

Graphene

L. Tetard^{1,2}

¹*Oak Ridge National Laboratory, Oak Ridge, TN 37831-6123 USA*

²*Department of Physics, University of Tennessee, Knoxville, TN 37996, USA*

(Dated: April 7, 2009)

'Diamond, graphite, charcoal, coke, lampblack, fossile fuels, carbon dioxide, DNA...'

Allotrope or not, carbon can be found in many forms (about 10 million compounds) and is a very abundant element in our lives. Its very complex behavior has been extensively studied throughout the years. If diamonds (from the greek adamas - the invincible) are believed to be of very ancient knowledge, graphite was not recognized until the 18th century. In modern times, Carbon has been identified as a key component of natural compounds (such as DNA) and processes (such as photosynthesis). Carbon also takes part in reactions in the universe (collisions of alpha particles or sun). As new center of interest emerge, nanoscale science took the step with respect to material properties. A myriad of studies elaborate on the properties of properties of carbon allotropes at the nanoscale (diamond nanorod is the hardest material reported, graphite is one of the softest). Surprisingly it was not until the 16th century that graphite was used in the form of a pencil, and not until the 18th century that it was identified as such. Important discoveries, including that of fullerenes (R. Curl, H. Kroto and R. Smalley in 1985) and carbon nanotubes (S. Iijima for first time fabrication in 1991) (see FIG.1), led to a new perception of the world and hopes for a revolution in the field of material science with important repercussions in the form of applications (in particular transistors). The impact of these discoveries on the scientific community was unprecedented. There is a simple explanation though: the amazing properties of the new carbon-based materials.

I. TWO-DIMENSIONAL FORM OF CARBON: MODEL

The 2D form of Carbon, the Graphene, has been used and studied as building block for carbon-based materials for decades (see FIG.1). This two dimensional configuration consists of a real atomic monolayer of carbon atoms organized into a honeycomb lattice. Indeed after the 90s, carbon allotropes were available in 3D, 1D and 0D. As Figure 1 depicts so well, graphene is clearly the building block of each of these other compounds (stack several graphene layers and you get graphite, roll a graphene layer along a longitudinal axis and you get a nanotube, wrap it as a ball and you get a fullerene). As a consequence, the

theory for graphene has been developed for sixty years, first to explain the properties of the other dimensionalities and later as a quantum electrodynamics model. Although graphene was known to exist in graphite, the scientific community believed for the longest time that it would be impossible to ever isolate a stable atomic monolayer of graphene. Landau and Peierls first formulated the arguments that 2D crystals were (thermodynamically) unstable and thus could not exist in the 1930s [1]. Thermal fluctuations were calculated to have a divergent contribution in the lower dimensional system and the resulting displacement would approach interatomic distances and push the system to change its state for finite temperature. Mermin further developed this theory in 1968 and also presented experimental results to validate the hypothesis [2].

II. TWO-DIMENSIONAL FORM OF CARBON: DISCOVERY OF GRAPHENE

Although graphene is the building block of graphite, a material studied for many years because of its interesting mechanical properties, it is only recently [3] that a free-standing stable atomic monolayer of carbon was observed experimentally, proving wrong the theories of Landau and Mermin [1, 2]. Despite all the skepticism numerous attempts to make graphene took place over the years. Chemical exfoliation was used for a long time with no success. It consists in inserting molecules to graphite by chemical treatment hoping that it would allow a separation of single monolayers of carbon held together by van der Waals forces. Novoselov et al. proved in their work published in Science in 2004 [3] that it was indeed possible to produce graphene in various environment (growth on monocrystals with matching lattice or on non-crystalline materials, in liquid suspension and free in the air). The ease of the approach (pretty crude) of their work accentuated the impact of their discovery. Graphene is a flat monolayer of carbon atoms organized into a honeycomb lattice (see FIG.1). All attempts of chemical preparation of graphene had failed until Novoselov and coworkers used micromechanical cleavage of graphite (a stable allotrope 3D form) to isolate monolayers of graphene. Isolation of the graphene layers would not suffice without a way to observe them. Eventhough it is possible to find in the literature AFM, SEM, TEM

of graphene flakes, these techniques are not suitable to both locate graphene and assess the thickness (number of layers) of the sample. By taking advantage of its optical properties it is possible to do so using a simple optical microscope. This method requires to use an extremely clean silicon wafer, covered of a controlled thickness of SiO_2 , to deposit the flakes from the tape. Interferences are responsible for high contrast of the graphene flake with respect to the substrate in this case. As a consequence, this is not trivial to achieve and all the parameters (thicknesses and cleanliness of the layers in particular) must fulfill strict requirements. For example, 315nm of SiO_2 instead of 300nm makes the graphene invisible [4]. Recently Raman spectroscopy was reported to allow the identification and help determine the number of layers of graphene present in the flake considered [?] (see FIG.2). In order to build up a 'library' (experimentally) for graphene it is crucial to have access to such characterization tools. The experimental discovery of graphene, which contradicted theory, led to a complete revolution in the physics world. Graphene is not only the thinnest material ever fabricated, its properties are incredible. We will present some current studies on the subject in the section 'Recent Measurements'. Before going into more details of recent papers, let's go through the major aspects of graphene.

Let us consider only crystal with high purity here. Such crystals are stable at room temperature. In addition interatomic bonds are very strong and flexible. It will accommodate important deformations before having to self-adjust its atoms to strain. These properties are expected to permit nice flexibility in the measurements. The crystalline structure of the layers (benzene rings) presents no defect. The first and most important element responsible for the excitement over graphene is the exceptional electronic properties of atomic monolayers of graphene. It has an amazingly good electrical conductivity. Surprisingly it never falls to zero independently of the concentration of charge carriers present (see literature details on Quantum Hall Effect) [5, 6]. Because of the quality of the crystal (partly) the scattering of the charge carriers is inexistent. We can make a simple analogy here: crossing an empty room is easy, while crossing a room full of people and furniture is a lot less efficient. In addition to their free displacement, charge carriers in graphene are known to be relativistic

particles (their speed is 1/300 of the speed of light). They are massless Dirac fermions. In such a case, Dirac equation replaces the famous Shrodinger equation to describe the behavior of the system, which obviously has important consequences in the properties of the material. It is in fact very rare to find an exception to the universality of the Shrodinger equation. Importantly, we point out that the periodic potential created by the honeycomb lattice of carbon atoms is the source of the unique behavior of the system; the carbon atom itself and the electrons moving around it do not have such (relativistic) behavior *a priori*. The system can be viewed as two sublattice of electrons and holes to form a new type of quasiparticles, which are relativistic at low energy (FIG.3). FIG.3 shows the particular energy bands of the structures associated with the sublattice (in blue), which happens to intersect at zero energy at K and K', the edges of the Brillouin Zone (BZ). In other words, the relation dispersion is linear at these particular points of the system: $E = \hbar v_f k$.

A conical section of the energy spectrum is associated with each of the carbon atom of the system (see yellow 3D representation in FIG.3 for one hexagon). Frequently the conical section is represented alone (see blue representation in FIG.3). This is true for $E \leq 1eV$. Quantum electrodynamics (QED) is on the verge of a new era. QED is not new. It was first formulated around the 1920s. The phenomena predicted by the theory required so far very high energies to eventually reach very weak responses of the systems. With graphene, QED is observed on the table of the lab, with low energies and relatively simple preparation and setups. It is an enormous step for the field of QED, which was confined to cosmology (black holes) and high-energy particle accelerators before this discovery.

FIG.4 gives a simple picture of the difference between classical and quantum mechanics as well as quantum electrodynamics. In general a charge carrier with low energy which faces a high potential can be treated classically and the model predicts that it will bounce back on the wall (represented on the top part of the figure by the green ball) because its energy is not sufficient to carry it over the top. Its is pretty easy to determine using conservation of energy. In the case of quantum mechanics, there is a non zero probability that the particle will be found on the other side of the potential-energy barrier. It is the tunnelling principle (middle section of FIG.4). The probability varies with the height and the width of the bar-

rier. In the case of QED, the relativistic particle will show perfect tunnelling regardless of the characteristics of the energy-barrier potential (bottom sketch in FIG.4) . This is called the Klein paradox [6].

III. LARGE SCALE GROWTH AND FABRICATION OF GRAPHENE-BASED DEVICES

An enormous amount of research went to carbon nanotubes since their discovery. This is an important base to consider for the advances to be made with graphene. One major drawback from nanotubes is the difficulty to reach industrial production (in terms of control, quantity and reproducibility). It is projected that it will be easier to overcome this issue with graphene far better. For this reason, today considerable efforts are put into fabrication of graphene. This kind of "easy fix" process of fabrication of graphene is well suited for research grade applications but does not meet the requirements for large-scale (eventually patterned) of commercial production. A important part of the present research focuses on this aspect. Different attempts aimed at producing macroscopic-scale graphene films have been reported in the recent literature. An interesting work by Kim K.S. et al. describe the problems associated with large-scale pattern growth and propose to use chemical vapor deposition of graphene films on thin nickel layers to circumvent these obstacles [7]. Unlike graphene layers chemically derived from graphite or graphene oxide, the deposited graphene layers exhibit the properties comparable to "ideal" (i.e. mechanically cleaved) graphene: low sheet resistance, optical transparency, large electron mobility at room temperature, and the half-integer quantum Hall effect. To date, no group has reported a successful fabrication of a graphene wafer of quality comparable to the ones described above. Despite different attempts, samples derived from the original method (mechanically cleaved layers) are still used in majority. The typical sizes of the 'sheets' have been increased to $100\mu\text{m}$ after optimizing the procedures. Four different techniques have been used to make graphene: (1) Chemical vapor deposition (CVD), (2) (mechanical) peel-off method, (3) Epitaxial growth on electrically insulating surfaces such as SiC and (4) colloidal suspensions [8]. Each of them

present advantages and disadvantages. For example, (2) is perfectly adapted for fundamental studies: it is "easy" to prepare and the quality of the small flakes of graphene is impressive. (1) provides larger samples but the quality of the layers cannot compete with the one in (2). The uniform growth of single layer graphene at a larger scale is still a challenge. Importantly, apart for the peel-off method, a complex chemistry problem is ahead of you if you want to make graphene layers at the macroscale.

Among various applications envisioned for this new material here are the main ones: mechanically improved composites, improved (faster) transistors, ... Each of the applications mentioned in the current literature reflects a particular property of graphene. It is very possible that after the first devices are fabricated, researchers will be able to simultaneously take advantage of the various interesting properties of the material. It is very difficult to predict as they are so many. Nevertheless, it is important to keep in mind that many obstacles are to be overcome before graphene expresses its full capacities. Similar to Carbon Nanotubes, the work ahead is exciting, but also very complex. The very unique properties of a monolayer of carbon compared to the superposition of several of these layers is very important, but could be detrimental if one does not find a way to make high (enough) quality graphene in homogeneous layer at large scale.

IV. RECENT MEASUREMENTS

It is impossible to be inclusive in this report, regarding all the publications related to graphene and its different aspects during the past year only. Here only a few measurements that were reported recently will be presented. Graphene is now believed to be a potential solution to the limits of the silicon-based semiconductors industry. Indeed, it is possible to increase the performance of silicon-based devices (Moore's law) by reducing their size, but the device will eventually reach the size of molecules and quantum effects will lead the process. The surface of bulk, crystalline semiconductors has profound consequences on the manufacturing of electronic devices [9]. Surface states are very important bulk materials. Similarly the edge structure plays a crucial role at the nanoscale. In the case of graphene, several

experimental results (on micrometer-size graphene sheets) are in contradiction with the predictions of the theory. In particular, for zigzag edge graphene calculations show a metallic behavior when experiments proves that it is in fact semiconductor. In addition experimental results now show that the electronic properties of graphene are independent of the crystallographic orientation of the system. It has been shown, by studying the edges effects on a nanometer size graphene sheet, that the metallic behavior can be observed for graphene quantum dots of 7-8nm. The metallic states decay into the graphene interior (1.0-1.2 nm decay length). These measurements are typically performed using a Ultra High Vacuum-STM. The results highlight the need for controlled fabrication of the future graphene-based nanodevices. There is an urgent need to investigate the potential applications and possibilities of quantum-based transistors. IBM launched a part of their research of graphene, after focusing on carbon nanotubes for many years. In a paper by Lin et al. this year [10], they report the fabrication and characterization of a top-gated graphene transistor operating at gigahertz frequencies (see FIG.5). Nanotubes has main restrictions that required a great amount of work in order to be circumvented: their high impedance and their properties at high frequencies. Graphene is not as complex in these matter, which make it easier to work with. Another important advantage to the eyes of the semiconductors industry is the fact that graphene is planar, and as a consequence more suitable to the existing processes and instruments for a eventual transition. The device exhibits interesting properties, and raises the expectation for graphene to be used in transistors. An important amount of work is necessary to find the best characterization tools to use for graphene. Low-energy electron diffraction (LEED), photon-electron spectroscopy, Raman spectroscopy and Angle-Resolved photon spectroscopy (ARPES) are possible solutions that could be useful for graphene [11] (see FIG.6). Finally, it might be interesting to note that one of the original papers about the isolation of graphene by micromechanical exfoliation was not restricted to carbon. Other crystals were reported for successful isolation of 2D structures. It is possible that interesting properties can be discovered for these compounds as well [4]. In addition, Elias et al. reported in Science [12] evidence for a new compound derived from graphene : Graphane (see FIG.7). In graphane a hydrogen atom is attached to each site of the graphene lattice. The

hybridization of C changes from sp^2 to sp^3 . It has for consequence to remove the π -band, responsible for the zero-gap. New applications could derive from this discovery. Clearly, the discovery of graphene is important, not only for the new property of the material itself, but also for the ideas that could derive from this new area of 2D-materials, and how it could shine light on other materials.

V. CONCLUSION

Who would have thought that such beautiful physics was contained in a simple pencil? Graphene is one of the hottest new material in physics today. Although it is still too early to predict its future, the purity of the atomic monolayer is such that beautiful fundamental physics will continue to be observed. Its commercial aspect will only be made possible by the development of large scale processes for graphene wafers or sheets. To date, graphene is probably the most expensive material to produce (1000 dollars for 100 microns). Nevertheless beautiful fundamental physics has been and will be studied thanks to this discovery. The remarkable properties of graphene, such as its Young's modulus (of around 1100 GPa), its thermal conductivity (of around 5000 W/mK), the mobility of its charge carriers (200 000 cm^2/Vs) and a high predicted specific surface area, together with the exotic transport phenomena it exhibits make it a serious candidate for numerous future studies. It is difficult to predict exactly the future of this material, but one can expect to see further research in QED, transistor-based devices, material sciences... This literature research turned out to be a very good source of useful information and learning.

-
- [1] Landau, L.D. *Phys. Z. Sowjet.* **11**, 26 (1937).
- [2] Mermin, N.D. *Phys. Rev.* **176**, 1 (1968).
- [3] Novoselov, K.S. *et al. Science* **306**, 666 (2004).
- [4] Novoselov, K.S. *et al. PNAS* **102**, 10451 (2005).
- [5] Katsnelson, M.I. *et al. Solid State Communications* **143**, 3 (2007).
- [6] Katsnelson, M.I. *et al. Nature Physics* **2**, 620 (2006).
- [7] Kim, K.S. *et al. Nature* doi: 10.1038/nature07719
- [8] Park, S. *et al. Nature Nanotechnology* doi: 10.1038/NNANO.2009.58
- [9] Ritter, K.A. *et al. Nature Material* doi: 10.1038/NMAT2378
- [10] Lin, Y.M. *et al. Nanoletters* **9**, 422 (2009).
- [11] Emtsev, K.V. *et al. Nature Material* doi: 10.1038/NMAT2382
- [12] Elias, D.C. *et al. Science* **323**, 610 (2009).
- [13] *Physics Today* (August 2007) and *Scientific American* (April 2008).

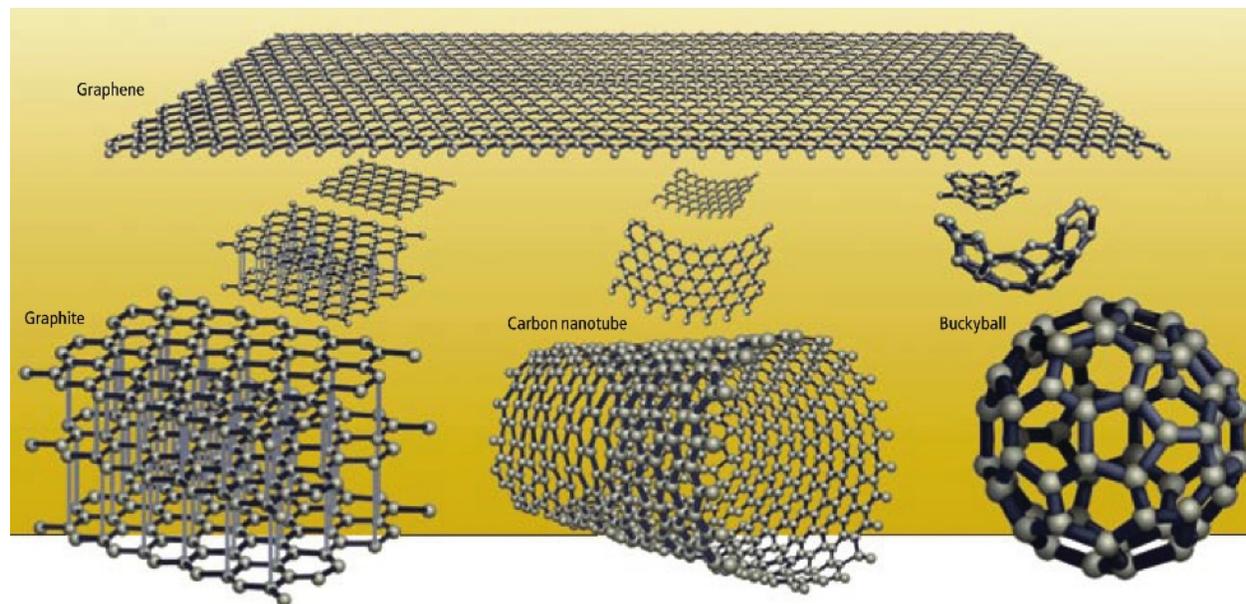


FIG. 1: Graphene: Building block of the various form of Carbon Allotropes. (top) Graphene, (bottom from left to right) Graphite, Nanotube and Fullerenes (adapted from Scientific American (2008)).

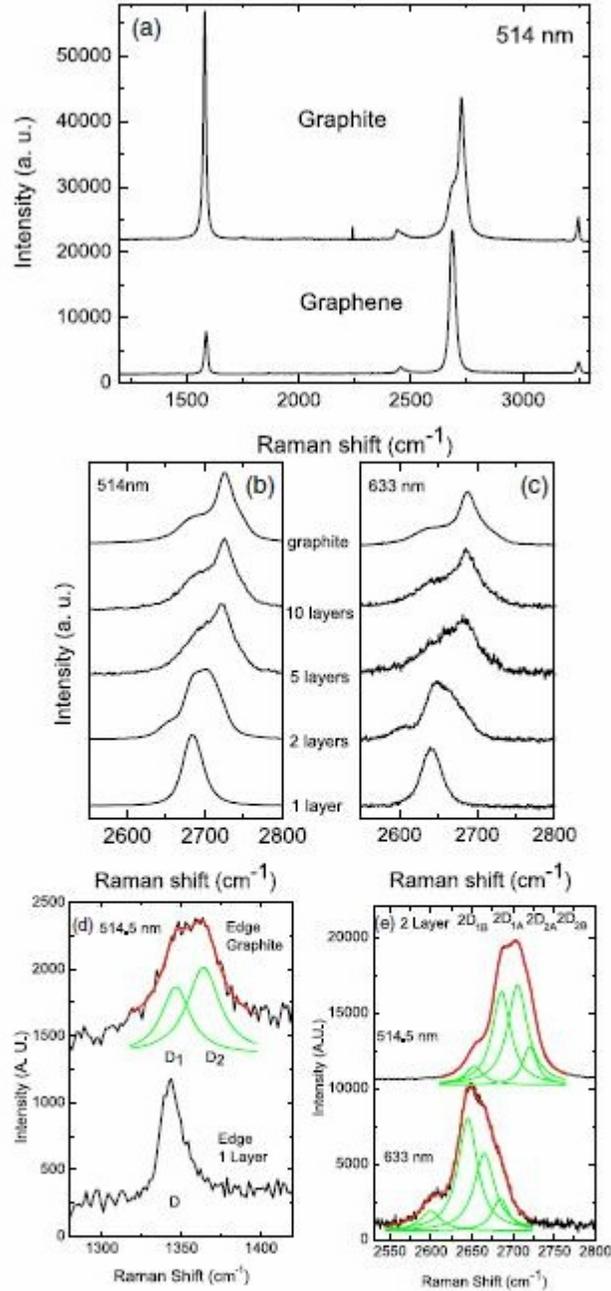


FIG. 2 (color online). (a) Comparison of Raman spectra at 514 nm for bulk graphite and graphene. They are scaled to have similar height of the 2D peak at ~ 2700 cm^{-1} . (b) Evolution of the spectra at 514 nm with the number of layers. (c) Evolution of the Raman spectra at 633 nm with the number of layers. (d) Comparison of the D band at 514 nm at the edge of bulk graphite and single layer graphene. The fit of the D_1 and D_2 components of the D band of bulk graphite is shown. (e) The four components of the 2D band in 2 layer graphene at 514 and 633 nm.

FIG. 2: Raman Spectroscopy to identify graphene (in Phys. Rev. Lett. (2006)).

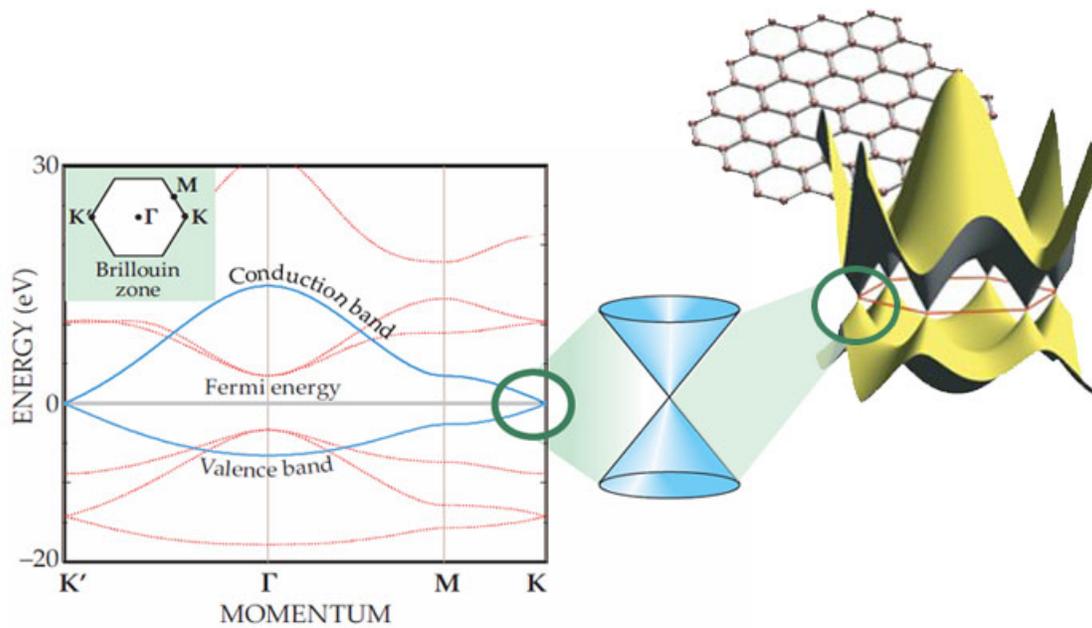


FIG. 3: **Electronic Structure of Graphene** Charge carriers are massless Dirac fermions. The dispersion relation is linear at the edges of the BZ for $E \ll 1$ eV (adapted from Physics Today (2007)).

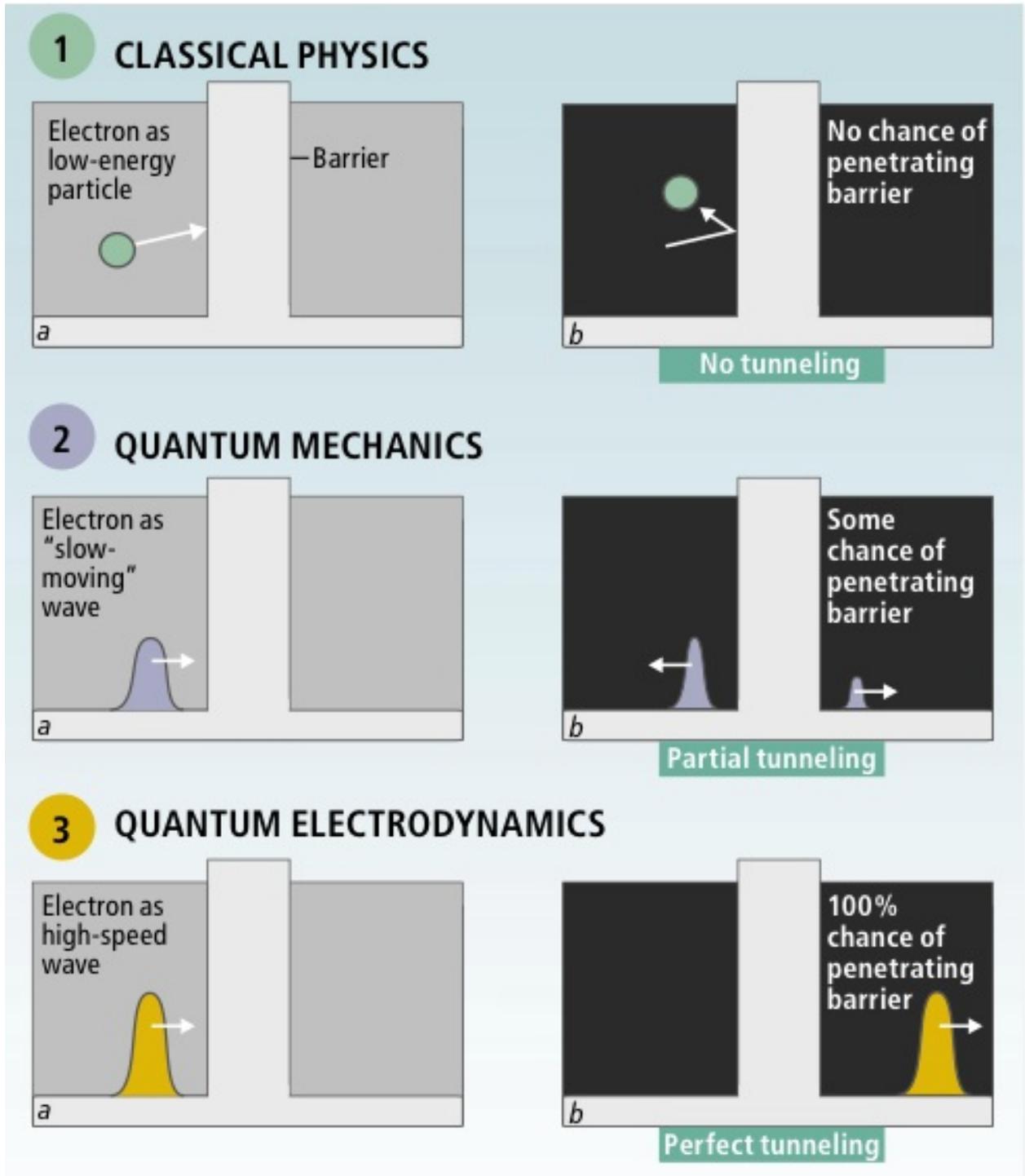


FIG. 4: Massless Dirac Fermions in Graphene: Quantum Electrodynamics in a pencil trace (in Scientific American (2008)).

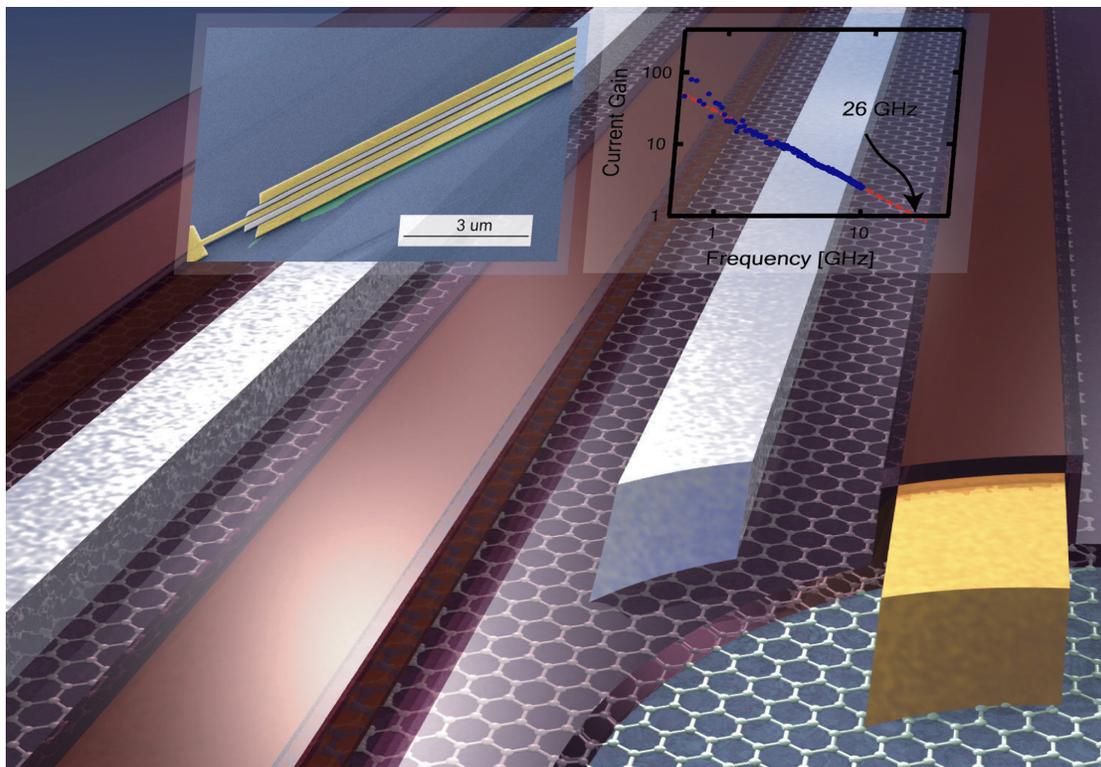


FIG. 5: First graphene transistor by IBM (in Nanoletters 2009).

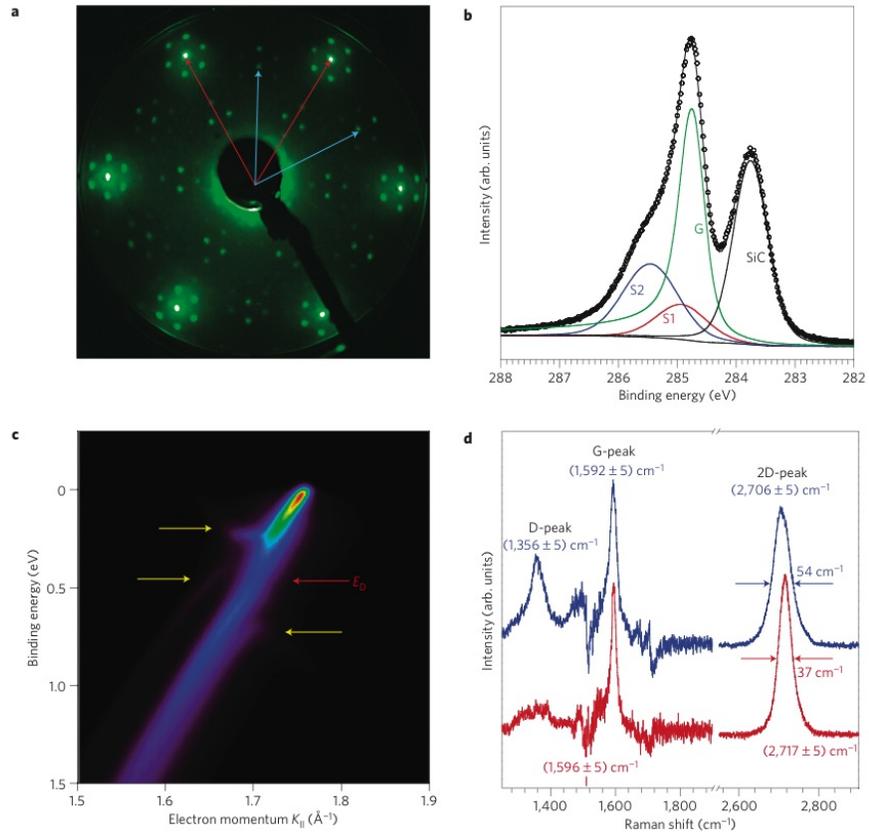


FIG. 6: Different techniques of characterization of graphene properties (in Nature Materials 2009).

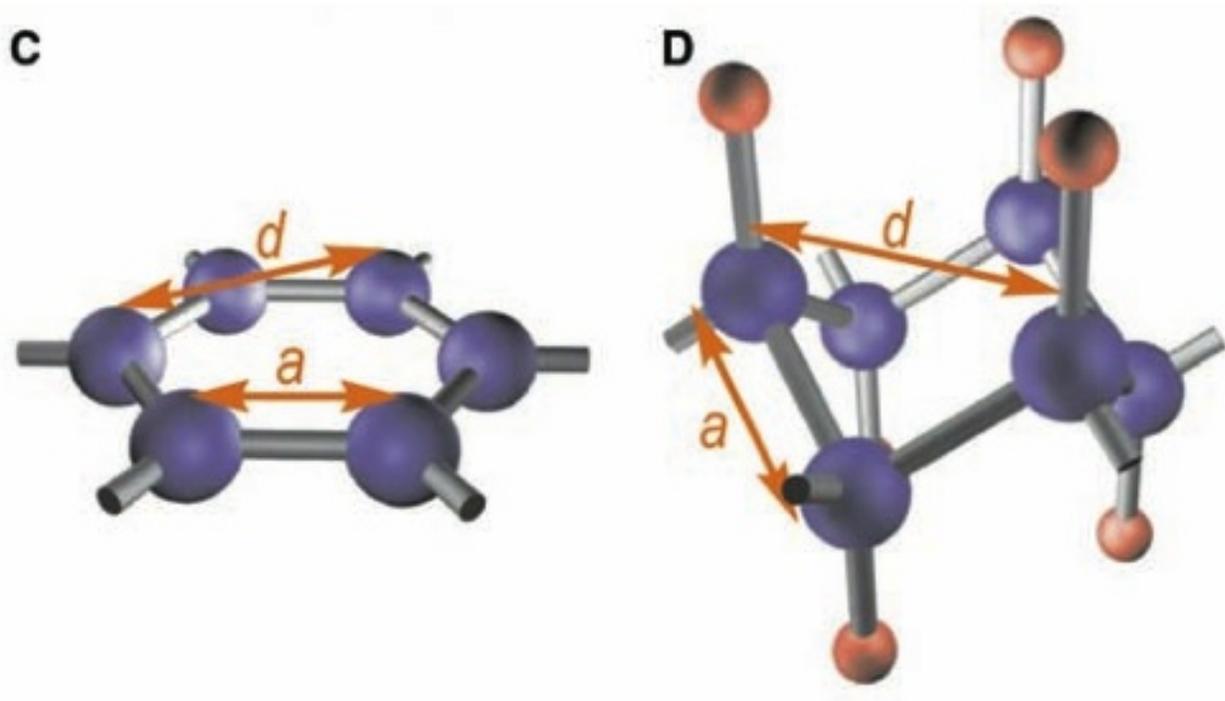


FIG. 7: Introduction of Graphane (in Science 2009).