Graphene - a fascinating new material of great future potential

Two Dimensions of Graphene

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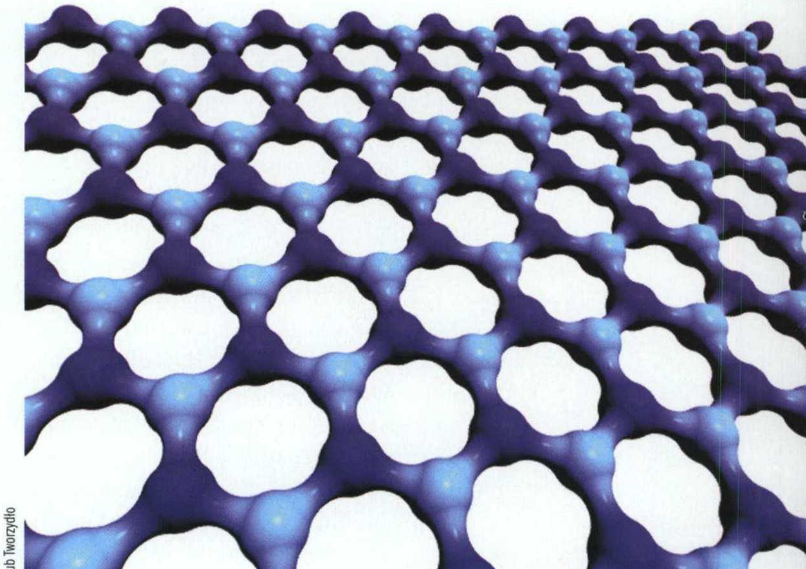
Last year, the Nobel Prize in physics was awarded for research on graphene – a two-dimensional, flat form of carbon, forming a honeycomb crystal just a single atom thick

Graphene had been known for many years as a one-atom-thick planar layer of carbon in a hexagonal crystal, forming the basic building block of graphite. The first report on the creation of graphene dates back to the year 1975, when van Bommel and his colleagues from the Philips laboratory in the Netherlands confirmed the presence of mono-atomic layers of carbon atoms arranged in hexagons on the surface of silicon carbide. Unfortunately, these researchers did not take any further interest in this achievement and we had to wait until 2004, when two physicists from the University of Manchester in the UK obtained graphene using graphite and adhesive tape. For the research work initiated by this experiment, Andre Geim and Konstantin Novoselov were awarded the Nobel Prize in 2010. The result of their experiments surprised the physics community because it ran against theoretical predictions, which ruled out the existence of free, thermodynamically stable, two-dimensional crystals.

After the enthusiastic news was reported that such a flat, single layer of carbon had indeed been obtained, the properties of the new material began to be studied. A year later, the journal Nature published confirmation of its unique properties. The first flakes of the graphene obtained were relatively small, roughly in the tens of micrometers. These proved to be good enough, however, to



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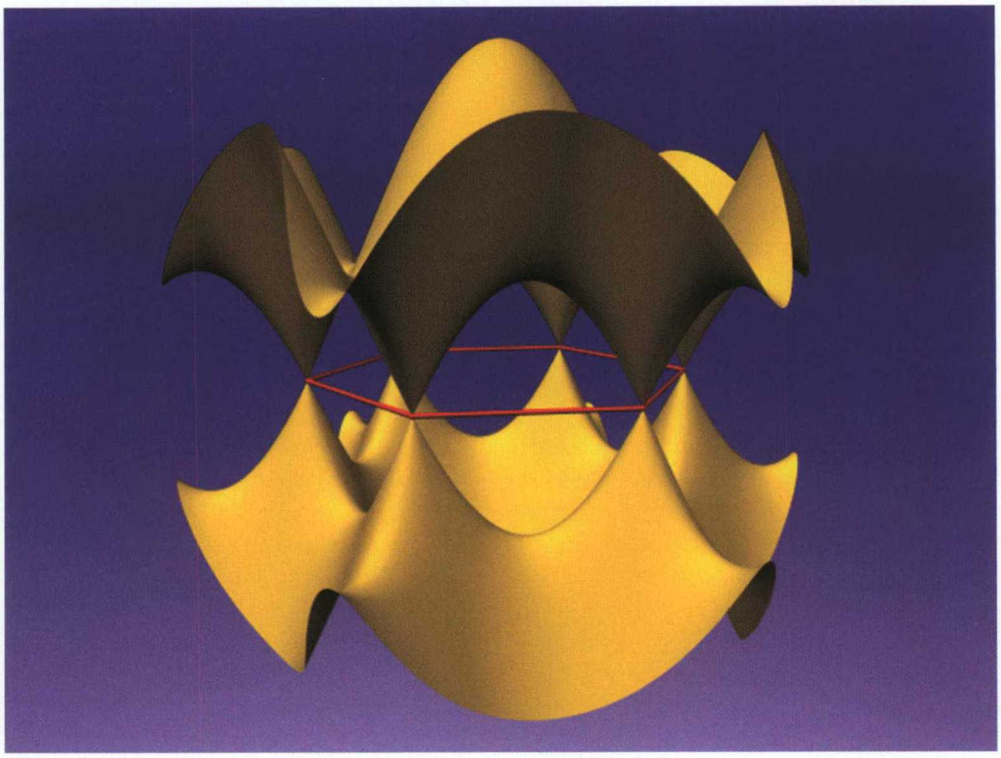
Graphene's crystalline network: atoms forming two sub-lattices shown in different colors



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Graphene's band structure in the Brillouin hexagonal zone (marked in red between the conduction and valence bands)

carry out many measurements. Preliminary results immediately suggested that graphene is a promising candidate for future applications in electronics, such as ballistic transistors. Such applications, however, require graphene samples covering a larger surface area, suitable for electron lithography techniques. One of the most promising methods for achieving this is to obtain graphene by sublimating silicon from silicon carbide (SiC). This technique originated in 2004 at the Georgia Institute of Technology in the US. In 2007, the Institute of Electronic Materials Technology in Warsaw, in collaboration with the Institute of Physics at the Faculty of Physics, University of Warsaw, launched research on obtaining graphene by sublimating silicon on the 6H and 4H polytypes of silicon carbide.

Band structure

Graphene's crystal structure is characterized by the organization of carbon atoms into a "honeycomb" lattice, involving a two-atom elementary cell. The lowest conduction band and highest valence band are formed from *p*-type orbitals. These orbitals lie perpendicular to the plane of the carbon and have a small overlap between neighboring atoms, which leads to the formation of π-type band states. The bands meet at six points, which corresponds to the emergence of a zero-energy interval. We can select just two of these points for consideration, since the rest are equivalent. In the vicinity of these points, the dispersion dependence is of conical shape and corresponds to the linear energy relationship $E = vp$, from the length of the two-dimensional quasimomentum $p = \hbar|k|$. The dispersion dependence is, therefore, the same as for the photon, and the constant v plays the role of the speed of light ($v = c/300$). Although the speed v is significantly lower than the speed of light, the electron excitations in graphene are described by the wave equation of relativistic quantum mechanics (the Dirac equation for particles with zero mass).

One consequence of the inversion symmetry of the atoms in the hexagonal elementary cell of the crystal lattice is particle-hole symmetry of excitations in graphene. Each energy state E (electron) corresponds to an energy state $-E$ (hole) with a reverse direction of pseudospin. Both electron (in the conduction band) and hole (in the valence) excitations are characterized by a linear relation of dispersion and zero mass. For this reason, both the electrons and the holes in the graphene will behave differently than in typical semiconductors or metals, where the energy is a parabolic function of the wavevector.

Advancing the State of the Art

The electronics industry has high hopes for the unusual electronic properties of graphene. The experimentally determined motilities of media in graphene are more than an order of magnitude greater than for silicon transistors. The expected theoretical values of media motility at room temperature are on the order of 10^5 cm^2/Vs. This allows for ballistic transport at distances on the order of several microns. This is expected to lead, with the help of electron lithography, to the development of a new standard of electronic instruments.

Another interesting avenue of research involves the spin properties of graphene strips, which can be semiconductors or metals, depending on how they are cut. Because of the negligible spin-orbit interaction, spin polarization in graphene can persist over large distances. By cutting an appropriate strip of graphene layers, opposite spin polarizations can be obtained on the two edges of the bar, which creates a half-metal with a spin balance in the media. The application of an electric field can destroy this balance, which provides an opportunity to tune the concentration of media with a specified spin. This allows graphene bars to be used in spintronics.

It is also worth mentioning potential immediate practical applications of graphene. It has recently been shown that graphene can absorb particles from the surrounding atmosphere, leading to its "doping" with electrons or holes depending on the type of gas adsorbed.

Graphene in Warsaw

We started obtaining graphene in Warsaw in 2007 while studying the controlled decomposition of SiC at high temperatures, as part of a collaboration between the Institute of Electronic Materials Technology (ITME) in Warsaw and the Institute of Experimental Physics at the Faculty of Physics University of Warsaw. Carbon layers grown at ITME were tested using experimental techniques available at the UW Faculty of Physics, such as atomic force microscopy (AFM), scanning tunneling microscopy (STM), inelastic light scattering (Raman Effect) and optical transmission. Poland's first graphene layer was obtained on an atomically smooth surface from the crystallization front of 6HSiC(0001) bulk crystal with silicon polarity. STM images of the samples grown at ITME clearly show a lattice of bright points occurring at distances of 2.45 Å, related to the atomic lattice of graphene. A "macroscopic" structure is imposed on the graphene structure, at distances of 17.5 Å, originating from the interaction between the graphene and the SiC foundation. This means that the resulting layer of graphene is thin – one or two atoms. Later, we obtained graphene layers on other polytypes of SiC, and also on epitaxial layers.

Currently, ITME is one of the few centers in Europe producing graphene on SiC. The enormous interest in this material has helped us forge broad scientific contacts with the best laboratories in Europe and worldwide. Thanks to collaboration with the Grenoble High Magnetic Field Laboratory, the samples from Warsaw were measured magnetooptically in the far infrared. These results have proved essential to the understanding of graphene's properties.

Fascinating properties of graphene have also been shown by absorption tests in visible light. A one-atom layer of graphene absorbs 2.3% of light regardless of wavelength. This difference in light intensity is easily detectable by the human eye. Considering the pre-conditions at the air-graphene and graphene-SiC borders, we can also confirm that transmission through N layers of epitaxial graphene does not de-

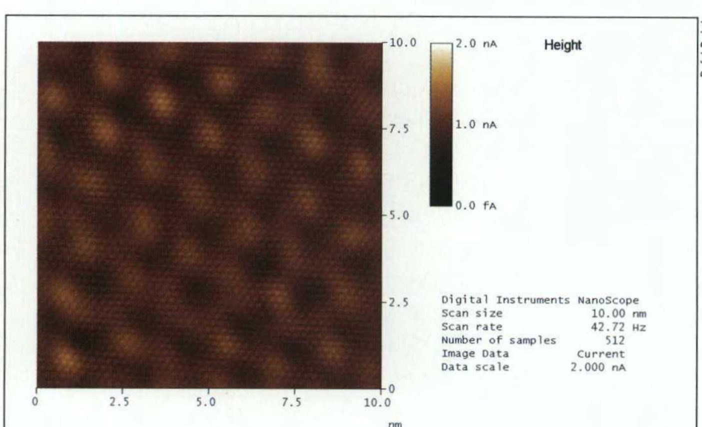

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Image obtained using a scanning tunneling microscope at the Faculty of Physics, University of Warsaw, for a graphene layer on a 6HSiC(0001) crystal from ITME

pend on the wavelength; instead each layer of epitaxial graphene absorbs not 2.3%, but 1.29% of the incident light. This means that a simple absorption measurement can serve as a source of information about the number of graphene layers grown on the SiC substrate.

Although Poland has significant coal deposits, unfortunately they cannot be converted into graphene any more than they can be turned into diamonds

CVD approach

While working on improving the sublimation method, Dr. Włodzimierz Strupiński from ITME proposed that instead of sublima-

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tion, chemical vapor deposition (CVD) could be used to lay down carbon layers on SiC substrates. One advantage of using the CVD method on silicon carbide is that it utilizes existing solutions applied in SiC electronics technology. In this method, the quality of obtained layers may be less sensitive to defects in the SiC substrate.

The ability to block the sublimation process using argon flow turned out to be key. After sublimation was blocked, a small admixture of propane was added to the argon, with the propane depositing carbon layers on the SiC surface.

Preliminary studies using various techniques have shown that the proposed method can provide very high quality graphene layers. Studies using angle-resolved photoemission spectroscopy (ARPES) indiciate that in layers produced using the CVD method, media behave like zero-mass Dirac fermions, for which the relationship between energy and momentum is linear. Raman studies show that samples obtained using the CVD method are significantly less stretched by the substrate, and exhibit far better homogeneity than layers obtained by sublimation. The high quality of the CVD layers is confirmed by studies using STM.

The intensive research now being conducted into graphene across the globe confirms that it is a fascinating material in terms of processes and phenomena occurring within it, as well as its potential applications. It is extremely important that Poland has been able to stay abreast of global trends and grow high quality graphene, whose optical and electrical properties do not deviate from the best structures available globally. ■

Further reading:

Drabińska A., Borysiuk J., Strupiński W., Baranowski J.M. (2010). Optical Transmission of Epitaxial Graphene Layers on SiC in the Visible Spectral Range. *Materials Science Forum*, 645-648, 615-618.

Drabińska A., Grodecki K., Strupiński W., Bożek R., Korona K.P., Wysmołek A., Stępniewski R., Baranowski J.M. (2010). Growth kinetics of epitaxial graphene on SiC substrates. *Phys. Rev. B* 81, 245410.

Strupiński W., Grodecki K., Wysmołek A., Stępniewski R., Szkopek T., Gaskell P.E., Grneis A., Haberer D., Bożek R., Krupka J., and Baranowski J.M. (2011). Graphene Epitaxy by Chemical Vapor Deposition. *Nano Lett.* 11 (4), 1786-1791.

Tworzydło J., Trauzettel B., Titov M., Rycerz A., and Beenakker C.W.J. (2006). Sub-Poissonian shot noise in graphene. *Phys. Rev. Lett.* 96, 246802.

Wysmołek A., Tworzydło J., Drabińska A. (2011). Grafen - nowy dwuwymiarowy materiał [Graphene - A New Two-Dimensional Material]. *Postępy Fizyki*, 62, 3, 94-103.