Modeling of defective graphene to investigate 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. Several routes are currently pursued to synthesize graphene, but the samples are often found to be polycrystalline. The 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, 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 tunneling 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 [1], while a grain boundary with a misorientation angle $\theta = 21°$ could be characterized as a flat array of 5-7 ring complexes [2]. The shape and properties of the defects may be further tailored by controlled oxidation [3]. 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.

Our density-functional (DFT) calculations[4] showed that point defects in graphene form a complex of non-hexagonal rings in the hexagonal graphene lattice [5]. Further analysis revealed that these defects form semi-localized defect states, indicating that defects in graphene would have an increased chemical activity. This was later confirmed by our investigation of oxidation of graphene, which revealed a two-step process for the low temperature oxidation of graphene[6]. Bare vacancies are very reactive towards O_2, such that the vacancies quickly get saturated by ether groups. These O-groups are stable with respect to CO-desorption at low temperatures, but they are more reactive towards additional O_2-molecules. The dissociation of the oxygen molecules at the ether groups forming more volatile O-groups, which as a second step leads to desorption of CO_2.

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 [7]. The combination of force field, bond order potential and DFT calculations[4] showed that low energy grain boundaries in graphene can be identified as dislocation arrays. Grain boundaries with small misorientation angles tend to form hillocks in agreement with STM observations of grain boundaries in epitaxial grown graphene [1]. Our calculations have also shown that contrary to the usual bulk behaviour, there is an attractive interaction between dislocation cores in graphene. This interaction decreases the strain energy, so dislocation arrays flatten out with increasing misorientation angles. The attractive interaction decreases the formation energy for grain boundaries with large misorientation angles so that a minimum occurs for $\theta = 32.2°$.

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