Thesis of doctoral (PhD) dissertation:

Charge propagation in graphene nanosystems

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1. Introduction and objectives of the work

Graphene, a single layer of graphite, is made out of carbon atoms arranged on a honeycomb lattice. This two-dimensional (2D) material was first isolated in 2004 using a simple exfoliation technique of graphite [1]. It is remarkable that only six years after the first measurements the Nobel Prize in Physics 2010 was awarded jointly to Geim and Novoselov “for groundbreaking experiments regarding the two-dimensional material graphene”. Besides the interesting physical phenomena such as the anomalous quantum Hall effect, graphene has a great potential for industrial applications, e.g. in nanoelectronics, which explains the special attention to this new material. The mobility of the charge carriers can reach the 200,000 cm²/Vs value even at room temperature [2] which is two orders of magnitude higher than in silicon. This property may open a new way for the development of graphene-based nanoelectronics with high operating frequency and lower dissipation.

In order to use graphene for practical applications we need to develop different techniques which are able to produce macroscopic samples on an industrial scale. Nowadays, chemical vapor deposition (CVD) [3] is one of the most promising methods to produce macroscopic graphene samples. With this technique several research groups have demonstrated the scaling up of graphene production even to meter scale [4]. The disadvantage of the method comes from the quality of the samples. Due to the growing mechanism of the CVD process the graphene lattice breaks into many single crystal regions with grain boundaries (GBs) between the domains. Therefore, investigating GBs and understanding their effects on the charge transport in graphene plays a central role both in the theoretical and experimental graphene research [5]. Another important issue in nanoelectronics is that how a local electron source affects the charge spreading in a nanosystem. This situation occurs in several experimental measurements where the nanosystem is locally contacted with electrodes. A similar geometrical arrangement is realized during the scanning tunneling microscope (STM) imaging where the electrons tunnel locally from an atomically sharp STM tip onto the graphene surface.

The above mentioned different types of defects make physical phenomena in graphene rather complex. The aim of my PhD thesis was to better understand the transport- and electronic properties of graphene containing defects with the help of wave packet dynamical (WPD) simulations and numerical electronic structure calculations.
2. **Applied methods**

Wave packet dynamics (WPD) is an effective method to investigate electron propagation in nanostructures [6]. The time-dependent wave function is computed from the time-dependent 3D Schrödinger equation. From the calculated wave function all measurable quantities can be obtained, such as the probability density and the probability current density which are significant in the study of transport phenomenon. This conceptionally simple method contains no perturbative approximation but includes all interference and multiple scattering effects which can be important in nanosystems. Furthermore, the visualization of the spreading wave packet gives a deep insight into the dynamics of the electrons and identifies the main scattering centers in complex systems. Compared to other transport methods, WPD is able to handle systems containing a large number of C atoms (more than 10,000) where *ab-initio* calculations are difficult to realize.

In order to better understand the transport mechanism I also applied tight-binding and *ab-initio* electronic structure calculations for the investigated systems. In the case of larger systems containing several defects the local density of states (LDOS) has been computed with the recursion method [7] within the tight-binding approximation. In order to investigate the electronic structure of the defects more precisely, I also performed DFT calculations where our computational resources allowed it. Comparing the results of these different methods proved to be fruitful in the interpretation of the numerical transport calculations.

3. **Results and conclusions**

By modeling the scanning tunneling microscope (STM) measurements of graphene I have examined the time development of the WP injected from a simulated STM tip onto the graphene surface. The results have shown anisotropic charge spreading on the graphene in the energy region far from the Femi energy and also near the Fermi energy. I showed that the anisotropy along the zigzag directions at high energy levels follows from the graphene band structure, while the anisotropy along the armchair directions at the Fermi-energy is related to the combined geometrical and electronic structure effects of the STM tip–graphene system. Utilizing these anisotropic conduction effects and patterning the graphene sheet into specific ribbons and junctions may open further opportunities for graphene-based nanoelectronic devices.

I have investigated different graphene grain boundaries (GBs) and their effects on the electronic and transport properties. In order to generate model geometries for different types
of GBs we developed a Monte-Carlo based technique. My results highlight the significance of the atomic-scale disorder inside the GBs, especially the role of the twofold coordinated C atoms and the four membered carbon rings which considerably diminish the electron transmission through the GBs. In contrast, I have found a high transparency for GBs containing only pentagons and heptagons, independently of their detailed configuration. The better understanding of these transport mechanisms is essential for the development of high mobility graphene-based nanoelectronics.

Finally, I performed DFT calculations to study the electronic and structural properties of GBs. I have shown that GBs containing two-coordinated C atoms have density of states peaks around the Fermi level compared to GBs containing only pentagons and heptagons. These localized states, together with the finite curvature of the STM tip, cause that the individual atomic sites at the boundary cannot be distinguished in the STM images. These results are in good agreement with low temperature STM measurements of graphene prepared by chemical vapor deposition.

**Thesis statements**

I. **By using a variety of model potential within the framework of the wave packet dynamical method I have investigated the tunneling process which occurs during the STM imaging of graphene and its effect on the charge spreading on graphene surface [T1, T2].**

a. I have shown that both in the simple jellium potential model describing the geometrical effects of the STM tip and the graphene system, and in the local one-electron pseudopotential model where the electronic structure is taken into account, the tunneling is characterized by a selection process. During this process a part of the wave packet tunnels from the tip onto the graphene sheet then the majority of this part tunnels back into the tip. Only those part remaining on the sample can later spread on it. The selection process is determined by both geometrical and electronic structure effects of the system.

b. Wave packet dynamical calculations have revealed anisotropic charge spreading on the graphene surface. I showed that the anisotropy along the zigzag directions far from the Fermi energy follows from the graphene band structure, while the
anisotropy along the armchair directions at the Fermi-energy is related to the combined geometrical and electronic structure effects of the STM tip–graphene system.

c. I have shown that the initial symmetry of the different STM tip positions (twofold, threefold and sixfold symmetry) appears in the angular distributions of the probability current on the graphene surface at the Fermi energy while a background armchair sixfold symmetry specific to the graphene lattice is always present.

II. **I have studied the effect of different graphene grain boundaries on the electronic- and transport properties utilizing wave packet dynamical method and electronic structure calculations** [T3, T4].

a. I have demonstrated that the transmission values of periodical grain boundaries containing pentagons, heptagons and octagons around the Fermi energy are determined by the detailed atomic positions and the related electronic structure effects. In contrast, far from the Fermi energy where the electrons are spreading along the zigzag directions, the transmission is independent from the detailed atomic structure of the GB and depends only on the lattice mismatch of the two graphene grains.

b. I have shown that the grain boundaries containing only pentagons and heptagons and preserving the sp² lattice have a high transparency. This property is not affected considerably by the aperiodic structure or the non-rectilinear shape of the grain boundary.

c. I have demonstrated that in the case of disordered grain boundary containing two-coordinated C atoms and other structural defects, the transmission near the Fermi energy decreases by about 80% compared to the periodical grain boundary previously studied. I identified the four membered carbon rings and the vacancy type defects as main scattering centers which considerably diminish the electron transmission.
III. Applying density functional method I have modelled the atomic and electronic properties of grain boundaries and compared the results with low temperature STM measurements of graphene prepared by CVD [T5].

a. I have shown that GBs containing two-coordinated C atoms have density of states peaks around the Fermi energy. Our calculations revealed that in most cases both $sp^2$ and $p_z$ type states contribute to the formation of the peak close to the Fermi energy.

b. The different formation energies of the modelled grain boundaries were taken into account to calculate the statistical average of the DOS functions. This averaged DOS function was in good agreement with the scanning tunneling spectroscopy (STS) results measured on different grain boundaries.

c. The STM image of the modelled grain boundaries simulated by the Tersoff-Hamann approximation have shown that the increased STM current around the two-coordinated C atoms together with the finite curvature of the STM tip leads to the lack of atomic resolution on the disordered GB.

I. Publications related to the thesis:


II. Other papers:


References


