CHAPTER 4

Graphene and Quantum Dots

4.1 GRAPHENE NANOSTRUCTURES AND QUANTUM DOTS

This chapter describes the fabrication methods and experiments on graphene nanostructures and quantum dots, with focus on the role of edges and size quantization effects. Considerable interest in graphene is related to potential electronic applications, e.g., as transistors, transparent electrodes or photodetectors [52]. In the case of, e.g., switching transistor on and off, energy gap is needed to control the current. However, since graphene is a semiconductor with a zero-energy band gap and a minimum conductivity at the Dirac point, the current cannot be switched off.

Additionally, as a result of the Klein paradox, it is difficult to confine electrons by an electrostatic gate. The problem of zero-energy gap can be solved by reducing the lateral size of graphene. As a result of size quantization, an energy gap opens. Finite-size semi-metallic graphene becomes a semiconductor. Among graphene nanostructures, graphene ribbons (strips) and graphene quantum dots (islands) are of particular interest. Cutting graphene nanostructures out of graphene results in two types of edges, armchair and zigzag, as illustrated in Fig. 4.1. The graphene nanostructure can also be characterized by the sub lattice symmetry whether it is conserved or not. As we will show, both types of edge and presence or absence of sub lattice symmetry play an important role in determining electronic properties of graphene nanostructures.

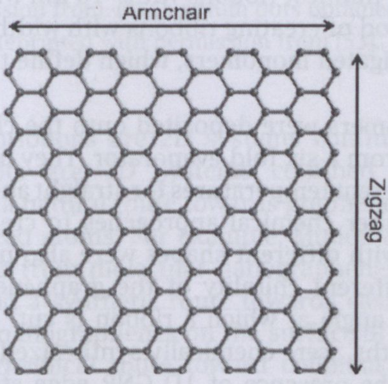

Fig. 4.1. Schematic illustration of two possible edge termination of graphene quantum dot [53].

4.1.1 Fabrication Methods

Graphene can be patterned into ribbons (GNR) with different widths by use of electron-beam lithography and an etching mask, as proposed by [53]. One starts from high-quality graphene obtained by mechanical exfoliation. Next, graphene is deposited onto heavily p-doped Si substrate covered by SiO_2 layer. Strips of graphene are covered by a protective etch mask made with cubical shaped molecules having one Si atom at each corner, with corners being linked via oxygen atoms, hydrogen forming silsesquioxane (HSQ). The unprotected graphene is etched away by the oxygen plasma. By using this technique, Kim's group was able to perform transport measurements on samples with widths from 20 to 500 nm and lengths ~1 μm. They noted that, transport properties strongly depend on both boundary scattering and trapped charges in the substrate.

A different method of creating ribbons was proposed by Jia *et al.* [54]. They used Joule heating and electron beam irradiation [55]. Samples were exposed to electron irradiation for 20 minute and heated by directional high electrical current. During the heating, carbon atoms on sharp edges evaporated and GNRs with smooth edges were created. Li *et al.* [56] chemically derived graphene nanoribbons with well-defined edges. The width of ribbons varied from ~10 to 50 nm with length ~1 μm. Graphene nanostructures with irregular shapes were also reported. They observed ribbons with 120◦ kink and zigzag edges. While the above work studied the thinnest ribbons with ~10 nm width, Cai et al. [57] have proposed a method of creating ribbons with width less than ~1 nm. They started from colligated monomers, which define the width of the ribbon.

These monomers were deposited onto the clean substrate surfaces by sublimation from a six fold evaporator. They used two step annealing process with different temperatures for straight and so called chevron type ribbons. Many other chemical approaches to create graphene quantum nanostructures with different shapes were also proposed [58]. Different shapes imply different chirality of the graphene nanoribbon. Chirality is related to the angle at which a ribbon is cut. GNRs, having different chirality and widths, were chemically synthesized by unzipping a carbon nanotube [59]. The presence of 1D GNR edge states was confirmed by using STM. The comparison of experimental results with the theoretical prediction based on the Hubbard model and Density Functional Theory (DFT) calculations provided an evidence for the formation of spin