Doping of graphene induced by boron/silicon substrate

Arezoo Dianat1, Zhongquan Liao1,2, Martin Gall2, Tao Zhang3, Rafael Gutierrez1, Ehrenfried Zschech2,4 and Gianaurelio Cuniberti1,5,6

1 Institute for Materials Science and Max Bergmann Center of Biomaterials, TU Dresden, D-01062 Dresden, Germany
2 Fraunhofer Institute for Ceramic Technologies and Systems (IKTS), D-01109 Dresden, Germany
3 Chair for Molecular Functional Materials, TU Dresden, D-01069 Dresden, Germany
4 Dresden Center for Nanoanalysis (DCN), TU Dresden, D-01187 Dresden, Germany
5 Dresden Center for Computational Materials Science, TU Dresden, D-01062 Dresden, Germany
6 Center for Advancing Electronics Dresden, TU Dresden, D-01062 Dresden, Germany

E-mail: zhongquan.liao@ikts.fraunhofer.de

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Abstract
In this work, we show the doping of graphene most likely from heteroatoms induced by the substrate using Raman spectra, x-ray photoelectron spectroscopy, energy dispersive x-ray spectroscopy and ab initio molecular dynamics (MD) simulations. The doping of graphene on a highly boron-doped silicon substrate was achieved by an annealing at 400 K for about 3 h in an oven with air flow. With the same annealing, only the Raman features similar to that from the pristine graphene were observed in the freestanding graphene and the graphene on a typical Si/SiO2 wafer. Ab initio MD simulations were performed for defected graphene on boron-doped silicon substrate at several temperatures. All vacancy sites in the graphene are occupied either with B atoms or Si atoms resulting in the mixed boron–silicon doping of the graphene. The MD simulations validated the experimental finding of graphene doped behavior observed by Raman spectrum. The electronic structure analysis indicated the p-type nature of doped graphene. The observed doping by the possible incorporation of heteroatoms into the graphene, simply only using 400 K annealing the boron-doped Si substrate, could provide a new approach to synthesize doped graphene in a more economic way.

Supplementary material for this article is available online

Keywords: graphene, annealing, doping, heteroatoms

(Some figures may appear in colour only in the online journal)

1. Introduction
Graphene, an allotrope of carbon, is a single layer of carbon atoms building a honeycomb lattice. Since its discovery, it has raised extensive interest worldwide, and has been investigated as a potential material for improving the performance of future devices [1]. In particular, the very high mobility [2], quantum Hall effect [3], massless carriers [4] etc, positions graphene as a main candidate for applications in post-silicon electronics. However, the absence of bandgap in pristine graphene hinders most of its potential electronic applications, because the switching off in any kind of device made from zero-bandgap graphene would be extremely difficult. Therefore, bandgap engineering is necessary for future graphene-based electronic devices.

Doping is a very mature method to control the semiconducting properties in the silicon semiconductor community, therefore, it has also been proposed to tune the bandgap of graphene. Theoretical studies have proven that the bandgap can be opened in graphene after substituting the carbon atoms using B and N atoms, and doped graphene shows ideal p- and n-type semiconducting electronic properties [5–7]. Subsequently, several groups tried to produce large area of doped graphene [8–15] using different approaches, such as chemical...
vapor deposition (CVD) [8, 14], segregation methods using embedded carbon and nitrogen sources [9], high power annealing in NH$_3$ [10, 11], among others [12, 13, 15, 16]. In comparison with many published approaches for the synthesis of N-doped graphene, the development for the synthesis of B-doped graphene falls far behind [14, 17]. Further investigation on the doping of graphene (both N-doped and B-doped) is necessary to control the induced defects and the microstructure in the doped graphene. The challenge to produce homogeneously doped graphene with silicon-comparable or higher mobility by an economic way for practical applications is still far away from being solved.

The possibility to open an energy gap in graphene through perturbations of the underlying substrates has raised increasing attention [18, 19]. Although the effect has been further demonstrated theoretically and experimentally [20–22], the influence of the underlying substrate on graphene layers is not fully understood. In particular, the feasibility of substituting carbon atoms by heteroatoms from the substrate using high temperature annealing may be expected, and this substitution can be realized by annealing in NH$_3$ [11], high power annealing in SiO$_2$, and annealing in a Si-SiO$_2$ system [12]. The ratio of intensities between the 2D and G peak is expected due to no influence from the substrate. Two typical Raman spectra from different positions of the graphene on the Si/SiO$_2$ substrate are shown in figures 1(d) and (e). With the same experimental conditions, the freestanding graphene without any support from the substrate shows similar Raman features as in figure 1(b), but with increased 2D/G ratio. The increased 2D/G ratio is expected due to no influence from the substrate. Since the graphene on the trench could not get heteroatoms from the highly boron-doped substrate, it does not produce homogeneously doped graphene with silicon-comparable or higher mobility by an economic way. The electronic structure is further investigated by the dynamical doping behavior of graphene and the corresponding electronic structure is further investigated by the dynamical doping behavior of graphene and the corresponding electronic structure is further investigated by the dynamical doping behavior of graphene and the corresponding electronic structure.

2. Methods

Monolayer graphene was produced in a CVD furnace using copper as the catalyst, and then was transferred to a Si/SiO$_2$ wafer and a highly boron-doped silicon substrate with patterned trenches using the polymethyl methacrylate (PMMA) method [23]. One step before the dissolving of PMMA, the graphene/PMMA on the substrates were annealed at 400 K for about 3 h in an oven with air flow. The final samples were dried in a critical point dryer to protect the delicate graphene layers against rupture due to the surface tension. A confocal Raman microscope was used to characterize the transferred graphene layers on substrates. The Raman spectrum was excited a 532 nm (2.33 eV) laser, and the spot size of the laser beam was about 0.5 μm. After the Raman measurement, the graphene on the highly boron-doped silicon substrate was transferred to Au substrate and TEM grid for x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray spectroscopy (EDX) measurement, respectively. XPS was measured by Kratos Analytical AXIS Ultra photoelectron spectrometer, and EDX was acquired in a Zeiss Libra (S)TEM using a Oxford Instrument EDX detector.

The investigation of the dynamical behavior of graphene on the boron-doped silicon surface and the corresponding electronic structure was carried out at the DFT level using the standard implementation in the CP2K package [24, 25]. A mixed basis-set approach is used, with the Kohn–Sham orbitals expanded into linear combinations of contracted Gaussian type orbitals and complemented by a plane-wave basis set for computing the electronic charge density. In our case, we use a (double zeta for valence electrons plus polarization functions) basis set complemented with a plane-wave basis with energy cut-off of 350 Ry. In all calculations, the BLYP exchange-correlation functional [26] and its corresponding norm-conserving pseudo-potential (Goedecker, Teter and Hutter) were used. Dispersion corrections were included through the standard D3 Grimme parameterization [27]. As the k-point sampling is not implemented in Cp2k and because of the large size of the unit cells, k-points schemes were not used. Born–Oppenheimer quantum molecular dynamics (MD) simulations were performed in the canonical ensemble, with a time step of 1.0 fs using a Nose–Hoover thermostat to control the temperature. Finally, periodic boundary conditions were used for the total energy calculations and MD simulations with a vacuum gap of about 15 Å in the slab direction to avoid spurious interactions between supercell images. To obtain the energy profiles for the replacement of a B atom from the substrate into the defected graphene, a climbing image nudged elastic band (NEB) approach was used for the calculation of the corresponding activation barrier. We have determined the reaction pathway with seven images connected via springs (fixed spring constants of 0.05 atomic units).

3. Results and discussion

Figure 1(a) shows the optical microscope image of a monolayer graphene transferred on a Si/SiO$_2$ substrate. A typical Raman spectrum of the graphene on the Si/SiO$_2$ substrate is provided in figure 1(b), which is acquired at the position indicated by a red circle in figure 1(a). The two most prominent features observed are the G peak around 1580 cm$^{-1}$ and the 2D peak around 2680 cm$^{-1}$. Two very small peaks can also be observed, the D peak (defect peak) around 1350 cm$^{-1}$ and G’ peak around 2450 cm$^{-1}$. The negligible D peak indicates good quality of graphene used in the experiment. The ratio of intensities between the 2D and G peak (2D/G) is about 1.8. Apparently, the annealing at 400 K for about 3 h in an oven with air flow did not cause noticeable changes in the Raman spectrum of the graphene on the Si/SiO$_2$ substrate. Two typical Raman spectra from different positions of the graphene on a highly boron-doped silicon substrate are shown in figures 1(d) and (e). With the same experimental conditions, the freestanding graphene without any support from the substrate shows similar Raman features as in figure 1(b), but with increased 2D/G ratio. The increased 2D/G ratio is expected due to no influence from the substrate. Since the graphene on the trench could not get heteroatoms from the highly boron-doped substrate, it does
not show any doping behavior from the corresponding Raman spectrum (figures 1(c) and (d)). However, the typical Raman spectrum of graphene (figure 1(e)) directly on the highly boron-doped silicon substrate, which is acquired at position 2, shows the features similar to the ones observed in the doped graphene after substituting the carbon atoms by B and/or N atoms [7, 9, 13, 14, 28]. The uneven background in the spectrum is due to the disturbance from the substrate (see figure S1, available at stacks.iop.org/NANO/28/215701/mmedia). The spectrum exhibits a very pronounced D peak and an accompanied D' peak with a obviously decreased intensity ratio of 2D and G peaks about 1.1, which are consistent with the expected doping effect from heteroatoms [28], and can be explained by the elastically scattered photo-excited electron generated by heteroatoms embedded in the graphene lattice and intravalley double resonance scattering processes [29]. As a comparison, a Raman spectrum of the graphene supported on the highly boron-doped silicon substrate before annealing at 400 K was also acquired (see figure S1), only Raman features of pristine graphene could be observed. Therefore, it is inferred that the annealing of graphene on the highly boron-doped silicon substrate at 400 K for about 3 h may dope the graphene effectively. Relatively weak bonds between the B atom and Si atom may break and B and Si atoms could dope the graphene by substituting some carbon atoms of graphene.

XPS and EDX were chosen to confirm the incorporation of heteroatoms into the graphene. The doped graphene on the highly boron-doped silicon substrate was transferred to Au substrate and TEM grid for XPS and EDX measurement. The quantitative XPS results from the used pristine CVD graphene on copper and the doped graphene after annealing experiment are shown in tables 1 and 2. The corresponding spectra are shown in figures S2 and 3. Si (2.89 at%) is clearly observed in the doped graphene, while no Si could be observed in the used pristine CVD graphene. Cu or Au is from the corresponding substrate, and Sn or S is the residue (very small peaks in figures S2 and 3). O is normal to be observed in graphene sample due to physisorption, PMMA residue could be extra source for O in the transferred graphene sample (table 2). EDX results in the STEM (online supplementary figure S4 and table S1) also tend to show the incorporation of

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heteroatoms (Si atoms) into the graphene. B could not be detected from XPS and EDX, probably because the concentration of B in the doped graphene is very low which is lower than the detection limit. The concentration of B in the typically highly doped Si wafer from the market is usually lower than 1%, which means more than 99% Si in our used highly boron-doped Si substrate. In our experiment, very high concentration of B in the substrate resulted in only about 2.89% doping level of Si (table 2). Therefore less than 1% B in the substrate would result in a much low concentration of B in the doped graphene, which is expected to be lower than the detection limit of XPS and EDX. However, it is believed that B atoms should be introduced in the graphene as well due to the easier thermal excitation compared to Si atoms. The doping by the possible incorporation of heteroatoms into the graphene, simply only using 400 K annealing the boron-doped Si substrate, could provide a new approach to synthesize doped graphene in a more economic way.

In order to understand the doping behavior of graphene on the boron-doped silicon surface, theoretical calculations and simulations were performed. Our starting reference silicon structure in the simulation is a reconstructed (2 × 1) Si(100) surface, where buckled dimer rows are built; we have then considered the cases where (i) a full layer of bulk silicon atoms is replaced by boron atoms, and (ii) the surface silicon atoms forming the dimer rows are replaced by boron atoms. It is clear that cases (i) and (ii) represent two ideal extreme situations; in a more realistic substrate a random positioning of boron atoms may be expected. This would however require the study of disorder average quantities and goes beyond the scope of the present study. Our main goal at this stage is to compare the energetic stability of these two extreme configurations via total energy calculations. The two structurally relaxed structures are shown in the figure 2; notice that the buckling in the dimer rows has been suppressed upon replacement of silicon by boron. The total energy difference between them was calculated to be 2.6 eV, the surface segregated state being energetically preferred. This result is in agreement with the boron surface segregation behavior in various unpassivated silicon nanowires previously reported [30]. In the next step, we have then considered the structure from figure 2(b) as the starting conformation to perform quantum MD simulations.

In order to investigate graphene–surface interaction, graphene is placed on the 3 × 3 boron-doped Si(100) surface (see figure 3(a)) with periodic boundary conditions. First, an MD run was performed to adjust the graphene lattice vectors to the underlying surface lattice. This resulted in a stretching of graphene by less than 7%. This specific procedure of dynamically adapting the graphene lattice to the substrate and not vice versa avoids artificial interactions in the substrate. The vertical distance of the graphene plane to the surface was determined to be 3.3 Å indicating the weak non-binding interaction between the two systems. In the next step, we generated single and double vacancies in graphene to address the possible transfer of substrate impurities (the boron atoms) into the graphene membrane (see figure 3(b)). MD simulations were then carried out at different temperatures (400, 700, 1000, and 1500 K) and selected results are summarized in figure 4. We find that all vacancy sites in the graphene are occupied either with B atoms or Si atoms. The concentration of boron atoms is almost twice larger than Si because of the lower atomic weight of B atoms and consequently the easier thermal excitation.

In order to confirm the MD simulation results, the energy profile for the replacement of a B atom from the substrate into the defected graphene was calculated by the NEB method for the structure shown in figure 3(a) with only one vacancy position in graphene. The energy landscape for different reaction coordinates is presented in figure 5. The activation barrier of about 0.6 eV has been found for the transition state where the vertical distance between B and graphene is about 2.9 Å and the B–B distance about 1.76 Å. This activation barrier is rather small and the reaction is expected to occur relatively fast.

Due to the high interest of graphene nanoribbons, we have also considered finite size graphene structures obtained from the previously studied periodic conformations by removing periodic boundary conditions in the direction of the substrate dimer rows. We have considered m = 10 atomic armchair chains in order to have a semiconducting nanoribbon. The total density of states of the pristine armchair nanoribbon indicates a band gap of about 0.7 eV (see figure 6(a)). For 3.44% B doping, the density of states shifts...
to the unoccupied states, indicating the p-type nature of doped graphene. It should be noted that in this case the band gap is reduced to about 0.45 eV (see figure 6(b)). In the case of mixed B and Si doping, the electronic states are still shifted towards the conduction band, however by a smaller amount than only with B doping, thus resulting in the lower degree of p-type doping. The calculated band gap, in this case, has been found to be around 0.2 eV (see figure 6(c)).

4. Conclusions

Annealing at 400 K for about 3 h in an oven with air flow did not affect the Raman features of the freestanding graphene and the graphene on typical Si/SiO₂ substrate. The same annealing induced a doping into the graphene on the highly boron-doped silicon substrate, which is caused by possible substituting carbon atoms by heteroatoms from the substrate. A very pronounced D peak and an accompanied D’ peak with an obviously decreased intensity ratio of 2D and G peaks about 1.1 were observed in the doped graphene. XPS and EDX provided indirect evidence of the possible incorporation of heteroatoms into the graphene from the substrate. It is inferred that relatively weak bonding between the B atom and Si atom may break during the high temperature annealing, and Si and B atoms could dope the graphene by substituting some carbon atoms of graphene. The first-principle MD calculations at different temperature showed that all vacancy sites in the graphene are occupied either with boron atoms or with mixed boron and silicon atoms from boron-doped silicon substrate. The MD simulations validated the experimental finding of graphene doped behavior observed by Raman spectrum. The electronic structure analysis also confirmed the p-type nature of doped graphene. The observed doping by the possible incorporation of heteroatoms into the graphene, simply only using 400 K annealing the boron-doped Si substrate, could provide a new approach to synthesize doped graphene in a more economic way.
Acknowledgments

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