NANO

MIKRO- ÉS NANOTECHNIKA II

Dr. Pődör Bálint

Óbudai Egyetem KVK Mikroelektronikai és Technológia Intézet

6b. ELŐADÁS: GRAFÉN ÉS ALKALMAZÁSAI

2012/2013 tanév 1. félév
Nem-szerkesztett (ideiglenes) változat!

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GRAFÉN ÉS ALKALMAZÁSAI

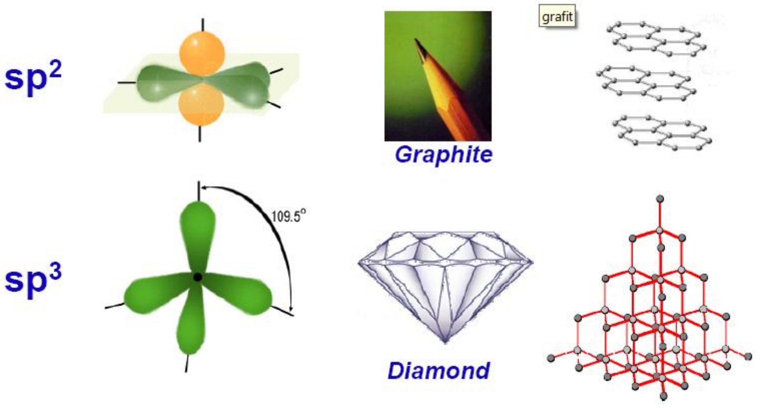
Biró László Péter: Graphene: The route from touch screens to digital nanoelectronics

Nemes-Incze Péter: Két-dimenziós szén kristály

Mindkét előadás letölthető: www.nanotechnology.hu

Az előadás részben ezen anyagok felhasználásával készült.

A KARBON 1985 ELŐTT



A SZÉN KÜLÖNBÖZŐ MÓDOSULATAI

Carbon is arguably the most fascinating element in the periodic table. It is the base for DNA and all life on earth. Carbon can exist in several different forms. The most common form of carbon is graphite, which consists of stacked sheets of carbon with a hexagonal structure. Under high pressure diamond is formed, which is a metastable form of carbon.

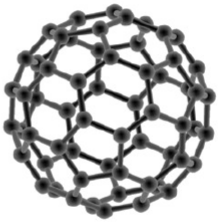
A new form of molecular carbon are the so called fullerenes[8]. The most common, called C60, contains 60 carbon atoms and looks like a football (soccer ball) made up from 20 hexagons and 12 pentagons which allow the surface to form a sphere. The discovery of fullerenes was awarded the Nobel Prize in Chemistry in 1996.

A related quasi-one-dimensional form of carbon, carbon nanotubes, have been known for several decades[9] and the single walled nanotubes since 1993.[10,11] These can be formed from graphene sheets which are rolled up to form tubes, and their ends are half spherical in the same way as the fullerenes. The electronic and mechanical properties of metallic single walled nanotubes have many similarities with graphene.

It was well known that graphite consists of hexagonal carbon sheets that are stacked on top of each other, but it was believed that a single such sheet could not be produced in isolated form. It, therefore, came as a surprise to the physics community when in 2004, Konstantin Novoselov, Andre Geim and their collaborators[1] showed that such a single layer could be isolated and that it was stable. The single layer of carbon is what we call graphene.

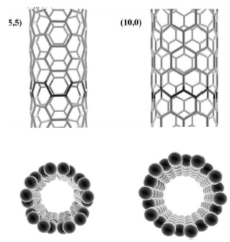
A KARBON 1985 UTÁN: FULLERÉN, CNT, GRAFÉN

Fullerének
0D



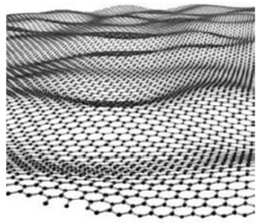
1985
H.W. Kroto

Szén nanocsövek
1D



1991
S. Iijima

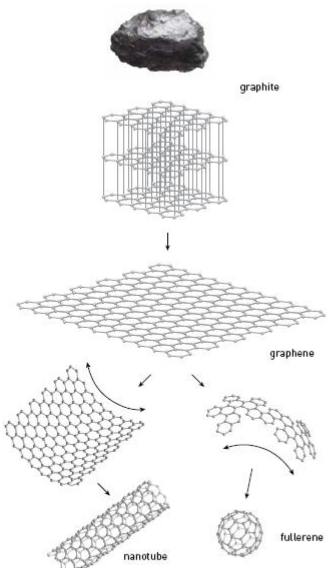
Grafén
2D



2004
K.S. Novoselov

Grafén: a szén nanoszerkezetek családjának új tagja

C (SZÉN): MOLEKULÁRIS ALAKZATOK



Graphite is a basic material found in nature. When taken apart graphite sheets become graphene. A rolled up layer of graphene forms a carbon nanotube, folded up it becomes a small football, fullerene.

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FULLEREN ÉS GRAFÉN

C_{60} fullerén vagy ”buckyball” vagy buckminsterfullerén (R.B.Fuller építész nevéről, aki hasonló szerkezeteket tervezett).

60 szénatom, 20 hatszög, 12 ötszög, futball-labda alak.

Kémiai Nobel díj 1996: H. Kroto, K. Smalley, R. Curl

Grafén: egy atomréteg ”vastag” lemez

Fizikai Nobel díj 2010: A. Geim és K. Novoselov

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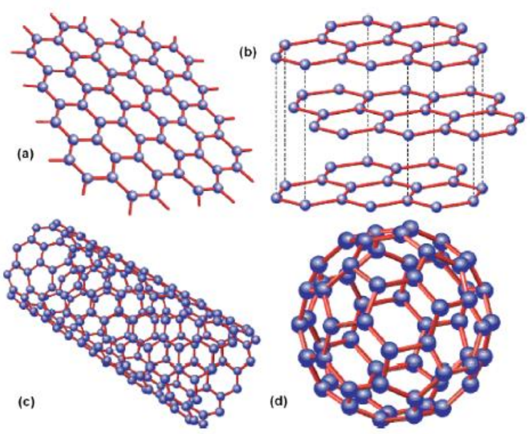
GRAFÉN



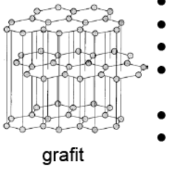
Graphene (a) is a 2D building block of other carbon allotropes: graphite (b), nanotubes (c) and fullerene (d).

ELŐZMÉNYEK

Although graphene has been a topic of study for about the last 60 years, its existence in the free state remained elusive. But, ultimately in 2004, a group of researchers led by Dr Andrei Geim from the University of Manchester isolated graphene from graphite for the first time. Since then, graphene has spurred great excitement in the chip research

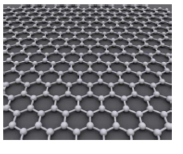
GRAFIT- GRAFÉN

Grafén: egy atomréteg ”vastag” lemez

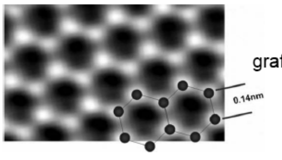


grafit

- Gyengén kölcsönható síkokból áll.
- A síkokon belül hatszöges elrendezés.
- *c*-síkban a grafit vezetőként viselkedik.
- A síkokat gyenge *van der Waals*-erők kötik össze.
- A síkok egymáshoz képest eltolva.
- A síkok „vastagsága” ~*0,3 nm*. Egy-egy sík *1D* nanostruktúrának tekinthető.



grafén sík



grafén TEM kép

Ha egy síkot leválasztunk, akkor annak különleges tulajdonságai lesznek.

- Elektromos vezetőképessége jobb mint az ezüsté
- Kétdimenziós vezetési tulajdonságok
- A grafén réteg a fehér fényre átlátszatlan, és az átlászóság elektronos térrel változtatható.
- Hővezetőképessége kb. 10-szerese mint az ezüsté
- Szakító szilárdsága ~ 200 szorosa az acélénak


Andre Geim és Konstantin Novoselov
fizika Nobel-díj 2010

Megoldották az egy atomsíknyi grafitlemez tömbről való leválasztását!

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GRAFÉN PIKKELYEK

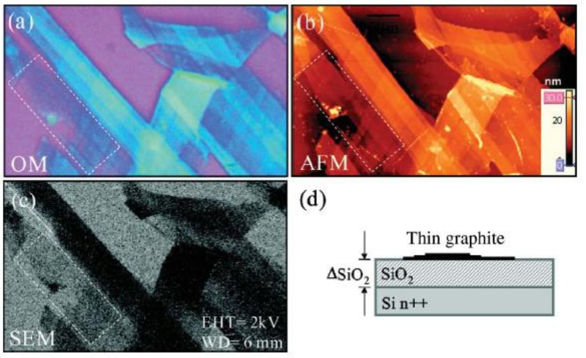
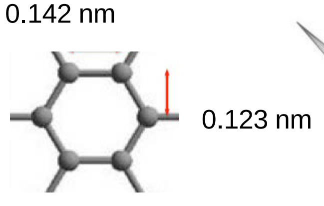
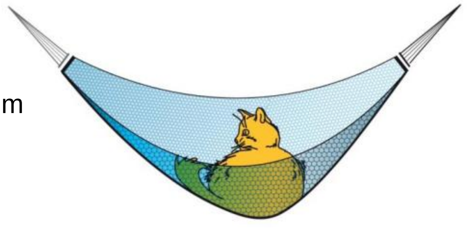


Image of a big mechanically exfoliated graphite flake containing regions of different thicknesses taken using an optical microscope (a), an atomic force microscope (b), and a scanning electron microscope (c). An ultra thin graphite region (thickness below 2 nm) is highlighted by a dashed rectangle. (d) The flake is deposited on top of an SiO2/Si substrate with an oxide thickness SiO2 = 500 nm [17].

DENSITY OF GRAPHENE



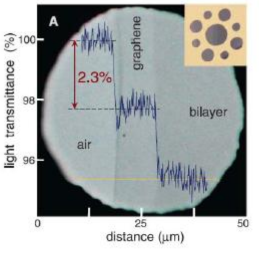


The unit hexagonal cell of graphene contains two carbon atoms and has an area of 0.052 nm^2. We can thus calculate its density as being 0.77 mg/m^2.
A hypothetical hammock measuring 1m^2 made from graphene would thus weigh 0.77 mg.

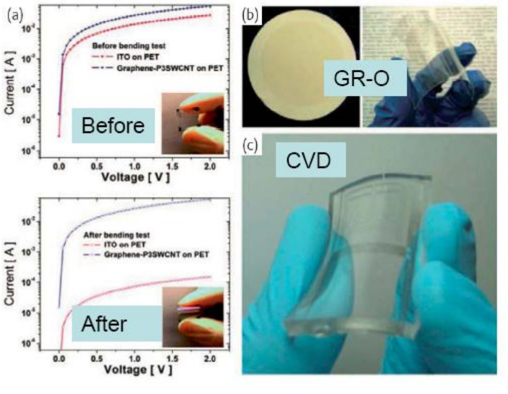
OPTICAL TRANSPARENCY OF GREPHENE

Graphene is almost transparent, it absorbs only 2.3% of the light intensity, independent of the wavelength in the optical domain. This number is given by $\pi\alpha$, where α is the fine structure constant. Thus suspended graphene does not have any colour.

TRANSPARENT AND FLEXIBLE MATERIAL



Nair, R. R. et al. *Science* **2008**, *320*, 1308.



Bending graphene vs. ITO on PET

Wassei, J. K.; Kaner, R. B. *Materials Today* **2010**, *13*, 52-59.

STRENGTH OF GRAPHENE

Graphene ha a breaking strenth of 42 N/m. Steel has a breaking strength in the range of 250-1200 Mpa. For a hypothetical steel film of the same thickness as graphene (which can be taken to be 3.35 Å = 3.35×10^{-10} m, i.e. the layer thickness in graphite), this would give a 2D breaking strength of 0.084-0.40 N/m. Thus graphene is more than 100 times stronger than the strongest steel.

In our 1 m^2 hammock tied between two trees you could place a weight of approximately 4 kg before it would break. It should thus be possible to make an almost invisible hammock out of graphene that could hold a cat without breaking. The hammock would weigh less than one mg, corresponding to the weight of one of the cat's whiskers.

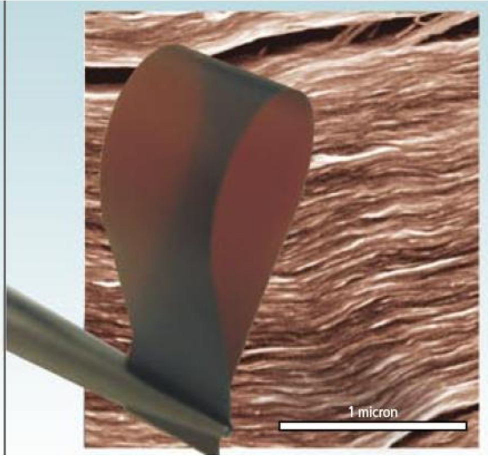
THERMAL CONDUCTIVITY

The thermal conductivity of graphene is dominated by phonons and has been measured to be approximately 5000 $Wm^{-1}K^{-1}$. Copper at room temperature has a thermal conductivity 400 $Wm^{-1}K^{-1}$. Thus graphene conducts heat 10 times better than copper.

ALKALMAZÁS: KOMPOZITOK

: the list of prospective graphene-based

COMPOSITE MATERIALS ▸
Two or more complementary materials can often be combined to obtain the desirable properties of both. Typically a bulk matrix and a reinforcement are used: think of a fiberglass boat hull made of plastic infused with strong glass fibers. Investigators are testing the physical properties of composites fabricated from polymers reinforced with graphene-based materials such as graphene oxide, a chemically modified version of graphene that is stiff and strong. Unlike graphene, graphene oxide "paper" (*right, inset*) is relatively easy to make and may soon find its own useful applications in laminated composites (*right, background*). The scale bar is one micron long.



GRAFÉN KOMPOZITOK

The unique combination of graphene's electronic, chemical, mechanical, and optical properties can be utilized in full in composite materials. It is also relatively easy to prepare graphene for such an application: One can either use the direct chemical exfoliation of graphene, which allows a rather high yield of graphene flakes in a number of organic solvents, or go through an oxidation process to prepare graphite oxide—which can be easily exfoliated in water—with subsequent reduction in a number of reducing media.

GRAFÉN KOMPOZITOK

The strongest and simultaneously one of the stiffest known materials, with a Young's modulus of 1 TPa, graphene is an ideal candidate for use as a reinforcement in high performance composites.

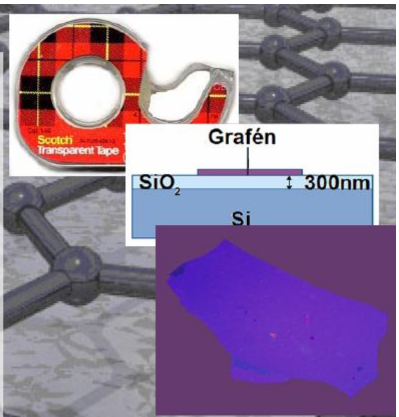
There is a huge advantage in its being exactly one atom thick: It cannot cleave, giving it the maximum possible strength in the out-of plane direction. Its high aspect ratio also allows graphene to act as an ideal stopper for crack propagation. As for interaction with the matrix—the central issue for all nanocomposite fillers such as carbon fiber or carbon nanotubes—chemical modification of the surface or edges may significantly strengthen the interface between the graphene and a polymer.

GRAFÉN KOMPOZITOK

Using chemical derivatives of graphene would not only broaden the range of possible matrices but also widen the functionality of the possible composites. Given that the mechanical strength of fluorographene is only slightly smaller than that of pristine graphene, one can obtain composites with similar mechanical properties but a range of other characteristics, from optically transparent to opaque, and from electrically conductive to insulating.

PRODUCTION OF GRAPHENE

- Micromechanical cleavage
- Epitaxy on SiC
- **<u>CVD</u>** <u>(Ni, Pt, Rh, **Cu)**</u>
- Chemical exfoliation (G-O, oxigene removal!)
- CNT „unzipping"
- and many other exotic methods ….



"ROLL-TO-ROLL LARGE SIZE CVD GRAPHENE

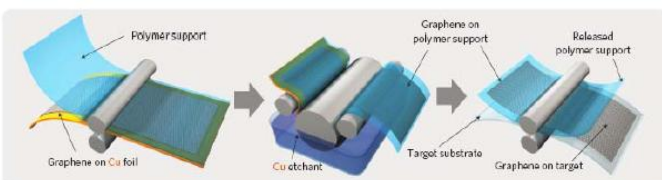
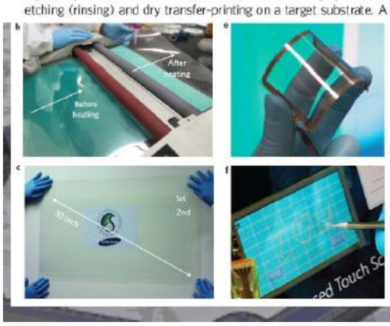


Figure 1 | Schematic of the roll-based production of graphene films grown on a copper foil. The process includes adhesion of polymer supports, copper etching (rinsing) and dry transfer-printing on a target substrate. A wet-chemical doping can be carried out using a set-up similar to that used for etching.



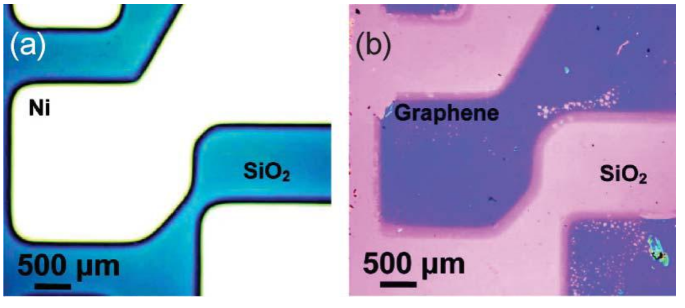
Bae, S. et al.,. *Nature Nanotechnology* **2010**, *5*, 574 .

The quality of the material is well suited for transparent conducting & flexible electrodes => market ready!

GRAPHENE: CHEMICAL VAPOUR DEPOSITION

Low-cost synthesis of large-scale graphene films using chemical vapor deposition (CVD) on thin (less than 300 nm) metal layers (e.g. Ni, Co, Pt, Ru, etc.) is another alternative technique. The metal film (e.g. Ni film on SiO2/Si substrate) is exposed to a flow of a hydrocarbon gas (e.g. methane) at high temperatures (900–1000◦C) causing carbon saturation of the metal. This is followed by rapid cooling of the sample, leading to a decrease in the solid solubility of carbon in Ni and, thus, precipitation of carbon in the form of ultrathin graphitic films (1–10 layers) over the metal surface occurs as a consequence.
The deposited films can be transferred to arbitrary substrates by etching the underlying metal film, and can also be patterned using standard lithographic processes. The quality of graphene obtained by CVD is almost as high as mechanically cleaved graphene. Another option is to prepattern the metal surface producing graphene patterns of desired geometries at precise locations and hence favoring device fabrication.

CVD OF GRAPHENE



Chemical vapor deposition of graphene using prepatterned transition metal films. (a) Optical microscopic image of the nickel catalyst film on SiO2/Si. CVD graphene is grown on the same nickel pattern. (b) Optical image of this graphene when transferred from the nickel surface to another SiO2/Si substrate.

EPITAXIÁS NÖVESZTÉS

Graphene can be grown over specially chosen support substrates. The advantage of such substrate-based synthesis techniques is their compatibility with the present CMOS technology and their scalability, which can help in realizing the dream of incorporating graphene in the mainstream electronics industry.

One such method uses ultrahigh vacuum (UHV) annealing of single-crystal SiC causing its thermal reduction and eventually producing graphene as an epitaxial layer. Silicon desorbs from SiC at about 1000◦C and the carbon-enriched surface undergoes reorganization, leaving behind small islands of graphitized carbon. The process is called vacuum graphitization. The size of the film produced depends on the size of the substrate used.

GRAFÉN

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The evolution of graphene-based electronic devices

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(*Received 29 April 2010; final version received 21 July 2010*)

Successful isolation of single-layer graphene, the two-dimensional allotrope of carbon from graphite, has fuelled a lot of interest in exploring the feasibility of using it for fabrication of various electronic devices, particularly because of its exceptional electronic properties. Graphene is poised to save Moore's law by acting as a successor of silicon-based electronics. This article reviews the success story of this allotrope with a focus on the structure, properties and preparation of graphene as well as its various device applications.

Keywords: electronic device; FET; field effect; graphene; nanoelectronics

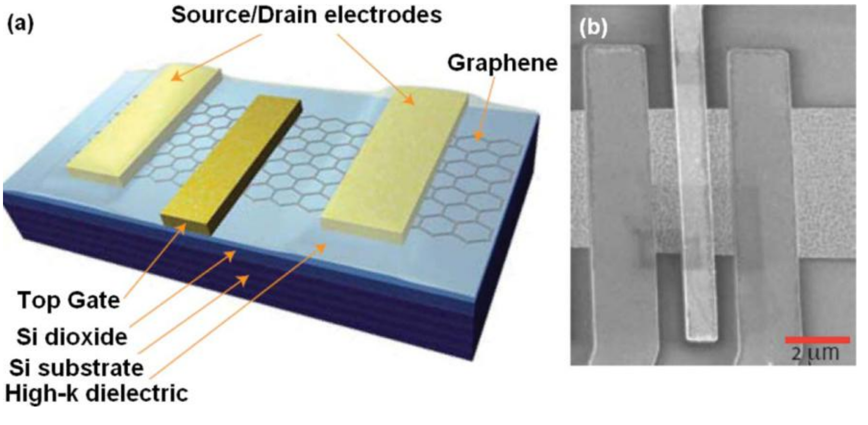
GRAFÉN ELEKTRONIKAI ESZKÖZÖK

Successful isolation of single-layer graphene, the two-dimensional allotrope of carbon from graphite, has fuelled a lot of interest in exploring the feasibility of using it for fabrication of various electronic devices, particularly because of its exceptional electronic properties.

Graphene is poised to save Moore's law by acting as a successor of silicon-based electronics.

Azért itt is érvényes, hogy a jövő eldönti, hogy ez igaz lesz-e, da a múlt arra tanít, hogy a legtöbb jóslat nem vált be…

GRAFÉN FET



A top-gated graphene field effect transistor on a SiO2/Si substrate: (a) schematic diagram;
(b) SEM image

GRAFÉN ÉS NÉHÁNY FÉLVEZETŐ FONTOSABB TULAJDONSÁGAI

Table 1. Comparison of the properties of graphene with those of some common semiconductors.

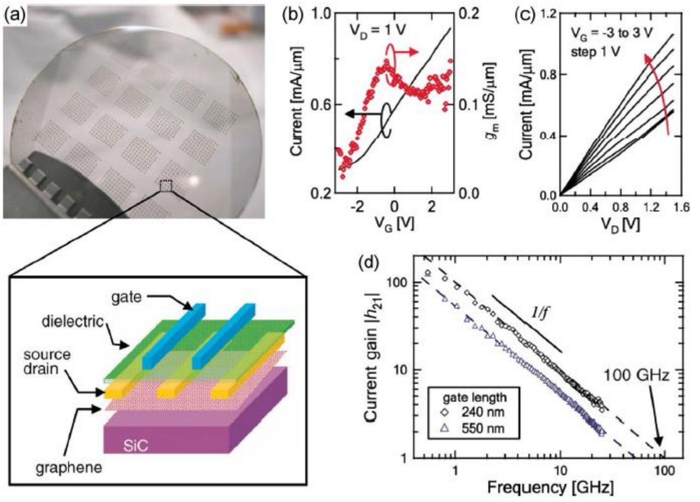
	Graphene	Si	Ge	GaAs	InAs	InP
Electron mobility ($cm^2\ V^{-1}\ s^{-1}$) @ 300 K	200,000	1400	3900	4600	16,000	2800
Band gap energy, E_g (eV)	0	1.12	0.66	1.42	0.36	1.35
Electron saturation velocity V_{sat} (10^7 cm/s)	>5	1	0.6	2.2	4.0	2.2
Density-of-states electron effective mass (m^*/m_o)	0	1.08	0.56	0.067	0.023	0.077
Relative dielectric constant, ε_r	2.4	11.9	16.0	13.1	14.6	12.4
Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	5000	150	60.2	46	27	68
Lattice constant (Å)	2.46	5.43	5.65	5.65	6.06	5.87

BEILLESZTÉS A Si TECHNOLÓGIAI SORBA…

Multilayered epitaxial graphene on insulating SiC substrate has been used for fabricating hundreds of transistors on a single chip. The world's first RF graphene field-effect transistor has been ccomplished using 1–2 layered EG on SiC.

Recently, IBM has reported the creation of top-gated transistors using graphene grown on the silicon face of a 2 inch thick SiC wafer that can operate at speeds of 100 GHz with an electron carrier density of about 3 × 1012 cm−2 and peak mobility of 1500 cm2 V−1 s−1 at room temperature.

This far surpasses the performance of the fastest GaAs transistors.



(a) Image and schematic cross-sectional view of the epitaxial graphene FETs. (b) The plot of drain current (ID) and transconductance (gm) of the device with gate voltage (VG) variation at fixed drain bias (VD) of 1 V and the source grounded. (c) The variation of ID as a function of VD for different values of VG. (d) Small-signal current gain (|h21|) variation with frequency.

VÉGE

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