Molecular Interactions on Epitaxial Graphene

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The growth of high quality epitaxial graphene will facilitate the development and commercialization of graphene nanoelectronics devices, and the main substrate-based approaches are chemical vapour deposition (CVD) on metal catalytic thin films and thermal decomposition of silicon carbide (SiC). We have performed detailed studies using *in situ* scanning tunnelling microscopy (STM), synchrotron photoemission (PES) and density functional theory (DFT) calculations to investigate the structure of the various reconstructions of 6H-SiC(0001) prior to its thermal decomposition to form epitaxial graphene (EG) [1-3] (Fig. 1). We show that the transition from monolayer EG to trilayer EG adopts a bottom-up growth mechanism [4], and x-ray absorption fine structure studies indicate an increase in disorder of Si atoms in the SiC substrate beneath the surface and the formation of Si clusters [5,6].

A major challenge in graphene-based devices is opening the energy band gap and doping. Molecular functionalization of graphene is one approach to modifying its electronic properties. Surface transfer doping by surface modification with appropriate molecular acceptors represents a simple and effective method to non-destructively dope graphene [7-9]. Surface transfer doping relies on charge separation at interfaces, and represents a valuable tool for the controlled and non-destructive doping of semiconductors and nanostructures at relatively low cost, thereby facilitating the development of hybrid organic-graphene nanoelectronics. Molecular self-assembly of bimolecular systems on epitaxial graphene and HOPG is demonstrated [10,11] (Fig. 2). Surface transfer hole doping of epitaxial graphene using oxide thin films is also discussed [12].

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Figure 1: LEED and corresponding STM images showing the evolution of various superstructures on 6H-SiC(0001) as a function of annealing temperature: 3×3 (panels a and e); (panels b and f); nanomesh (panels c and g); graphene (panels d and g). Incident electron beam energies (LEED) of 100 eV for panels a, b and c, and 175 eV for panel d. Adapted from Ref [9].



Figure 2: Molecularly resolved 15x15 nm2 STM images (top) and DFT simulated molecular models (below) of the F16CuPc molecular dot arrays with tunable intermolecular distance controlled by DIP molecular coverage. The scale bar in each STM image represents 5 nm. (from Ref [11])