

**The fabrication and investigation of graphene nanostructures and
other two dimensional materials with scanning tunneling
microscopic methods**

PhD thesis booklet

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Introduction and motivation

We live in a time when science and industry are developing at a rapid pace, new materials and technologies are emerging quickly. One of these new materials is graphene that was discovered in 2004. This one atomic layer thin material was isolated from bulk graphite crystal. Graphene is characterized by outstanding electronic [Neto, 2009] mechanical [Lee, 2008] and optical [Nair, 2008] properties, and a series of novel phenomena can be observed in it [Kim, 2011]. Several possible applications have been proposed for graphene, such as composite materials [Stankovich, 2006], transparent and flexible electrodes [Kim, 2009], and it can also be used combined with silicon based technologies to develop faster electronic devices with low power consumption.

In order to use graphene in digital electronics, first we have to transform this (semi-) metallic material, which has no bandgap, into a semiconductor. One can open a gap exploiting the quantum confinement phenomenon. In order to do so, we have to confine the charge carriers of the 2D graphene sheet into stripes of nanometer width, with edges running along a chosen direction of the graphene lattice. This can be achieved by cutting few nanometers wide nanoribbons out of the two-dimensional graphene sheet. Theoretical calculations predict that the properties of graphene nanoribbons are strongly dependent on both the width of the ribbon and the crystallographic orientation of the ribbon edges [Fujita, 1996]. The quality of the ribbon edges is also important, as the disorder on the edges can substantially alter the size of the bandgap, and it can also significantly degrade the electronic quality of the devices.

Several approaches have been proposed to define graphene nanoribbons [Wang, 2014], but for a long time it remained challenging to prepare nanoribbons with controlled width and crystallographic edge orientation, as well as sufficiently smooth edges. Researchers at the MTA EK MFA Nanostructures Department have developed such a nanofabrication method, based on Scanning Tunneling Lithography [Tapasztó, 2008]. They used graphite substrate, which due to the strong interaction with the nanoribbons makes it difficult to investigate their properties. In my PhD work, I have fabricated graphene nanoribbons on gold substrate by Scanning Tunneling Lithography. The gold substrate made it possible to systematically investigate the electronic properties of the fabricated graphene nanoribbons as a function of their atomic structure.

After the success of graphene, the research interest also shifted towards isolating monolayers from several other layered materials. The isolation of single layers has been

successful in several cases, such as for black phosphorus, hexagonal boron-nitride, and various transition metal dichalcogenides (TMDCs). The TMDCs show diverse physical properties even in their bulk forms, there are semiconductors (MoS₂, WSe₂), semi-metals (TiS₂, TiSe₂) or superconductors (NbS₂, NbSe₂) amongst them. The monolayer TMDCs are expected to show diverse properties as well, with the promise of making our electronic devices even more efficient. In my PhD work I have investigated the atomic structure of several TMDC monolayers mainly by Scanning Tunneling Microscopy (STM).

Objectives

The main objective of my PhD work was to systematically investigate the theoretically predicted dependence of the electronic band structure of graphene nanoribbons on their atomic structure (width and edge orientation). These results can be used to gain a deeper understanding of the physics of graphene nanoribbons; furthermore, they enable the engineering of the electronic properties (band gap) of the nanoribbons over a wide range by designing their geometry. This could serve as the basis of future nanoelectronic applications of graphene. In my PhD work I have fabricated graphene nanoribbons with nanometer precision and well-defined crystallographic orientation by using the Scanning Tunneling Lithography method, and investigated their electronic structure by Scanning Tunneling Spectroscopy (STS) to establish the atomic-electronic structure correlation.

The method used for the investigations of graphene can also be employed for other two-dimensional materials. The other important aim of my PhD work was to reveal the atomic scale defect structure of MoS₂ monolayers by STM measurements, as MoS₂ is the most intensely investigated member of the 2D TMDC crystals. To achieve this, I also had to develop an exfoliation method capable of yielding MoS₂ monolayers of high crystalline quality and with sufficiently large lateral dimensions to enable their STM investigations. In stark contrast to graphene, in case of MoS₂ I have observed a substantial concentration of point defects in the atomic structure, significantly altering its properties.

Methods

I have mainly used Scanning Tunneling Microscopy to investigate the structure of graphene nanostructures and MoS₂ monolayers. STM measurements enabled resolving the atomic structure of 2D crystals, as well as to investigate their electronic properties by Scanning Tunneling Spectroscopy. In the lithography mode it is also possible to define (cut)

graphene nanostructures with close to atomic precision. In this mode, instead of imaging, the tunneling current between the STM tip and sample is employed to activate the highly local chemical etching of the sample. This method is the most precise nanolithographic method available for the fabrication of nanostructures from 2D materials even today.

New scientific results

- 1) I have defined graphene nanoribbons with armchair edges and various widths, in the 3 - 10 nm range, using Scanning Tunneling Lithography into chemical vapor deposition grown graphene sheets transferred to Au (111) substrates. The results provide the first systematic experimental validation for the dependence of the quantum confinement induced band gap on the width of armchair graphene nanoribbon. The measurements show excellent fit to the values given by first-principles theoretical calculations.

These results are published in [T1], [T2].

- 2) I have defined graphene nanoribbons with zigzag edge orientation and various widths by Scanning Tunneling Lithography on Au (111) substrates. Scanning Tunneling Spectroscopy measurements revealed a sharp semiconductor-metal transition as a function of the ribbon width. Nanoribbons narrower than 7 nanometers display a band gap slightly varying as a function of ribbon width. By contrast, zigzag graphene nanoribbons wider than 8 nanometers show metallic behavior.

Theoretical calculations based on the Hubbard model, including the effect of temperature and doping, reveal that the basis of the experimentally observed band gap opening in the narrow zigzag ribbons is the magnetic order appearing on the zigzag edges. The sharp semiconductor-metal transition corresponds to the transition from antiferromagnetic (semiconductor) to ferromagnetic (metallic) coupling between the opposite spin-polarized ribbon edges. These observations provide the first indirect but conclusive experimental evidence on the room temperature magnetic order appearing on the zigzag edges of graphene nanoribbons.

These results are published in [T2].

- 3) I have developed a new exfoliation method to produce MoS₂ monolayers based on the chemically enhanced adhesion between the sulfur atoms of the MoS₂ sheet and a gold surface. This method typically yields MoS₂ monolayers with lateral sizes in the range of hundreds of micrometers instead of few micrometers characteristic to the widely used scotch tape exfoliation method, originally developed for graphene. This new exfoliation method can be generally applied to isolate single layers of transition metal – sulfide, selenide and telluride crystals.

These results are published in [T3].

- 4) I have successfully imaged the atomic scale point defects of MoS₂ monolayers by Scanning Tunneling Microscopy. The native point defects of exfoliated MoS₂ monolayers can be identified as single sulfur atom vacancies based on the atomic resolution STM images. Comparing STM measurements and Density Functional Theory calculations enabled us to identify the two localized electronic defect states induced by sulfur vacancies within the band gap of 2D MoS₂ crystals. The two defect states display triangular and circular symmetries in the topographic STM images.

These results are published in [T4].

References

- [Neto, 2009] Neto, AH Castro, et al. "The electronic properties of graphene." *Reviews of modern physics* 81.1 (2009): 109.
- [Lee, 2008] Lee, Changgu, et al. "Measurement of the elastic properties and intrinsic strength of monolayer graphene." *science* 321.5887 (2008): 385-388.
- [Nair, 2008] Nair, R. R., et al. "Fine structure constant defines visual transparency of graphene." *Science* 320.5881 (2008): 1308-1308.
- [Kim, 2011] Kim, Kinam, et al. "A role for graphene in silicon-based semiconductor devices." *Nature* 479.7373 (2011): 338-344.
- [Stankovich, 2006] Stankovich, Sasha, et al. "Graphene-based composite materials." *nature* 442.7100 (2006): 282-286.

- [Kim, 2009] Kim, Keun Soo, et al. "Large-scale pattern growth of graphene films for stretchable transparent electrodes." *nature* 457.7230 (2009): 706-710.
- [Fujita, 1996] Fujita, Mitsutaka, et al. "Peculiar localized state at zigzag graphite edge." *Journal of the Physical Society of Japan* 65.7 (1996): 1920-1923.
- [Wang, 2014] Wang, Xinran, and Yi Shi. "Fabrication Techniques of Graphene Nanostructures." (2014): 1-30.
- [Tapasztó, 2008] Tapasztó, Levente, et al. "Tailoring the atomic structure of graphene nanoribbons by scanning tunneling microscope lithography." *Nature nanotechnology* 3.7 (2008): 397-401.

Publications related to thesis statements

- [T1] P. Nemes-Incze, L. Tapasztó, G. Zs. Magda, Z. Osváth, G. Dobrik, X. Jin, C. Hwang, L. P. Biró: Graphene nanoribbons with zigzag and armchair edges prepared by scanning tunneling microscope lithography on gold substrates, *Applied Surface Science*, **291**, 48-52, (2014)
- [T2] G. Zs. Magda, X. Jin, I. Hagymási, P. Vancsó, Z. Osváth, P. Nemes-Incze, C. Hwang, L. P. Biró, L. Tapasztó: Room-temperature magnetic order on zigzag edges of narrow graphene nanoribbons, *Nature*, **514**, 608–611 (2014)
- [T3] G. Zs. Magda, J. Pető, G. Dobrik, C. Hwang, L. P. Biró, L. Tapasztó: Exfoliation of large-area transition metal chalcogenide single layers, *Scientific Reports*, **5**, 14714 (2015)
- [T4] P. Vancsó, G. Z. Magda, J. Pető, J. Y. Noh, Y. S. Kim, C. Hwang, L. P. Biró, L. Tapasztó: The intrinsic defect structure of exfoliated MoS₂ single layers revealed by Scanning Tunneling Microscopy, *Scientific Reports*, **6**. (2016)

Other publications

5. P. Nemes-Incze, G. Magda, K. Kamarás, L. P. Biró: Crystallographically selective nanopatterning of graphene on SiO₂, *Nano Research*, **3**(2), 110-116 (2010)

6. P. Nemes-Incze, G. Magda, K. Kamarás, L. P. Biró: Crystallographic orientation dependent etching of graphene layers, *Physica Status Solidi (c)*, **7**(3-4), 1241-1245 (2010)
7. P. Süle, M. Szendrő, G. Z. Magda, C. Hwang, L. Tapasztó: Nanomesh type graphene superlattice formation on Au(111) substrate, *Nano Letters*, **15**(12), 8295-8299 (2015)
8. A. A. Koós, P. Vancsó, G. Z. Magda, Z. Osváth, K. Kertész, G. Dobrik, C. Hwang, L. Tapasztó, L. P. Biró: STM study of the MoS₂ flakes grown on graphite: A model system for atomically clean 2D heterostructure interfaces, *Carbon*, **105**, 408-415 (2016)

To date, the publication I co-authored were cited more than 300 times.