

Theory and hierarchical modeling of defective graphene, the effects of grain boundaries and oxidation

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Graphene has extraordinary properties, but utilizing these properties in electronic applications requires the ability to grow large scale, defect-free graphene sheets. The ground breaking method to exfoliate graphene sheets from graphite crystals do provide defect-free graphene sheet over large length scales, but this method is not suitable for industrial scale production. Several other routes are currently pursued to synthesize graphene, such as annealing of SiC, CVD growth or oxidation of graphite, but the samples created in these ways are often found to be polycrystalline and may contain a variety of defects and functional groups. These defects in the as-grown polycrystalline graphene samples can, on the one hand, be detrimental for the properties of graphene, but on the other hand, offer a method to control its mechanical and electronic properties. However, the graphene research has up to now been focusing on perfect graphene and as-grown, defective graphene has only recently started to obtain some attention.

Point defect in graphene may be generated by electron beam irradiation [1], but grain boundary engineering at the atomic level is still very challenging because no general theory is available, which is able to describe the various structures that have been observed in experiments. Scanning tunnelling microscopy (STM) investigations of a variety of [0001] tilt grain boundaries in graphene have shown that small angle grain boundaries have the shape of periodic arrays of asymmetric hillocks with large separation as demonstrated in Fig. 1a) [2], while a grain boundary with a misorientation angle $\theta = 21^\circ$ could be characterized as a flat array of 5-7 ring complexes [3] and a grain boundary with a misorientation angle of 60° had the shape of an array of 5 and 8 rings [4]. The shape and properties of the defects may be further tailored by controlled oxidation [5], as the basal plane of graphene is inert towards molecular oxygen and only vacancies are etched by O_2 [6]. However, oxidation of graphene is a very complex process, where the individual steps are not yet completely understood.

In order to improve the understanding of imperfect graphene, we have investigated the shape and effects of point defects and grain boundaries in graphene and how oxidation influence as-grown graphene.

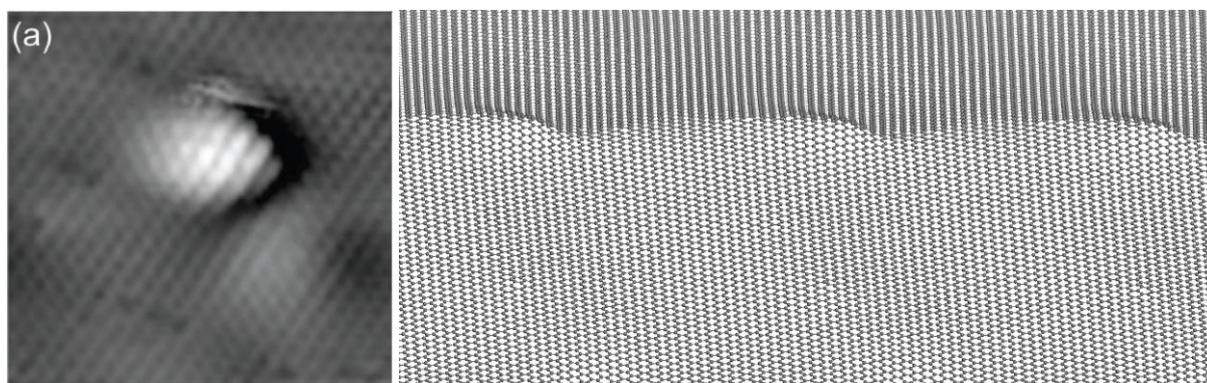


Figure 1 a). STM observation of the hillocks at a small angle grain boundary in graphene taken from [1]. b) Optimized structure of the atomistic grain boundary model having the same misorientation angle as the experiment. Taken from [4].

Our density-functional (DFT) calculations using the DMol-code showed that point defects in graphene form a complex of non-hexagonal rings in the hexagonal graphene lattice [7]. Further analysis revealed that these defects form semi-localized defect states, indicating that defects in graphene would have an increased chemical activity, which was later confirmed by our investigation of oxidation of graphene [8].

In addition, we have developed a general theory for the structure of [0001] tilt grain boundaries in graphene based on the coincidence site lattice (CSL)-theory [9]. The CSL-theory is convenient to derive supercell models for grain boundaries and we have implemented the method into a script in Materials Studio [10]. The script is able to generate grain boundary models for a particular misorientation angle θ with two grain boundaries per supercell. The structure of a large set of the grain boundary models were geometry optimized by force field and bond order potential calculations and selected models were also optimized by DFT calculations using the CASTEP-code for reference. Our force field and DFT calculations show that low energy grain boundaries in graphene can be identified as dislocation arrays. Grain boundaries with small misorientation angles tend to form hillocks as shown in Fig. 1b). This occurs due to the strain at the dislocation cores in agreement with STM observations of small misorientation angle grain boundaries in epitaxial grown graphene [2]. Our calculations have also shown that contrary to the usual bulk behaviour, in graphene there is an attractive interaction between dislocation cores that decreases the strain energy, so that the dislocation arrays form ridges for misorientation angles $10^\circ < \theta < 25^\circ$ and flatten out for misorientation angles larger than $\theta = 25^\circ$. The structure of the grain boundary corresponding to the STM observation in [4] is then approximately a flat array of 5-7 dislocation core rings. The attractive interaction decreases the formation energy for grain boundaries with large misorientation angles so that a minimum occurs for $\Sigma = 13$ at $\theta = 32.2^\circ$.

Finally, we have investigated oxidation of graphene. Our DFT calculations using the CASTEP-code showed that dissociation of O_2 of the basal plane of graphene is strongly endothermic, which provides an explanation to the inertness of defect-free graphene [8]. Further calculations for oxidation of vacancies indicated that low temperature etching of graphene proceeds through a two-step mechanism. Bare vacancies are very reactive towards O_2 as our previous analysis indicated [7]. The O_2 molecules get dissociated, such that the vacancies quickly get saturated by ether and carbonyl groups. These O-groups are stable with respect to CO-desorption below the critical temperature T_c , and they can be considered as the ground state in an oxygen atmosphere. The saturation of the bare vacancies is the first step in the oxidation reaction. The oxygen saturated vacancies are less reactive towards oxygen compared to the bare vacancies, but significantly more reactive than the basal plane. The oxygen molecules can be dissociated at the ether groups and this leads to the formation of larger O-groups, primarily lactones, which either desorb directly as CO_2 or the lactones are further activated by additional O_2 dissociation forming anhydride groups. The anhydride groups decompose rapidly and the CO_2 desorption exposes new sites for O_2 -dissociation, thus driving the etching reaction further. The dissociation of the oxygen molecules at the ether groups forming lactones and anhydrides is the second step in the oxidation process.

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