1 Title of the Project

Strain engineering of graphene electronic structure for creating a band gap and study of charge and spin transport through it

2 Applicant

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References
Master Thesis "Non-linear interactions between spin, heat and charge in graphene nanostructures", *Rijksuniversiteit Groningen*, The Netherlands (2011)

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4 Abstract

Achieving a bandgap in graphene is critical to developing active electronics made out of it. Graphene is a major contender for future generation electronics and circuitry because of the extremely good conducting properties that come from the fact that it exhibits pseudo-relativistic behaviors of carrier and can withstand high current densities [1]. Furthermore, it possess extremely high thermal conductivity and Young modulus. However, there is still a lack of control to completely pinch off the charge transport at will due to the presence of a minimum conductivity. We propose to experimentally tune the electronic structure of graphene to have a gapped spectrum by patterning, not the graphene, but the substrate on which it rests [2]. This approach relies on the generation of strain in the graphene layer causing anisotropic changes in hopping amplitudes. Though the latter approach does not aim at creating bulk spectral band gap in graphene, it achieves all characteristics of the former by creating the bottleneck for electron transport using local strain effects. In particular, the broader area of strain induced changes in electronic structure with many other theoretical proposals [3, 4, 5, 6] awaits experimental realization. Besides charge transport, we also propose to study spin transport through strained graphene system. This is important in possible realization of Datta-Das spin field effect transistor (sFET) that relies on Bychkov-Rashba spin splitting that could occur in asymmetric quantum wells or in deformed bulk systems [7].

5 Duration of the project

4 years starting September 2011

6 Personnel

6.1 Senior scientists

Name	Task in Project	Time
Prof. dr. ir. Bart van Wees	Supervision and management	10%
Prof. dr. ir. Paul van Loosdrecht	Supervision and analysis	5%
Dr. Ivan J. Vera Marun	Supervision and analysis	10%

6.2 Junior scientists and technicians

Name	Task in Project	Time
PhD student	Experiment and analysis	90%
Johan Holstein	Technical support	5%
Martijn de Roosz	Techinical support	5%

7 Cost estimates

7.1 personnel positions

One *onderzoeker in opleiding* position for four years.

7.2 Running budget

15k€per year for conferences, summer school and maintenance.

7.3 Equipments

Equipments	Costs
Raman spectroscopy setup	≈ 10k€
Liquid Helium and Nitrogen	≈ 5k€
Stanford Research Systems SR830 DSP lock-in	≈ 5k€

7.4 Other support

The project will be part of a larger research programme of the Zernike Institute of Advanced Materials. Aforementioned personnel involved are employed by the same institute or associated research programmes.

7.5 Budget Summary (in k€)

	2010	2011	2012	2013	2014	Total
Personnel (positions)						
PhD student	15	43	43	43	28	172
Postdocs	-	-	-	-	-	-
Technicians	-	-	-	-	-	-
Guests	-	-	-	-	-	-
Personnel costs	15	43	43	43	28	172
Running budget	6	15	15	15	9	60
Equipment FOM-part	20	-	-	-	-	20
Total	41	58	58	58	37	252

8 Introduction

Interests in present day electronics are fueled by low fabrication costs, high speed operation and low power consumption. Use of organic substrates as the active substrate has become really important in this respect. Firstly, because these are abundant in nature and inexpensive. Secondly, devices can be conveniently fabricated using large scale printing which is not possible with inorganic electronics. For spintronics usage, organic systems can support very large spin lifetimes since the mechanisms that limit it i.e. spin-orbit interaction and the hyperfine interaction are expected to be small [8].

Graphene consists of a single planar sheet of carbon atoms tightly packed in a hexagonal lattice. Fermions in such a symmetry interact in a way that their behavior effectively follows the relativistic Dirac equation. Resulting conduction and valence bands have zero band gap conical spectrum and touch each other at zero charge carrier density so called Dirac points (see figure 1). One immediate consequence of the linear dispersion is that carriers become massless. Despite it being the thinnest known crystal, it is the strongest material ever measured. Its mobility can reach up to $2 \times 10^5 cm^2 V^{-1} s^{-1}$ at room temperature, even more than that of Silver and can sustain current densities six orders of magnitude higher than that of Copper. It shows record thermal conductivity and stiffness, is impermeable and inert to most of gases and stable even till $500^o C$ in air. These properties have attracted huge interest in the possible implementation of graphene in a myriad of devices, eg. high-speed and radio frequency digital devices, thermally and electrically conductive reinforced composites, sensors, and transparent electrodes for displays and solar cells.

The present era of digital electronics however demands an impressive on/off ratio in conductance. Due to zero band gap and presence of minimum conductivity in graphene, the former remains far from realization. What is needed is a control to completely turn on/off the charge density on demand. Creation of a band gap is therefore essential. One way to achieve this is by geometrical confinement using ribbons and quantum dots. But the electronic transport here shows large sensitivities to edge profiles. Fabrication of such devices with desired edge profile has been problematic so far and its limitations with respect to reliability, scalability and damage can not be ruled out [2].

We propose to experimentally realize the geometrical confinement of graphene ribbons and dots by patterning, not the graphene, but the substrate over which it
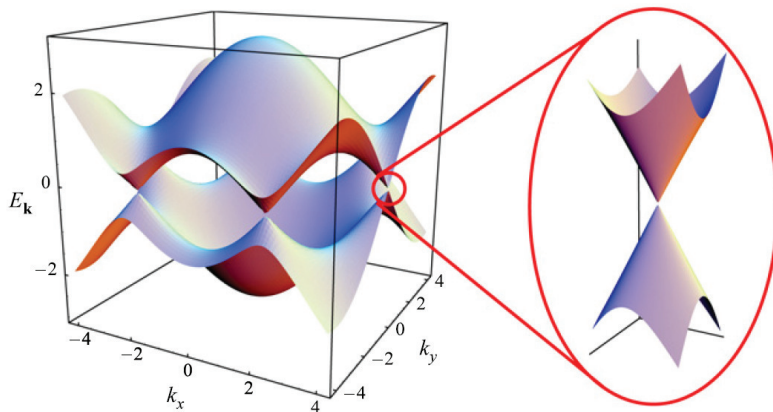
Figure 1: Band structure of gapless graphene. Conduction band and valence band meet each other at charge neutrality points. An enlarged image near these corners shows a Dirac cone with linear dispersion [10].

lies on [2]. This will involve engineering of the substrate to generate local strain in the graphene lattice. This local anisotropy will change the in-plane hopping amplitudes, eventually creating a band gap in the energy spectrum while still preserving the graphene strip. This focus of combining elastic properties and electronic transport will prove remarkable. Clearly, in this era of low power consumption, we do not want to control the device characteristics by any extra electric or magnetic field. Geim, Nobel laureate in physics 2010, rightly wrote the following in a review article [9] that "Research on graphene's electronic properties is now matured but is unlikely to start fading any time soon, especially because of the virtually unexplored opportunity to control quantum transport by strain engineering and various structural modifications."

8.1 Energy gap in graphene

Achieving an energy gap in graphene will be the foremost important goal of this research proposal. Theoretical predictions suggest that there are two main ways in which a band gap (E_G) can be created in graphene. A unit cell of graphene has two sublattices A and B which are chemically equivalent though different on symmetry [10]. The band structure correspondingly has conduction band and valence band that intersect each other at two inequivalent momentum K and K' points (Dirac points). The first way uses the inter-Dirac points hybridization (2a) and requires translational symmetry breaking [4]. This points out at reconstruction of sublattices on the substrate. This however has not been possible for many conventional substrates since the large scattering wavevector which is required to mix K and K' [4] is generally much longer than the reciprocal lattice vectors of reconstructed lattice. An Alternative approach to achieve inter-Dirac interaction is through impurity scattering and will strongly depend on the impurity concentration. Again this has been shown that energy gaps induced by underlying substrate did not change with impurity concentration [4] proving the lesser magnitude of this control.

The second way to create a band gap is by breaking A, B sublattice symmetry. The band structure here changes by rehybridizing valence and conduction band states present with the same Dirac point (K or K'). It therefore results in breaking of six-fold rotational symmetry and hence gap openings near each Dirac points (figure 2b). Such interaction can be achieved first by fabricating graphene super-structures like quantum dots [11], graphene ribbons [12] and devices from single and bilayer
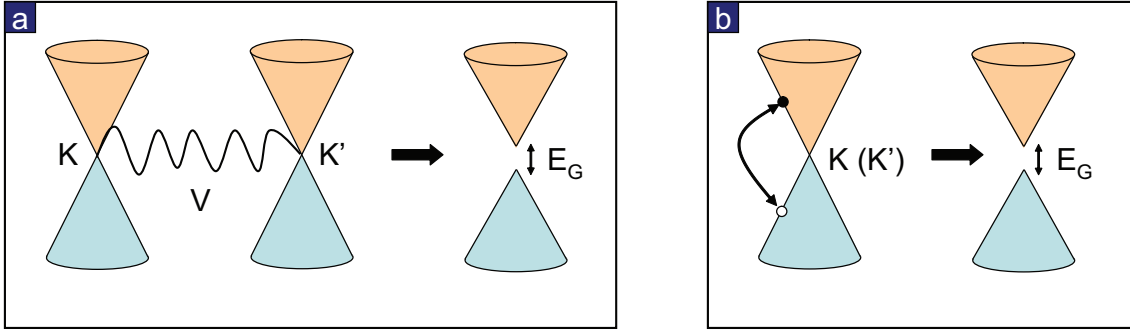
Figure 2: Two ways to create a band gap in graphene, first (a) by inter Dirac points hybridization effected by translational symmetry breaking, second (b) by rehybridization of conduction and valence band states associated with the same Dirac point brought about by breaking A, B sublattice symmetry.

graphene regions [13]. Alternatively, it can be induced by the substrate. The band gap reported for epitaxially grown graphene on SiC E_G was found to be $\approx 0.26eV$ [4]. However, one inherent problem here is the electron doping from the substrate and Fermi level always lie on the top of the gap. To make it a real semiconductor, one will need to apply backgate to keep Fermi level in valence band and below the gap. For a lattice matched case of Boron Nitride (BN) substrate [14], E_G was much lesser $\approx 53meV$. Here, the symmetry breaks since the most stable configuration has one carbon on the top of Boron atom and other centered on the BN ring.

Studies on substrate induced asymmetry in graphene are discouraged by the fact that this requires search for a suitable candidate that can create an appreciable bandgap without seriously disturbing the pseudo-relativistic nature of carriers and its high mobility. Graphene however shows a great sensitivity to type of substrates one chooses. Consequently, energy gap induced by a pristine susbtrate has not been difficult to realize so far. We therefore turn to engineering of substrates, which is easier, more controlled and transferable to suitable substrates. Besides, graphene strip is preserved in the fabrication process of the devices. This also poses minimum risk to contamination or reliability. Easier scalability of the effects directly from substrates will also allow to manipulate the electronic structure without the need to fabricate graphene superstructures. In short, once strain effects are realized, the substrates can be patterned with much ease in state of art systems and one would only need to transfer graphene on top of it.

9 Research Programme

9.1 Strain engineering of electronic structure in graphene

In principle, a presence of bulk spectral gap in graphene will work wonders. But, the effect of strain in graphene to induce a bulk spectral gap (figure 3a) is not really clear. Ni et al [15] showed using ultra sensitive Raman spectroscopy that E_G depends linearly on uniaxial strain (created by stretching a flexible polyethylene terephalate substrate over which graphene was deposited) and can reach 300 meV at 1% strain. The observed effect was attributed to breaking of sublattice symmetry under uniaxial strain using first principle electronic calculations. Further theoretical
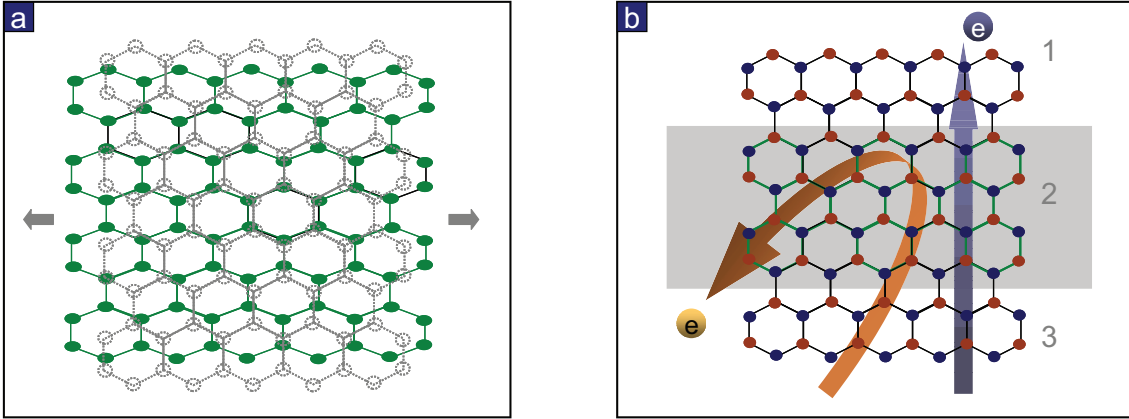
Figure 3: (a) A bulk spectral gap in graphene can be induced by an uniaxial strain ($> 20\%$ threshold value which is rather large and risks damage to graphene) along zigzag edge. Dashed and solid figures represent unstrained and strained graphene. (b) A local strain induced perturbed hopping in shaded region (2) forms a potential well with unperturbed parts (1,3) of graphene. This can select transmission of electrons only with certain energies and momentum, similar to an optical system of wavelength filtering with materials of different refractive indices.

works, that invoked pure tight binding model, on contrast suggest that uniaxial strain profile actually merges inequivalent K and K' points [6] and creates a band gap only above a threshhold value of 20% strain. Its magnitude, in addition, depends on the direction of applied tension such that strain along zigzag direction is more effective than that along armchair edges. More theoretical calculations [16] and no experimental reproducibility evidences [17] tend to support that band structure of graphene is rather robust and topologically protected against small perturbations (1% strain). Clearly 20% strain does not seem an option as it is close to critical straining and damaging of the material.

Due to limitations in bulk spectral gap, we propose to create local profiles of strain experimentally that can achieve all characteristics of a band gap [2]. In this case, a local strain can be translated into perturbations of nearest-neighbor hopping amplitudes. As shown in the figure 3b , a local shaded region has different hopping amplitude than unshaded part of graphene. This effectively gives rise to a tunneling barrier-like perturbation in the middle of a bulk graphene. Depending on the strength of perturbed hopping, tunneling transmission can be completely suppressed for certain momentum sectors and energy bands. Consequently, even in absence of a bulk spectral gap, this gap marked by the overlap of Fermi surfaces of channels acts as the bottle neck for transport. So if they do not overlap, there is no phase space for transmission of carriers through the shaded strained region. This is analogous to optical wavelength band filtering using materials with different refractive indices. Beside creating band gap properties, this effect will be instrumental in electron beam collimation and lensing [2]. Ultimately what is needed, and presents us with the challenge is a suitable geometrical configuration of such strain induced barriers that can amplify the filtering of energy of incoming electrons.

Further, we want to investigate effects of strain on spin transport in graphene. So far, there has not been any theoretical reports or experimental evidences studying this effect. Ever since Datta-Das sFET was proposed [18], there has been much
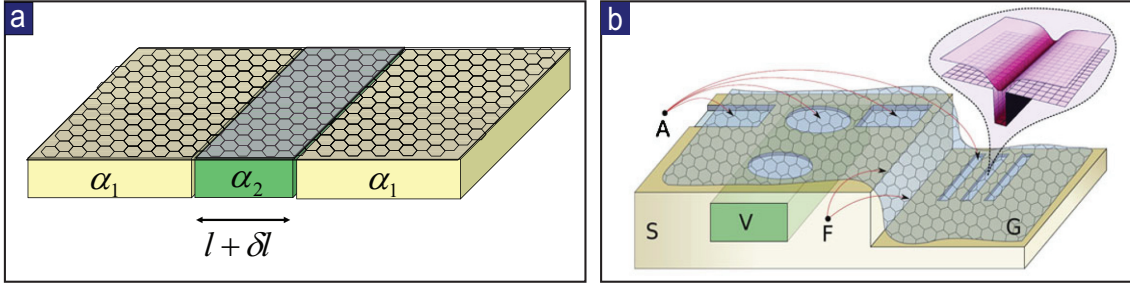
Figure 4: we propose to realize local strain effect in the substrates upon which graphene rests by two ways (a) Using different substrates with different thermal coefficients α_i, A temperature change will cause different expansions in two materials and create a local strain. (b) Using the same substrate with folds (F), trenches, dots and wells (A) [2] to change the In plane hopping amplitudes anisotropically.

effort in realizing this in systems which potentially support big spin lifetimes. Small spin orbit coupling in graphene indeed increases spin life times, but poses a big challenge for creation of Rashba spin splitting required for the realization of sFET. We propose that local strains may be the solution. Theoretical works suggest that gauge fields induced by strain further give rise to an uniform magnetic fields whose amplitudes are of $\approx 10T$. We propose to tailor and manipulate such fields to control spin transport.

9.2 Summary of the proposal

This research proposal aims to realize a band gap in graphene by strain engineering of the substrate over which it lies. Two fundamental questions in this respect are

- Theoretical studies show that local strain effects can collimate electrons with energy selectivity [2] and create uniform magnetic field [3] in graphene. Is it possible to use these properties experimentally in creating characteristics of band gap and realization of sFET respectively?

- Is it possible to achieve the former without disturbing other features of graphene like its pseudo relativistic carriers, noble reactivity and high mobility?

The research will hence involve nano-scale and low temperature investigation of electronic and magnetic property changes coming from strain and its optimization in various substrates' geometry.

9.3 Methods

Foundation: The current research will be continuation of my master thesis work on graphene. Here, I have studied both linear and non-linear effects of interactions between charge transport and spin, heat diffusion. Accordingly, I have demonstrated both theoretically and experimentally physics of interactions and its changes with electronic structures and doping. My proposal will benefit from active research on charge transport on different substrates such as Silicon oxide, Silicon carbide

and Boron Nitride running in my present group. The group had laid down foundations of spintronics in graphene and metal systems [19, 8]. Further, our group has successfully created a band-gap in graphene using chemical treatment [paper in preparation] and demonstrated quantized conductance in geometrical nanoconstrictions [20]. These expertise that stayed in the group together with my fabrication and measurements skills learned during my thesis are going to be useful in development, measurement and study of proposed effect.

Proposed sample fabrication: We propose to experimentally realize characteristics of a band gap using selective transmission of electrons with certain energy using local strain. Local strain could be achieved in two ways. Firstly, using a homogeneous substrate upon which graphene rests on, we will engineer grooves, wells, steps, creases, folds etc. on it [2]. Secondly, using two substrates with different thermal coefficients. Under a temperature change, two will expand differently causing a local strain near the junctions and altering the graphene over which it lies. These are listed in figure 4.

Proposed studies Before fabricating any graphene based FET, we will employ Raman spectroscopy on local graphene parts to study changes in electronic properties induced by strain. This will involve identifying characteristic Raman modes and its behavioral changes versus strain profiles. A first principle theory will also be developed to back up the experimental observations. Charge and spin transport measurements will be similar to that for a standard graphene FET with a highly doped Silicon backgate to control charge density on it and with source and drain electrodes to measure the transfer characteristics. A more sophisticated FET will involve use of a side gate and top gate to locally influence carrier densities. This will also help to make p-n junctions in our devices. Temperature dependent studies will form an important part of the project to only focus on a transport not limited by thermal and impurity scatterings. Studies on spin transports on similar substrate will depend on the success of charge transport measurements and will focus mainly on exploiting strain induced gauge fields [3] that effectively give rise to a uniform magnetic field.

9.4   Plan of work

Year 1   Preparation of substrates with well defined geometrical patterns grooves, folds etc. and its characterization with AFM and SEM studies. Transfer/deposition of graphene on these substrates and optimization of the fabrication methods. First principle calculation of expected results for particular geometry.

Year 2   Raman study of change on electronic structure of graphene caused by strain induced asymmetry. Further optimization of local strain effects. Fabrication of graphene FETs using the patterned substrates.

Year 3   Measurements and analysis of the charge transport measurements. Measurements on electron beam collimation using series of local substrates, similar to stacking optical materials with different refractive indices and measuring transmission of light through it.

Year 4   Fabrication of FET for spin transport measurements in graphene on strained substrates. Analysis and more investigation into strain engineering of electronic structure.

9.5   Infrastructure and Collaborations

For the above mentioned project, important fabricating and characterizing facilities like Electron beam lithography, Scanning electron microscopy, Atomic force microscopy and clean room processings like spin coating, liftoff and etching will be used. These are readily available in our group and I have used them during my master thesis.

Groups at Zernike institute are dynamic with respect to collaborating. For my project, we will collaborate with optical condensed matter physics group (group leader: Prof. Paul van Loosdrecht) for the use of Raman spectroscopy setup. This will be important to characterize the thickness of graphene and its electronic properties. For growth of desired patterns and study of surface modes arising from local strain, we will collaborate with Petra Rudolf's group for surface science. Moreover, if needed, we may collaborate with group of theoretical condensed matter physics group for first principle studies of strain.

9.6   Application perspectives in industry, other disciplines or society

Achieving a large on/off ratio of electron transport in graphene will open the gates for an era of all graphene made organic electronics, i.e. high-speed and radio frequency digital devices, thermally and electrically conductive reinforced composites, sensors, and transparent electrodes for displays, solar cells, electron beam lenses etc. This is because graphene now can be made to act like a metal or semiconductor at will. The strain effect is also important for fundamental studies of graphene. A zero field quantum Hall effect can be observed induced by strain gauge fields [3]. This holds promise in making of a ferromagnetic semiconductor and experimental realization spin FET with extremely low power consumption. Further, such a study will also investigate the fundamental aspects of edges and valley degeneracy.

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