattering potential for carriers, leading to very unique electrical properties. Moreover, coupling of the Gr/Gr interface via the “magic” angle results in correlated insulating states at half-filling and can be tuned to zero-temperature via electrostatic doping.

Recently, Gr/sapphire (α-Al2O3) has shown promising applications in electronic devices due to the relatively high dielectric properties of α-Al2O3 as a gate dielectric. In addition, Gr/α-Al2O3 is also applied as a platform for remote growth of third-generation semiconductors where Gr acts as a buffer layer to overcome the limitation of lattice mismatch. In generation semiconductors where Gr acts as a buffer layer to overcome the limitation of lattice mismatch, the van der Waals (vdW) gap, which results in a reduction of the tunnel barrier for carriers. Such an effect is also observed in 2D/2D heterostructures, e.g., the topological current is detected in the Gr/BN superlattice and the reconstruction at the Gr/BN interface provides a periodic scattering potential for carriers, leading to very unique electrical properties. Moreover, coupling of the Gr/Gr interface via the “magic” angle results in correlated insulating states at half-filling and can be tuned to zero-temperature via electrostatic doping.

To ensure the cleanness of the interface, we directly grew a Gr film on α-Al2O3 substrates via a chemical vapor deposition (CVD) method (see details in the Methods section). For better protection of the Gr/α-Al2O3 interface, a multilayer Gr film was obtained by prolonging the growth time. Raman mappings of I2D and I2D of the obtained Gr/α-Al2O3 in Supplementary Fig. 1a, b show a high uniform color contrast at the microscale, indicating the uniformity of the grown Gr film. The relatively low value of I2D/I2D (≤0.8) confirms the multilayer feature of Gr (Supplementary Fig. 1c). Moreover, the G and 2D peaks of CVD-derived Gr/α-Al2O3 are all upshifted with respect to those of transferred Gr on SiO2/Si substrates (Supplementary Fig. 1d), indicating that Gr experiences a compressive strain imposed by α-Al2O3.

We used the high-angle annular dark-field scanning TEM (HAADF-STEM) imaging mode of Cs-TEM to reveal the atomic structure of the Gr/α-Al2O3 interface. The atomically resolved image of the Gr/α-Al2O3 interface with a viewing direction of [100] is shown in Fig. 1a and the Gr layer can be clearly observed in an image with lower magnification in Supplementary Fig. 2. The corresponding atomic structures of α-Al2O3 and Gr are depicted in Fig. 1b from the [100] direction superimposed on the STEM image and are in good agreement with the simulated result. We observe additional atoms between the Gr layer and the topmost surface Al atoms. These atoms are further identified to be O, which will be explained later in detail. The distance between the topmost surface Al and the additional O is ~1.76 Å, whereas the spacing between the O and the Gr is also ~1.76 Å, indicating a strong interaction between Gr and the α-Al2O3 substrate.

The presence of the C–O bond at the interface is further confirmed by the C 1s X-ray photoelectron spectroscopy spectrum (Supplementary Fig. 3) of Gr/α-Al2O3, which shows an intense sp2 carbon peak (~284.8 eV), a weak C–H peak (~285.7 eV), and a weak C–O peak (~287.3 eV). Such a C–O peak suggests the existence of a C–O–Al configuration at the interface.

**Results**

**Characterization of the Gr/α-Al2O3 interface.** To ensure the cleanness of the interface, we directly grew a Gr film on α-Al2O3 substrates via a chemical vapor deposition (CVD) method (see details in the Methods section). For better protection of the Gr/α-Al2O3 interface, a multilayer Gr film was obtained by prolonging the growth time. Raman mappings of I2D and I2D of the obtained Gr/α-Al2O3 in Supplementary Fig. 1a, b show a high uniform color contrast at the microscale, indicating the uniformity of the grown Gr film. The relatively low value of I2D/I2D (≤0.8) confirms the multilayer feature of Gr (Supplementary Fig. 1c). Moreover, the G and 2D peaks of CVD-derived Gr/α-Al2O3 are all upshifted with respect to those of transferred Gr on SiO2/Si substrates (Supplementary Fig. 1d), indicating that Gr experiences a compressive strain imposed by α-Al2O3.

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**DFT calculation of the Gr/α-Al2O3 interface.** We perform DFT calculations to verify the Gr/α-Al2O3 interface structures. To construct the Gr/α-Al2O3 interface, we first added an additional atom on top of the surface Al atom according to the STEM results and then added the Gr layer (Supplementary Methods for details). We consider all the possibilities (O, H, C, and Al) for the additional atoms and find that only the O atoms can produce an interface structure consistent with the experimental results, as shown in Supplementary Figs. 4–6. The structure without...
additional atoms at the interface is also shown in Supplementary Fig. 7 for comparison. Figure 2a,b shows the top and side views, respectively, of the geometry of the Gr/α-Al2O3 interface with the additional O atoms obtained from DFT calculations. The additional O atoms directly bond to some of the C atoms of Gr with a bond length of 1.400 Å, as shown in Fig. 2b, whereas the other C atoms are further away from the α-Al2O3 surface. As a result, the average spacing between the additional O atoms and the Gr is 1.762 Å, which is in good agreement with the experimental results.

Fig. 2 Calculated interface structure of Gr/α-Al2O3. a Top view. b Side view. The unit of length is Å. Red: Al atom. Green: O atom. Gray: C atom

Effects on the surface structure of α-Al2O3. Figure 3 shows the quantitative analysis of the surface structure of α-Al2O3 along the [100] orientation based on the image shown in Fig. 1a. We measured the distance between Al atoms from different layers (Al–Al length) and the angle between the Al–Al direction and the normal direction of the interface (Al–Al angle). There are negligible deviations of the Al–Al distance and angle far below the surface compared with bulk α-Al2O3, whereas a significant difference is observed for the top surface layers, as shown in Fig. 3a,c. In our experiment, the Al–Al distance at the surface is ~2.3 Å, which is in sharp contrast to the bulk value of ~2.6 Å. Furthermore, a similar trend is observed for the Al–Al angles, i.e., the angle at the surface is ~36°, whereas it is ~32.5° in the bulk. The DFT calculations also show a large change in surface relaxation for α-Al2O3, i.e., 2.22 Å for the Al–Al distance at the surface and 2.58 Å inside the bulk and 38.64° for the Al–Al angle at the surface and 32.39° inside the bulk, which is in excellent agreement with the experimental results.

Indeed, the structure relaxation at the surface is an important physical phenomenon in many materials25–27, including α-Al2O3. We now compare the structure relaxation of α-Al2O3 near the interface with the bare surface case reported in the literatures in Fig. 4. In our case, the surface contraction is approximately −(35.3 ± 8.2)% for the top layer (distance from the first Al layer to the second O layer) compared with the bulk, whereas the relaxation rates become −(1.6 ± 0.3)%, −(27.1 ± 10.5)%, (16.6 ± 2.9)%, and −(8.2 ± 1.6)% for the second, third, fourth, and fifth layers, respectively. These measured values are very close to our DFT calculations and typically smaller than that of a bare α-Al2O3 surface reported in previous DFT calculations and experiments21, indicating that the strong interaction between the α-Al2O3 surface and the C atoms in Gr effectively suppresses the structure relaxation of the α-Al2O3 surface.

Fig. 3 Quantitative measurements of Al–Al length and angle. a Al–Al length mapping. b Averaged distance. c Al–Al angle mapping. d Averaged angle. The error bars are the standard deviation (SD)
The formation of C-O-Al bond can significantly change the properties of the interface. The adhesion force/energy of the Gr/α-Al2O3 interface is evaluated using a mechanical nanoscratch method with the aid of an AFM system (Cypher Asylum Research). The radius of the diamond tip used for the measurement was ~40 μm and a normal load of 11.9 μN was applied.

Data acquisition and analysis. The atomic scale HAADF-STEM images were acquired using a double aberration-corrected FEI (Titan Cubed Themis G2, spatial resolution up to 60 pm) operated at 300 kV with the convergence semiangle 21.5 mrad and collection semiaiangle 80–379 mrad. We also deliberately minimized the electron dose to avoid specimen damage using a small aperture, small beam current, and short scanning time. The atomistic models were generated by VESTA and XCrysDen software. The plots were created by Origin 2018C. Atom positions were determined by simultaneously fitting 2D Gaussian peaks to an a priori perovskite unit cell using a home-developed code running in MATLAB R2012b. The data mapping was also carried out by MATLAB R2012b.
HAADF-STEM image simulation. The multislice STEM simulation was performed using the software pack developed by Kirkland37. We used the single layer Gr/Al2O3 interface model shown in Fig. 2. In the simulation, the wave function size, sampling size, and image size were set to 1024 × 1024, 512 × 512, and 512 × 512, respectively. All microscope settings were the same as those in the experiments. The simulated image was then convolved with an 80 pm full width at half maximum Gaussian function considering the incoherent source broadening.

Data availability
All data supporting the findings of this study are available within the paper and its Supplementary Information.

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Author contributions
P.G., S.Y. and L.L. conceived the idea and designed the experiments. Z.D. and Y.S. prepared the TEM cross-sectional sample and did the STEM characterization assisted by Y.L., B.L. and Q.L. N.L. did the quantitative image analysis. S.Y. did the multislice STEM simulation performed using the software pack developed by Kirkland37. We used the single layer Gr/Al2O3 interface model shown in Fig. 2. In the simulation, the wave function size, sampling size, and image size were set to 1024 × 1024, 512 × 512, and 512 × 512, respectively. All microscope settings were the same as those in the experiments. The simulated image was then convolved with an 80 pm full width at half maximum Gaussian function considering the incoherent source broadening.

Competing interests
The authors declare no competing interests.

Additional information
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