Thermally controlled patterning of graphene by hydrogen

R. Balog, J. Jørgensen, L. Nilsson and L. Hornekær

Dept. Physics and Astronomy, Aarhus University, 8000 Aarhus C, Denmark.
balog@phys.au.dk

As a result of its unique electronic, mechanical, optical and chemical properties graphene attracts much attention both within basic and applied research and for actual applications [1-5]. However, the diversity of proposed applications require additional processing of graphene which is achievable by for example chemical functionalization.

We have extensively studied functionalization of graphene on Ir(111) by atomic hydrogen using STM, ARPES, XPS and *ab-initio* DFT calculations. What was found is that during the initial exposure of graphene to an atomic hydrogen beam, hydrogen clusters form at distinct parts of the moiré supercell of the graphene/Ir(111) interface. Hydrogen clusters formed this way therefore follow the periodicity of the moiré superstructure, which accordingly results in a substantial band-gap opening in graphene. The size of the gap, measured by ARPES, was estimated to be at least 0.4 eV at intermediate hydrogen coverage [6]. Further increasing of hydrogen dose destroys the periodicity of hydrogen clusters and turns graphene into an insulator.

Our newest XPS data reveal formation of two distinct types of hydrogen clusters at the graphene/Ir(111) interface, namely graphane-like and dimers [7]. While graphane-like clusters follow the moire periodicity, dimers tend to destroy the order. Fast-XPS data obtained *in situ* with hydrogen dose confirm the initial preferential formation of graphane-like clusters as observed in reference 6, but this preference is rapidly lost with increasing hydrogen coverage. On the other hand, temperature controlled fast-XPS revealed distinct thermal stability for both types of hydrogen clusters and indicate that one can obtain well-defined periodic (graphane-like) structures simply by annealing the sample to elevated temperatures.

The possibilities of thermally controlling the formation of well-defined hydrogen patterns on graphene are explored using STM experiments.

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