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Spin transport in graphene - hexagonal boron nitride van der Waals heterostructures

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Abstract

In this chapter I briefly discuss the basic electronic properties of the materials used in this thesis: graphene, hexagonal boron nitride, and their heterostructures. A brief overview on the crystallographic orientations of graphene, hBN, and their heterostructures has been provided and their importance in the transport properties is also discussed.

3.1 Graphene

Graphene is a two-dimensional (2D) material with a one atom thick layer of carbon atoms bonded with sp^2 hybridization and has honeycomb-like lattice structure. It is the first 2D material to be isolated from its bulk form. Graphene is considered as a building block for various carbon allotropes. In a layer-by-layer stacked structure bonded via van der Waals forces, it forms 3D graphite. When rolled into a cylindrical shape, it forms 1D carbon nanotubes. Whereas in a spherical shape, it forms 0D fullerenes.

The atomic structure of graphene can be visualized as a triangular lattice with a basis of two atoms per unit cell which are chemically equivalent but different with respect to lattice symmetry, denoted as A and B in Fig. 3.1(a). These two carbon atoms per unit cell result in the two inequivalent groups at the corners of the Brillouin zone, labeled as K and K' points in momentum space. From the tight binding calculations, the energy dispersion relation of the electrons in graphene close to Fermi energy, around K points can be expressed as:

$$E = \pm \hbar \nu_F |\vec{k}| \quad (3.1)$$

where \hbar is the reduced Planck constant, \vec{k} is the wave vector and $\nu_F \approx 1 \times 10^6 \text{ ms}^{-1}$ is the Fermi velocity of electrons in graphene. Moreover, this linear dispersion relation can also be obtained from the Dirac Hamiltonian that is used to describe the massless relativistic particles near K(K') points. Hence the electrons in graphene are often referred to as *Dirac fermions*. Due to a linear energy dispersion, the band structure of graphene around K and K' points is in cone shaped valleys. Both valleys have the same energy leading to a *valley degree of freedom*, in addition to the already existing

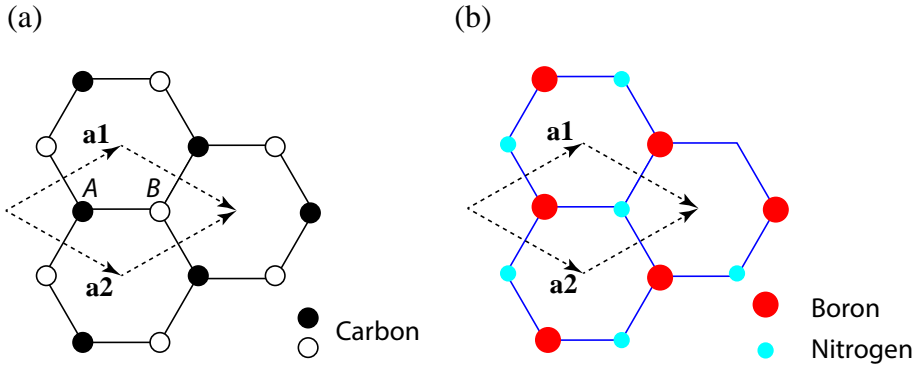


Figure 3.1: (a) Hexagonal crystal structure of graphene in real space with lattice parameters a_1 and a_2 , inequivalent atomic positions A and B . (b) Hexagonal crystal structure of boron nitride. The unit cell is represented by enclosed lattice vectors.

spin degree of freedom. Bulk graphite favours the AB stacking of layers where one carbon atom lies on top of a carbon atom from the bottom layer and one lies at the center of the hexagonal lattice [1].

Earlier studies have predicted that the two dimensional crystals were thermodynamically unstable to exist at room temperature [2, 3]. However, it was only in 2004 that the group of Geim from Manchester first isolated a single layer of graphene from a thick graphite crystal using a *scotch tape method* onto a commercially available SiO_2/Si substrate, and electrically characterized at room temperature. An optical microscope can be used for easy identification of graphene flakes down to a monolayer. This led to a surge of interest in identifying various other 2D materials [4] ever since revolutionizing the academic and industrial research [5], and the 2010 Nobel Prize in Physics was awarded to Geim and Novoselov [6].

The density of states of graphene can be tuned via an electrical gating of graphene when placed on an insulating substrate, typically a SiO_2/Si substrate. However, the electronic mobility of graphene has been found to be influenced by its interaction with the underlying SiO_2 substrate including the carrier scattering with the substrate roughness, interfacial impurities, atomic defects on substrate, surface optical phonons, and substrate induced charge inhomogeneities. The quest for an alternative substrate led to the usage of hexagonal boron nitride (hBN) substrates in 2010 for achieving high mobility graphene devices.

3.2 Hexagonal boron nitride (hBN)

Boron nitride (BN) is of great interest for electronics due to its fascinating properties such as extreme brittleness, low dielectric constant, high thermal conductivity, and large bandgap, that are highly valued for modern electronic devices. BN exists in various crystalline forms, including hexagonal, zincblende, and wurtzite, due to different hybridization modes of its constituent boron and nitrogen atoms. Only its hexagonal form, hBN, is stable at room temperature and exists in a layered structure and is isostructural with graphite.

Similar to graphene, boron nitride exists in various allotrope forms [7]: bulk hBN (3-dimensional), sheets (2-dimensional), nanotube (1-dimensional) and fullerene (0-dimensional). Both graphene and hBN are 2D crystalline materials, but there exist a few differences. hBN has a similar hexagonal layered structure to that of graphene with two chemically inequivalent atoms in a unit cell, i.e., boron and nitrogen atoms at A and B sublattices, respectively. Unlike graphene, hBN lacks inversion symmetry [8]. Moreover, the difference in electronegativity between boron and nitrogen sites in hBN leads to a finite band gap in the band structure of hBN [9]. While graphene is a zero bandgap semiconductor, hBN is a wide (indirect) bandgap insulator, also referred to as *white graphene* [10].

Even though BN has been known for sometime, 2D hBN has only been realized via *mechanical exfoliation* [11] after the discovery of graphene. Recently hBN has attracted a great attention due to its performance enhancement characteristics in vdW heterostructures with other 2D vdW materials.

Besides the excellent dielectric properties (wide bandgap, $\kappa \approx 4$) of hBN that are compatible with SiO₂, its atomically flat surface free from dangling bonds and charge traps, is attractive for using it as a dielectric substrate in place of a conventional SiO₂ substrate.

3.3 Graphene-hBN heterostructure

In order to improve the mobility and realize band gap engineering in graphene, various dielectric substrates have been studied including SiO₂ [14], suspended graphene (air), epitaxial graphene on SiC, mechanically transferred graphene on Al₂O₃, hBN [15], and other 2D materials [16, 17]. Among these substrates, hBN was found to be attractive substrate due to its dielectric properties and atomically flat and dangling bond free nature.

The discovery of the transfer techniques enabled to fabricate high mobility graphene devices on a hBN substrate [15, 18]. Moreover, these techniques allow us to stack various 2D materials in any desired order to make vdW heterostructures [17].

Graphene/hBN heterostructures have attracted much attention as a moiré super-

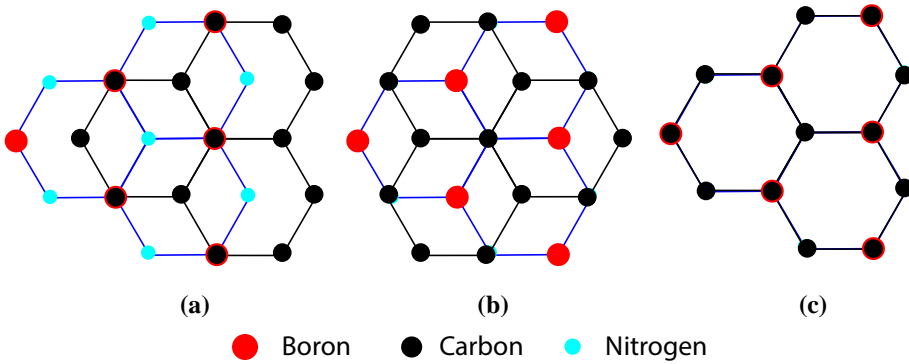


Figure 3.2: Three types of stacking order of graphene on hBN. (a) AB-stacking with a carbon on top of boron which is energetically stable. (b) AB' with a carbon on top of nitrogen. (c) AA-stacking with carbon on top of both boron and nitrogen. Besides, there exists other irregular stacking orientations [12, 13].

lattice system. Even though graphene and hBN are isostructural, the lattice parameter of hBN is about 1.8% larger than that of graphene. This lattice mismatch results in moiré pattern [19] and induces superlattice periodic potential field even in the unrotated graphene/hBN stack which is also realized experimentally in graphene/hBN heterostructures [20, 21].

The important features of a hBN substrate including an ultra flat surface, dangling bond free interface with graphene, and low charge inhomogeneities, allowed to realize exotic electronic phenomena in graphene such as Hofstadter's butterfly [22] when the crystallographic lattice orientation of graphene and hBN-substrate are perfectly aligned forming a moiré superlattice [23–25].

Different crystallographic stacking orientations are possible for graphene/hBN vdW heterostructures [Fig. 3.2] [26, 27]. Of all these, AB-stacking [Fig. 3.2(a)] is the energetically most favourable where one carbon is on top of the boron atom and one at the center of BN hexagon. This arrangement makes the two carbon sublattices of graphene inequivalent due to their interaction with the underlying hBN and is estimated to result in a bandgap of at least 53 meV [26]. The other stackings, AB' [Fig. 3.2(b)] with a carbon atom on nitrogen and one at the center, and AA [Fig. 3.2(c)] where carbon atoms lie on top of boron and nitrogen atoms, are energetically unstable.

In practice, during the assembly of graphene on hBN, a careful alignment of crystallographic directions (usually one can choose their straight edges) is required to find the superlattice features in transport experiments such as opening of a band gap, formation of the fractional quantum Hall state, and the Hofstadter quantization at high magnetic fields [21, 23, 25].

The interface of graphene/hBN creates an opportunity for a modulation of struc-

tural and electronic properties of graphene. However, the influence of the crystallographic alignment on spin transport in graphene has not been reported in literature. For the graphene/hBN devices prepared for spin transport studies in this thesis, a random transfer of graphene on hBN or hBN on graphene is chosen and thus the possibility of finding the superlattice features is very low [28].

On the other hand, the realization of the tunneling of electrons across graphene/hBN interface in a graphene-hBN field effect transistor device [29, 30] paved a way for new type of graphene devices [31, 32]. Interestingly, tunneling of spin polarized electrons across different thicknesses of hBN layers interfaced with graphene is predicted to enhance the spin polarization up to 100% [33]. Chapter 6 provides the experimental demonstration of achieving a large differential spin polarization in bilayer-hBN/graphene/hBN heterostructures. Moreover, Chapter 7 suggests the possibility of the influence of crystallographic orientation of a two-layer-CVD-hBN tunnel barrier on the electrical spin injection efficiency.

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