Modification of electronic properties of graphene by interaction with substrates and dopants

Submitted by Alexander Markevich to the University of Exeter as a thesis for the degree of Doctor of Philosophy in Physics.

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Abstract

First-principles calculations have been carried out to investigate structural and electronic properties of graphene on SiC and diamond substrates and for a study of doping of fluorographene with various surface adsorbates.

New insight is given into the problem of the decoupling of the graphene layers from SiC substrates after epitaxial growth. Mechanisms of hydrogen penetration between graphene and SiC(0001) surface, and properties of hydrogen and fluorine intercalated structures have been studied. Energy barriers for diffusion of atomic and molecular hydrogen through the interface graphene layer with no defects and graphene layers containing Stone-Wales defect or two- and four-vacancy clusters have been calculated. It is argued that diffusion of hydrogen towards the SiC surface occurs through the hollow defects in the interface graphene layer. It is further shown that hydrogen easily migrates between the graphene layer and the SiC substrate and passivates the surface Si bonds, thus causing the graphene layer decoupling. According to the band structure calculations the graphene layer decoupled from the SiC(0001) surface by hydrogen intercalation is undoped, while that obtained by the fluorine intercalation is p-type doped.

Further, structure and the electronic properties of single and double layer graphene on H-, OH-, and F- passivated (111) diamond surface have been studied. It is shown that graphene only weakly interacts with the underlying substrates and the linear dispersion of graphene $\pi$-bands is preserved. For graphene on the hydrogenated diamond surfaces the charge transfer results in n-type doping of graphene layers and the splitting of conduction and valence bands in bilayer graphene. For the F- and OH-terminated surfaces, charge transfer and doping of graphene do not occur.

Finally, the possibility of doping fluorographene by surface adsorbates have been investigated. The structure and electronic properties of fluorographene with adsorbed K, Li,
Au atoms, and F4-TCNQ molecule are described. It is shown that adsorption of K or Li atoms results in electron doping of fluorographene, while Au atoms and F4-TCNQ introduce deep levels inside the band gap. The calculated value of the fluorographene work function is extremely high, 7.3 eV, suggesting that $p$-type doping is difficult to achieve.
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Contents

List of Tables 9

List of Figures 11

List of Publications 20

1 Introduction 21

1.1 Graphene crystal structure .......................... 22
1.2 Electronic structure of graphene ...................... 22
1.3 Production of graphene ............................... 25
1.4 Doping of graphene .................................... 26
1.5 Effect of substrates on electronic transport in graphene . . 27
1.6 Band-gap engineering in graphene .................... 29
1.7 Goals of the present work ............................ 30
1.8 Thesis organisation ................................. 31
2 Method

2.1 Many body problem ........................................ 32
2.2 Born-Oppenheimer approximation .................................. 34
2.3 Variational principle ........................................ 35
2.4 Density Functional Theory ................................... 37
  2.4.1 Kohn-Sham equations ..................................... 38
  2.4.2 The exchange-correlation functional .......................... 39
2.5 Pseudopotentials ........................................ 42
2.6 The AIMPRO implementation of DFT ........................ 45
  2.6.1 The supercell method ..................................... 45
  2.6.2 Basis functions ........................................ 46
  2.6.3 Basis functions in reciprocal space ........................ 47
  2.6.4 Sampling of the Brillouin zone ............................ 48
2.7 Modelling graphene ...................................... 49
  2.7.1 Choice of k-points for the graphene Brillouin zone sampling .... 51

3 Intercalation of hydrogen and fluorine into graphene/SiC(0001) interface 54

3.1 Introduction ........................................ 54
3.2 Details of calculations ........................................... 57
3.3 Electronic and structural properties of the interfacial carbon layer on SiC(0001) according to the $R3$ and $4 \times 4$ models .................................................. 59
3.4 Effect of lattice strain on the binding energy and diffusion of hydrogen through a graphene layer ........................................ 62
3.5 Properties of a quasi-free-standing graphene layer on H- and F-passivated SiC(0001) ........................................... 66
3.6 Mechanisms for hydrogen penetration through the interfacial carbon layer on SiC(0001) ................................. 69
3.7 Hydrogen diffusion between the interfacial carbon layer and SiC substrate 75
3.8 A model of hydrogen intercalation into graphene/SiC interface ........... 76
3.9 Conclusions ............................................ 77

4 Graphene on diamond substrates ................................... 79
4.1 Introduction .......................................... 79
4.2 Details of calculations ................................... 81
4.3 Effect of the termination on the diamond (111) surface electronic properties 86
  4.3.1 Clean surface ........................................ 86
  4.3.2 Hydrogenated surface ................................ 87
  4.3.3 Fluorinated surface .................................. 89
  4.3.4 Hydroxylated surface ............................... 90
4.4 Graphene on passivated diamond substrates ....................... 92
  4.4.1 Graphene on the H-passivated diamond (111) surface .... 92
  4.4.2 Graphene on the F- and OH-passivated diamond (111) surfaces 95
  4.4.3 Bilayer graphene on the passivated diamond substrates ..... 96
4.5 Discussion .............................................. 97
4.6 Conclusions ............................................ 99
## 5 Doping of fluorographene by surface adsorbates

5.1 Introduction ........................................ 100
5.2 Details of calculations ................................ 102
5.3 Structural and electronic properties of fluorographene .......... 102
5.4 K, Li and Au atoms on fluorographene ..................... 105
5.5 F4-TCNQ on fluorographene .......................... 110
5.6 Effect of doping on structural parameters of fluorographene . . . . 112
5.7 Conclusions ........................................... 113

## 6 Concluding remarks

6.1 Summary ............................................. 115

   6.1.1 Graphene on SiC(0001) substrates ...................... 115
   6.1.2 Graphene on passivated diamond substrates .............. 117
   6.1.3 Doping of fluorographene by surface adsorbates ........... 119

6.2 Outlook ............................................. 119