Revealing the atomistic structure of grain boundaries in graphene by hierarchical simulations

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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].

We have developed a general theory for the structure of symmetric [0001] tilt grain boundaries in graphene based on the coincidence site lattice (CSL)-theory [3]. 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 θ=32.2°.

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