Applications of graphene in nanotechnology : 1D diffusion, current drag and nanoelectrodes

Vrbica, S.

Citation

Vrbica, S. (2018, December 12). *Applications of graphene in nanotechnology : 1D diffusion, current drag and nanoelectrodes*. *Casimir PhD Series*. Retrieved from https://hdl.handle.net/1887/68258

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Issue Date: 2018-12-12

1

INTRODUCTION

A poet once said, "The whole universe is in a glass of wine." We will probably never know in what sense he meant that, for poets do not write to be understood. But it is true that if we look at a glass of wine closely enough, we see the entire universe.

R. P. Feynman [1]

The surface of the wine in a glass appears calm to the naked eye. However, if we magnify it a billion times, the world of tiny particles will emerge and we will see all kinds of atoms and molecules moving around. The world down there, at the atomic scale, is quite different from what we experience in our macroworld. If we try to apply classical mechanics to it, it will lead to contradictions between theory and experiment. Atomic phenomena are, instead, governed by the laws of quantum mechanics which has a lot of peculiar implications. It unifies the idea of particles and waves into one [2], and introduces the concept of the wave function. Events that are forbidden in classical mechanics have a finite probability of happening in quantum mechanics. One such example is the phenomenon of quantum tunneling, in which a particle overcomes a potential barrier that classically would not be allowed. This concept was utilized in 1981 to image single atoms and molecules with a technique known as scanning tunneling microscopy (STM) [3, 4]. This was the birth of nanotechnology - engineering, technology and science carried out at the nanoscale. Studying properties of matter at nanoscale can offer insights into fundamental principles and answer many important questions. Questions of this kind that we will be addressing in this thesis are "what is the exact nature of electromigration?" or "can a liquid flowing over the surface of a conductor generate a voltage?". Answers to these questions will not only satisfy scientific curiosity, they will pave the way for inventions such as the creation of nanoelectrodes necessary for transport experiments through nanostructures, transport of nanomaterial or harvesting of electric power. Other practical applications may take advantage of enhanced properties of materials at the nanoscale (higher strength, lighter weight, better conductivity, atomic thickness, etc.) One of the most attractive approaches at this day and age is arguably the field of molecular electronics, which aims to incorporate molecular components as elements in electronic devices. Since the 1999 silicon industry has reduced channel length of transistor from 800 nm to 10 nm. The use of nanometer-sized molecules is therefore very appealing for electronic purposes. In 1974 a molecule was proposed that could work as a rectifier for the current when contacted by two electrodes [5]. Given the hard experimental task of fabricating molecular-scale electrodes, the first direct electrical measurement of a single molecule arrived only two decades later, when a current was sent through a single C_{60} molecule using an STM in UHV [6]. In 2000 researchers used the electromigration technique to sandwich the same molecule between two gold electrodes [7]. By applying a voltage on a third gate, the current between the source and the drain could be regulated, which resulted in the first single-molecule transistor. Applications could go as far as designing current-driven molecular motors or light-emitting gas sensors.

Advances in techniques for probing single molecules will also have a profound impact in the field of DNA sequencing. The sequence of the nucleobases in DNA encodes the genetic information, necessary for many applications in medicine, biology and other life sciences. With the motivation to find an efficient and inexpensive method for the whole genome analysis, the field of nanopore research has gained a lot of interest in the past two decades. In 1996, Kasianowicz *et al.* [8] first demonstrated translocation of single-stranded DNA molecules through a biological nanopore. DNA is a highly charged molecule, so it can be driven in a solution through the nanopore in a head-to-tail fashion by an electric field. When DNA enters the nanopore, the ionic current is reduced because the liquid volume that carries the ionic current is partially blocked by the translocating DNA. If the passage of each nucleotide of DNA produces a characteristic modulation of the ionic current, the sequence of current modulations would reflect the sequence of bases in DNA. However, single nucleotide discrimination could not be achieved with this technique because the ion-current blockades were found to be the consequence of several nucleotides (rather than a single nucleotide). Great effort has been made to find alternative materials to obtain thinner solid-state nanopores (such as SiN and SiO_2) with higher spatial resolution, ultimately reaching single-base resolution. Graphene is considered to be the most promising candidate, as the membrane thickness (0.34 nm) is comparable to the height of a nucleotide, which makes single nucleotide discrimination possible [9]. Initial experiments [10, 11] provided proof of concept that it is possible to realize and use graphene nanopores for DNA translocation. Recently, it was proposed that characterization of single nucleotides in DNA could be done via transverse electron tunneling through a nanogap between two graphene electrodes [12].

Despite significant progress during the last three decades, nanometer-scale electron transport still faces challenges. All current techniques for contacting molecules (STM, mechanically controllable break junction (lithographic and notched-wire), electromigration, ultra-high electron-beam lithography, focused ion-beam lithography, etc.) have some drawbacks. The biggest hindrance so far is the lack of reliable and easily reproducible way to create a gap between electrodes comparable to the size of the nanostructure itself.

1.1. OUTLINE OF THE THESIS

The initial motivation and the main aim of our research was electromigration at the atomic scale. Knowledge gained from such experiments would give clues to many unanswered questions about current-induced forces. Graphene on an insulating substrate was the first choice for the substrate material since the current would be confined within an atomic layer. Graphene on Si/SiO_2 that we initially used, however, came with a few limitations which inspired us to utilize graphene nanoribbons instead. Electromigration was also the motivation for the second part of the research presented in this thesis. The fact that drawing a droplet of ionic liquid along graphene induces a voltage [13] inspired us to ask the question: would it be possible to do the opposite? This approach required knowledge on adsorption of ions, formation of electric double layer and a pseudocapacitor, which was an incentive to expand the experiment and investigate voltages induced with several different types of ionic liquids. And as it often happens when doing scientific research, looking into certain problems sometimes leads to gaining knowledge (and interest) on concepts that are far from the initial objective. After doing many experiments with graphene, we were motivated to take it a step further and attempt to design atomically thin nanoelectrodes with a reproducible and reliable fabrication method. This project was particularly attractive in having a prospect for applications such as transport measurements on single molecules and sequencing of biopolymers.

The research in this thesis is accordingly split into three parts:

- **Chapter** 2 (*One-dimensional diffusion of Co adatoms on graphene nanoribbons*) focuses on the investigation of electromigration forces at the scale of single atoms. This is realised with Co adatoms on graphene nanoribbons (GNR) on a Au(111) substrate with the use of an STM technique. We find that the presence of a potential barrier at the edges of GNR confines Co adatoms to a GNR and provides a path for one-dimensional diffusion. We study current-induced migration of single Co adatoms on GNR and on Au(111), and look for evidence of directional asymmetry related to the presence of electromigration forces.

Comparison of Co migration on GNR and on Au(111), together with results from temperature-dependent diffusion measurements, gives information on relative diffusion barriers of the two substrates.

- **Chapter** 3 (*Inducing voltage by moving a droplet of liquid along graphene*) discusses the concept of an electrical double layer formed at the interface of a liquid and graphene on polyethylene terephthalate (PET), so-called "pseudocapacitor", which is responsible for a voltage signal induced in graphene when a droplet of liquid is set into motion. Experiments with different ionic liquids give information on the type of ions which dominantly adsorb to graphene. We find that certain types of ions adhere to graphene/PET so strongly that they leave the droplet and form a layer of charges on graphene. This is detected by the induced voltage signal when moving a droplet of distilled water along charged graphene surface. We find that the reason for this is the polarizability of water which has a large contribution to the voltage signal. Additionally, we attempt to induce motion of an ionic liquid droplet by applying a voltage across graphene, however no electromigration-induced motion of the droplet occurs. The reason lies in the additional layer of charges above the pseudocapacitor which neutralizes the charges, making the whole system neutral and unable to experience a net direct force. Our estimates show that the so-called *wind force* is much smaller than our detection limit.

- **Chapter** 4 (*Dynamic tunneling junction at the atomic intersection of two twisted graphene edges*) demonstrates a method for creating two atomically thin graphene electrodes on Si/SiO_2. All techniques used to characterize graphene edges (Raman spectroscopy, SEM, AFM and electrical measurements) unanimously confirm that graphene reaches up to the edge within the respective resolutions of each of the techniques. Using a modified STM and a twisted-sample approach, we created the first tunable tunneling nanogap between graphene electrodes. The nanogap size is detected with STM and can be tuned by moving the electrodes closer to each other by means of a piezo actuator. By bringing the crossed edges into contact we determine the single-atom contact resistance between the two graphene edges as 11 ± 3 kΩ, *i.e.* the quantum of resistance to within the experimental accuracy. This technique could, in principle, be used to probe single molecules via transverse electron tunneling and also achieve resolution of a single nucleotide in a DNA strand.

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