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«Научные и научно-педагогические кадры инновационной России
2009-2013 гг» Соглашение 8683 от 21.09.2012

Использовать как факультативное дополнение к учебным курсам
«Углеродные наноматериалы», «Нанотехнологии», «Микроэлектроника»

Оксид графена: синтез, свойства, возможности

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Ю.Кудашова, Д.Кириенко, А.Мейлахс, В.Микушкин,А.Швидченко,
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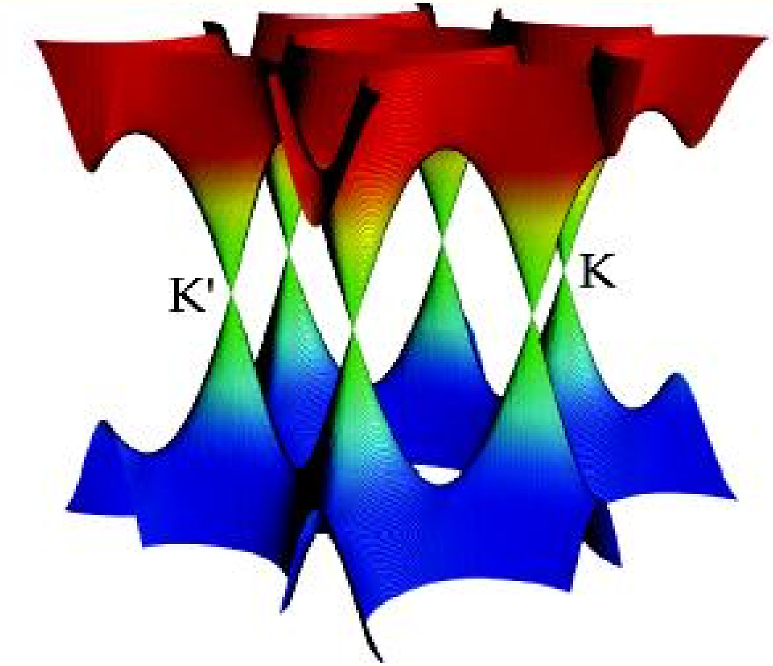
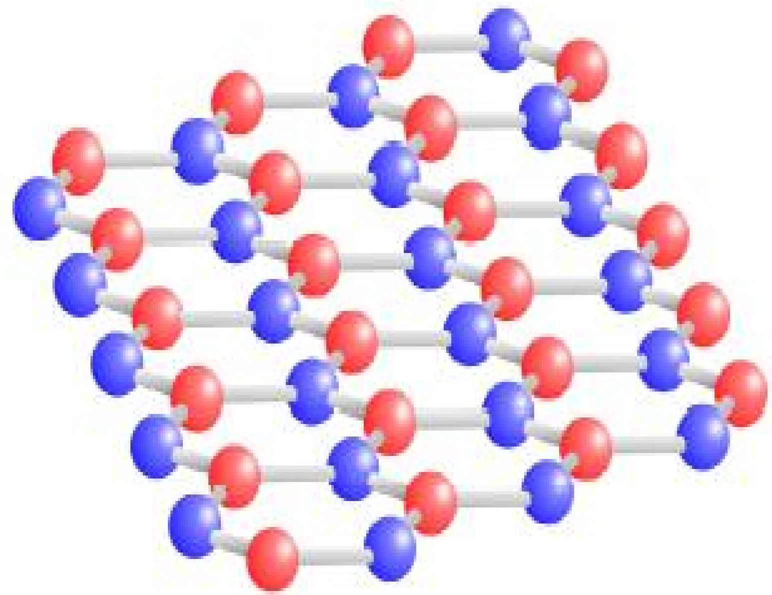
ФТИ им.А.Ф.Иоффе РАН
194021, С.-Петербург, Россия

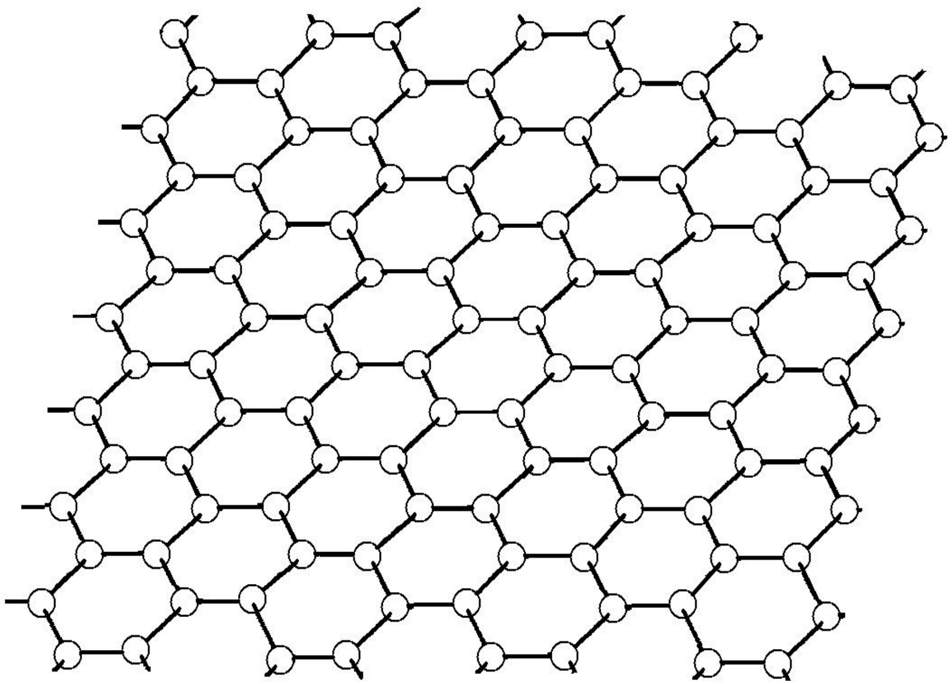
Кристаллическая и электронная структура графена

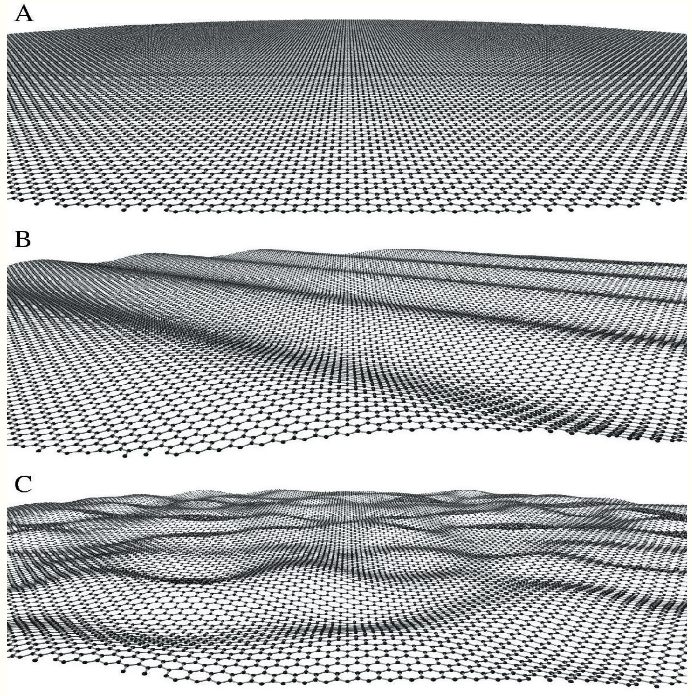




- High electron mobility
- High thermal conductivity
- High tensile strength

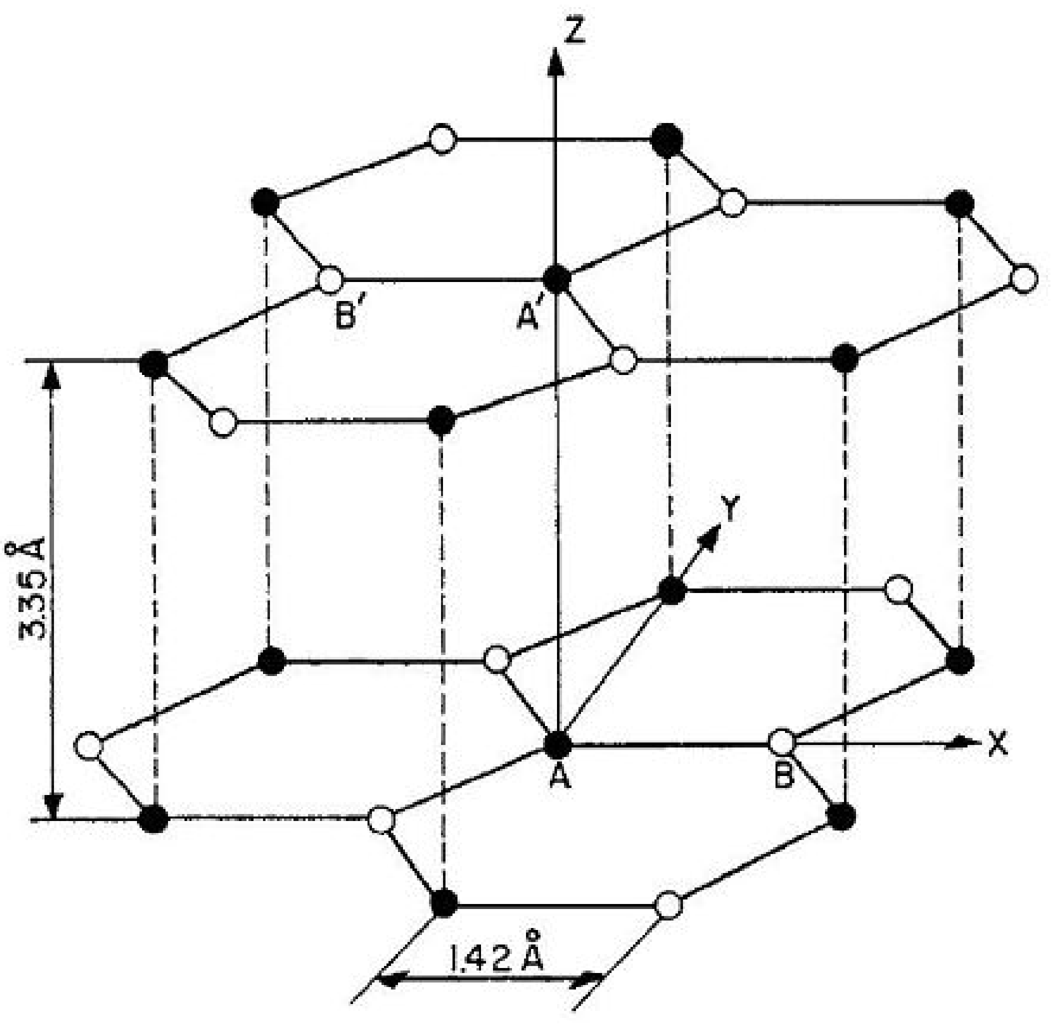
Графен – двумерная пленка



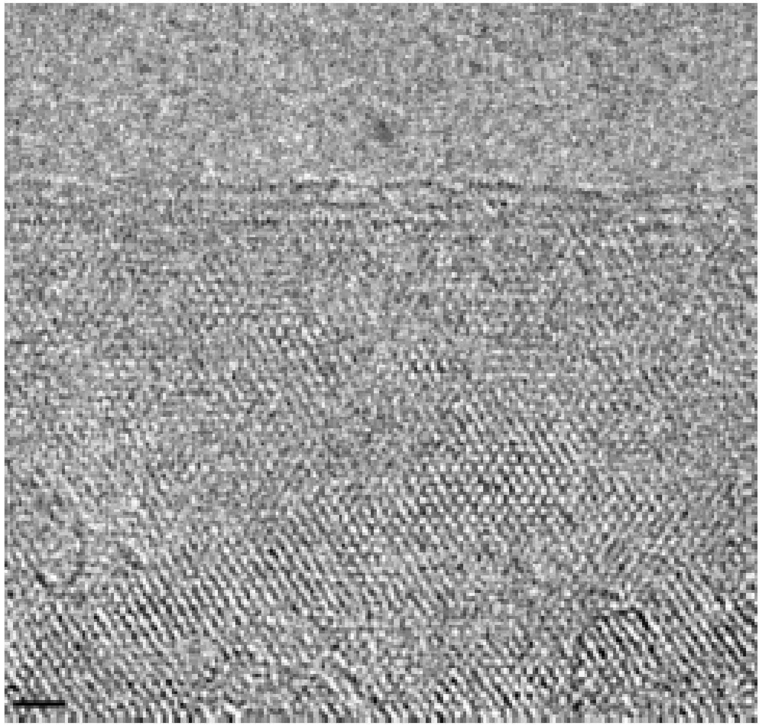


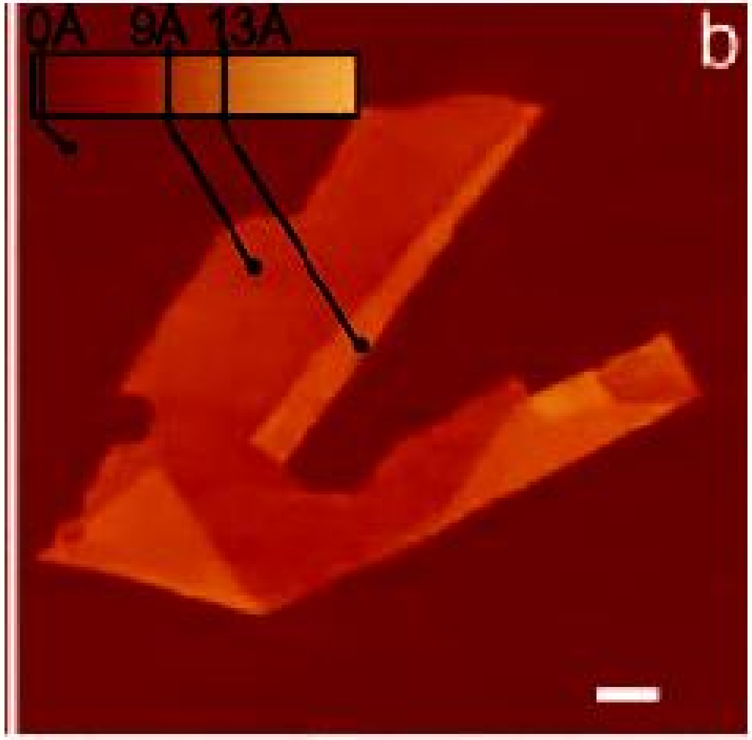
J.C.Meyer A.K.Geim, M.I. Katsnelson, K.S.Novoselov, T.J.Booth, S.Roth, The structure of suspended graphene sheets. Nature nanotecnology Vol 446| 1 March 2007| doi:10.1038/nature05545

Структура кристаллического графита



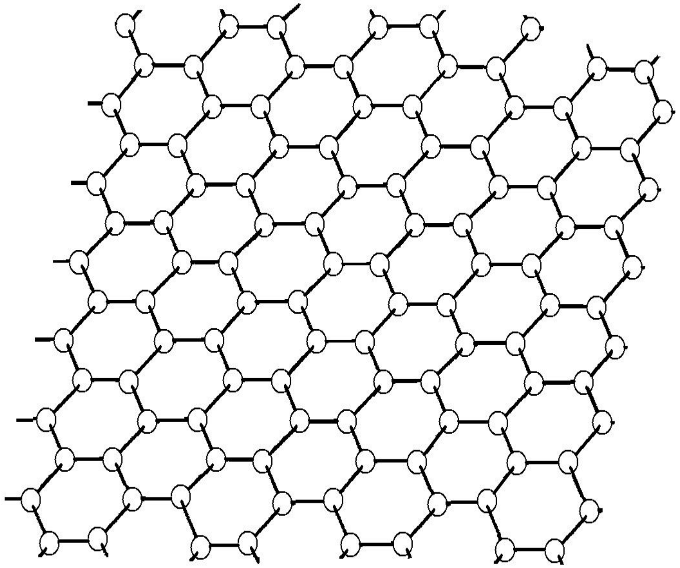
Графен из графита



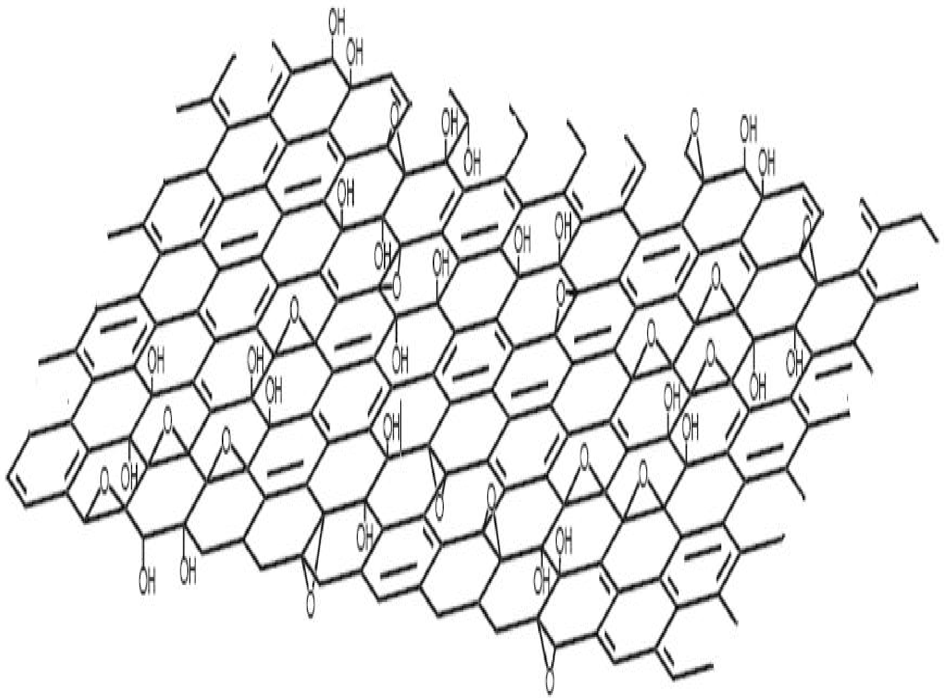


www.pnas.orgcgidoi10.1073pnas.0502848102

Графен и оксид графита

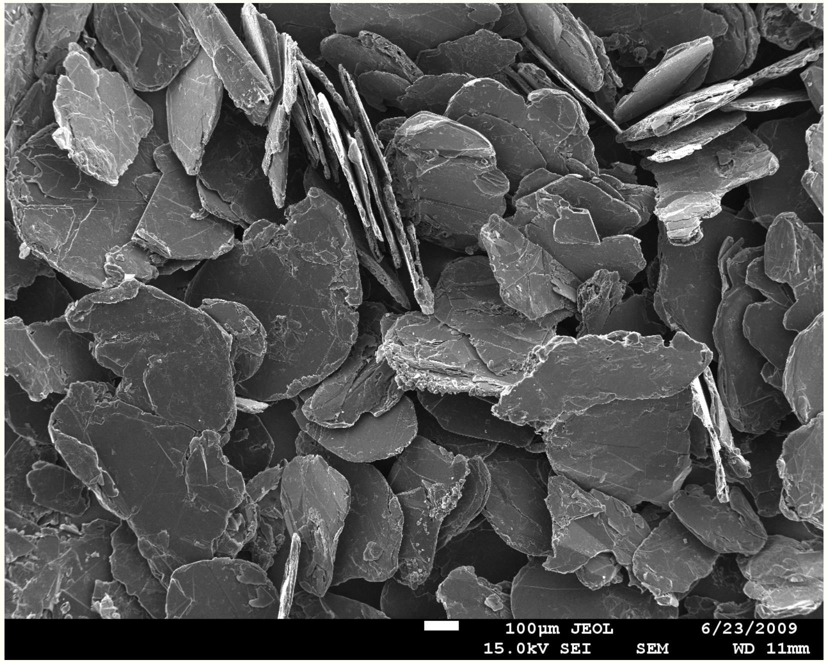


Graphene

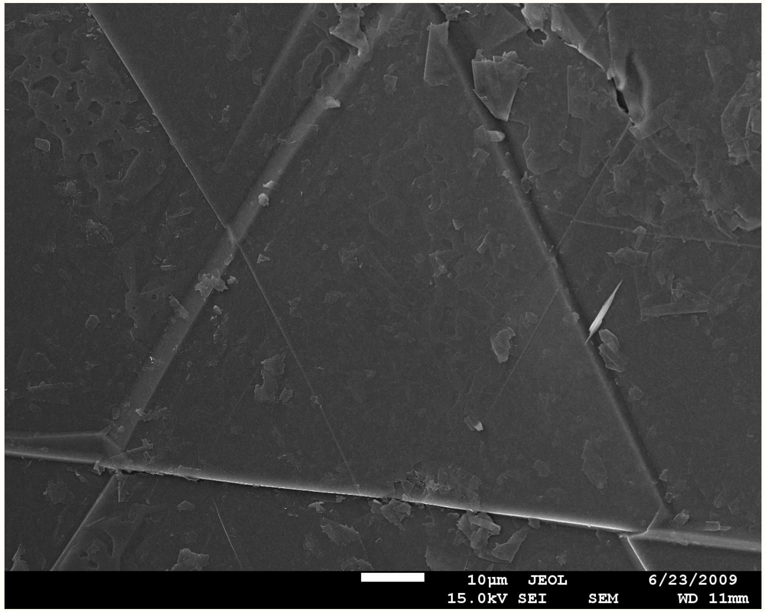


Graphite oxide $(C_2O)_X\,(COH)_{(1-X)}$

Природный кристаллический графит- исходный материал для получения оксида графена

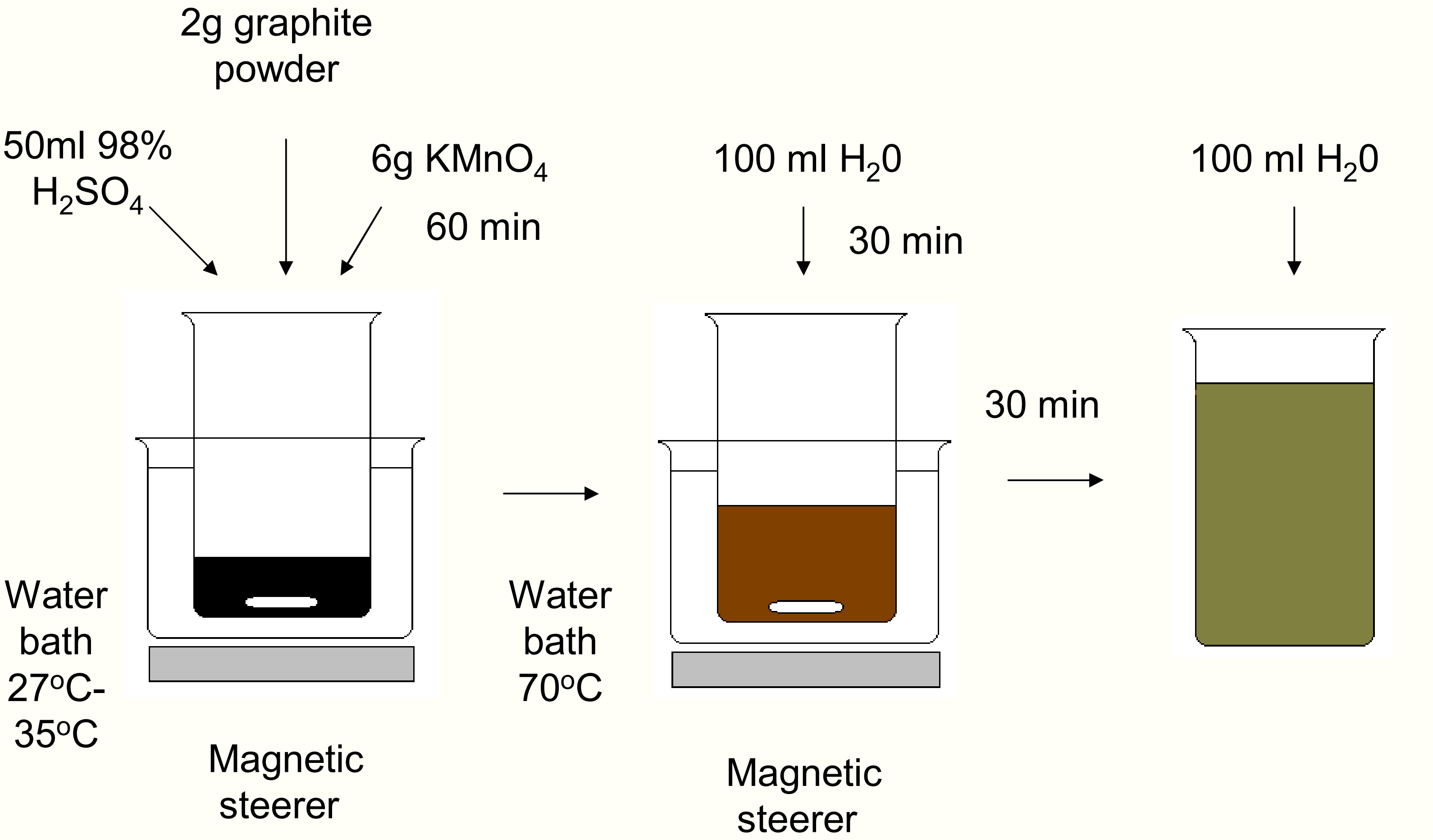


General view of natural crystalline graphite particles

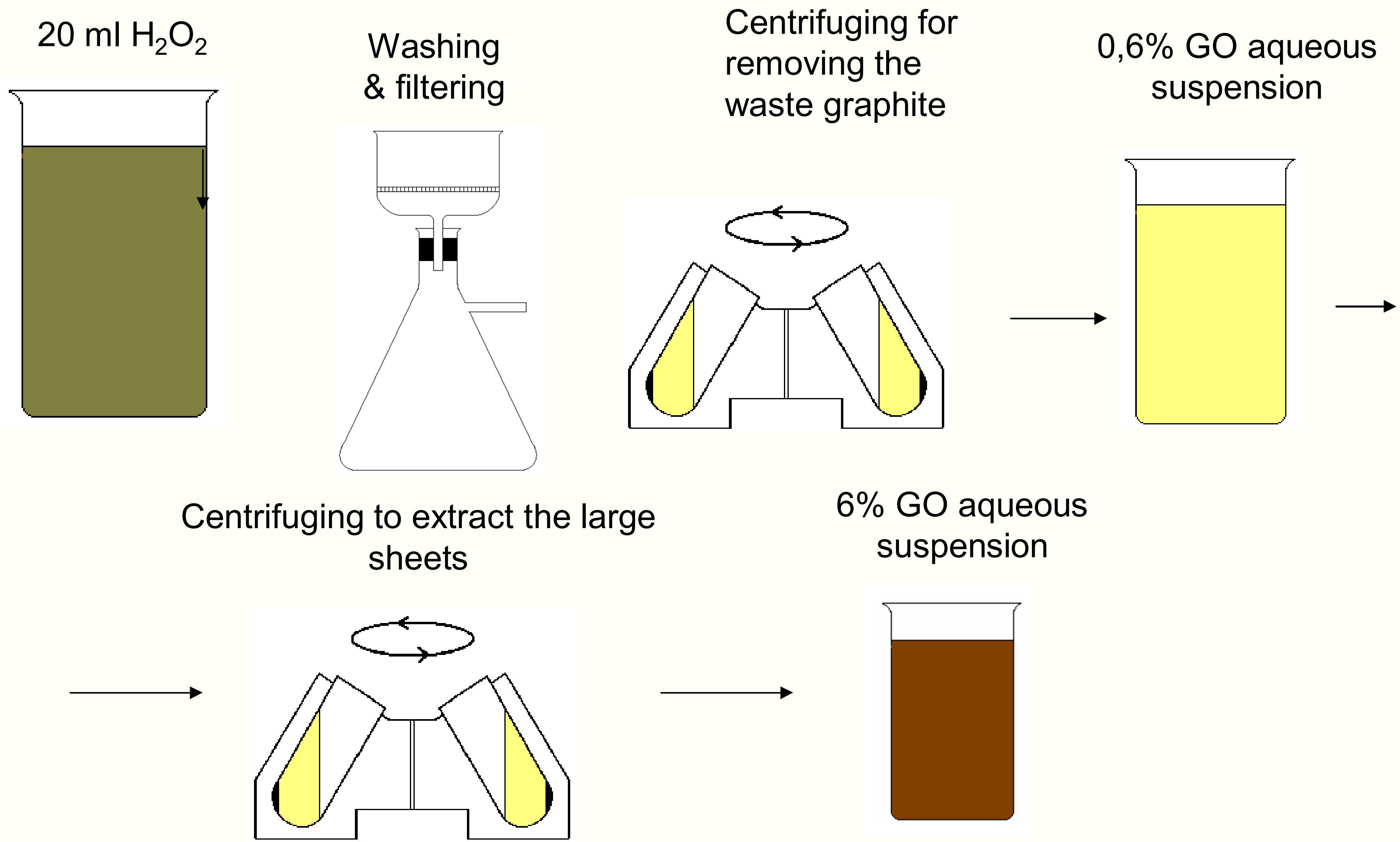


SEM image of [0001] surface of starting graphite

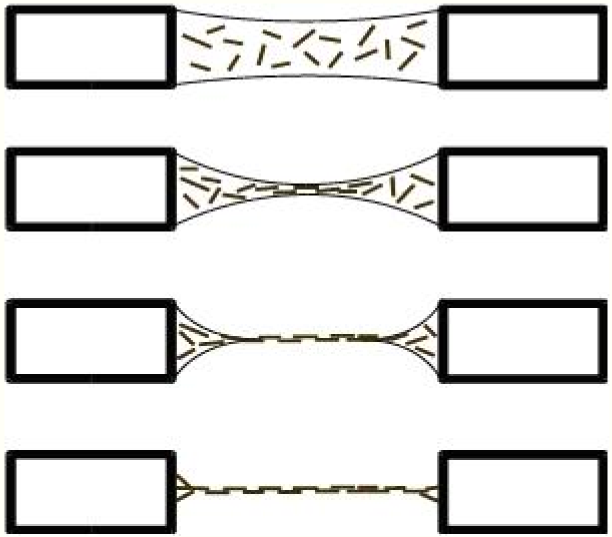
Последовательность окислительной интеркаляции графита



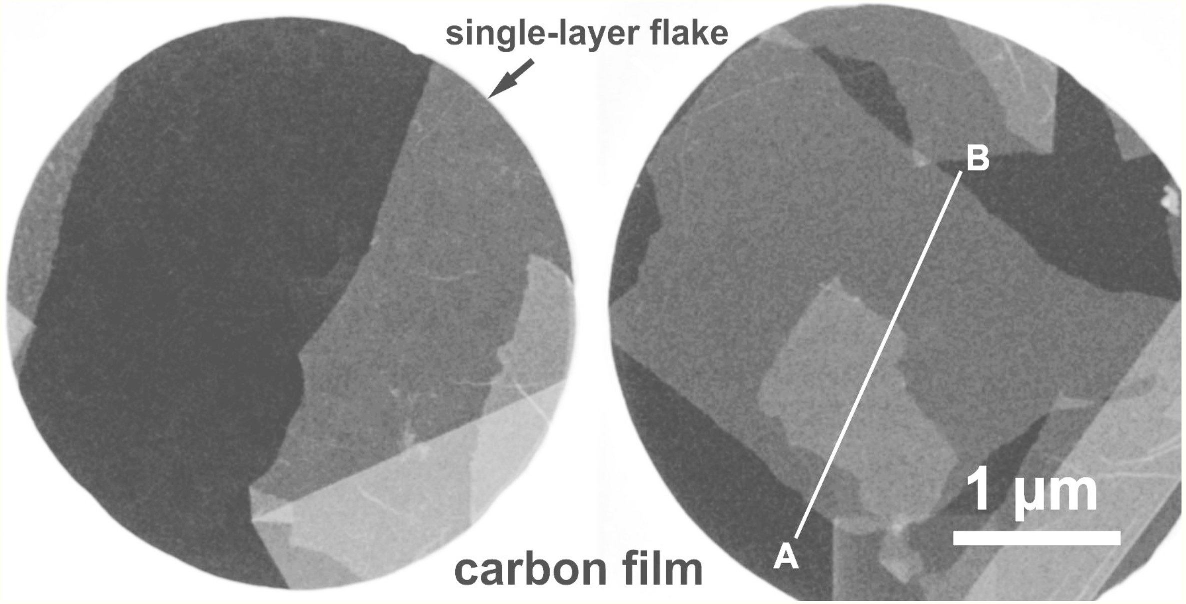
Выделение водной суспензии оксида графена

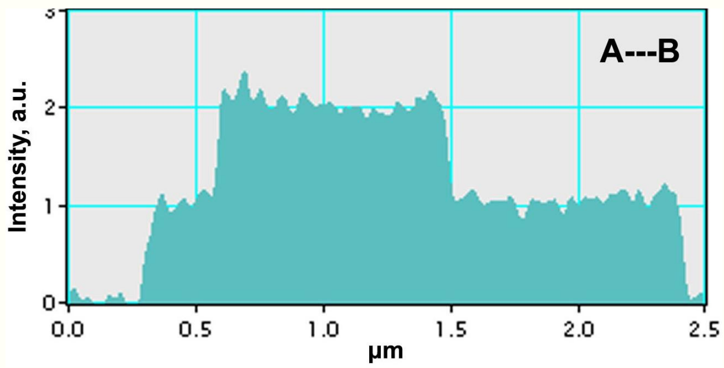


Свойства свободных пленок оксида графена

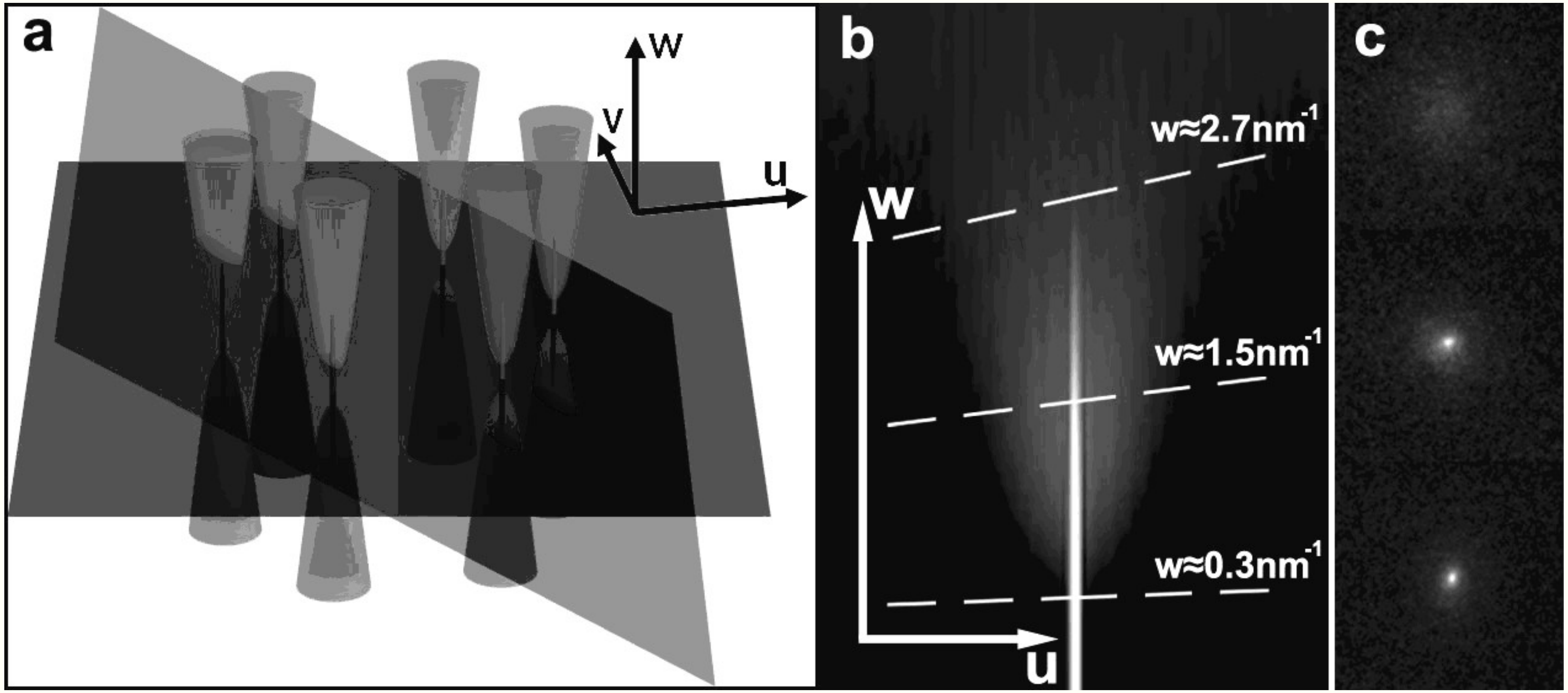


Formation of free standing GO membranes from aqueous suspension

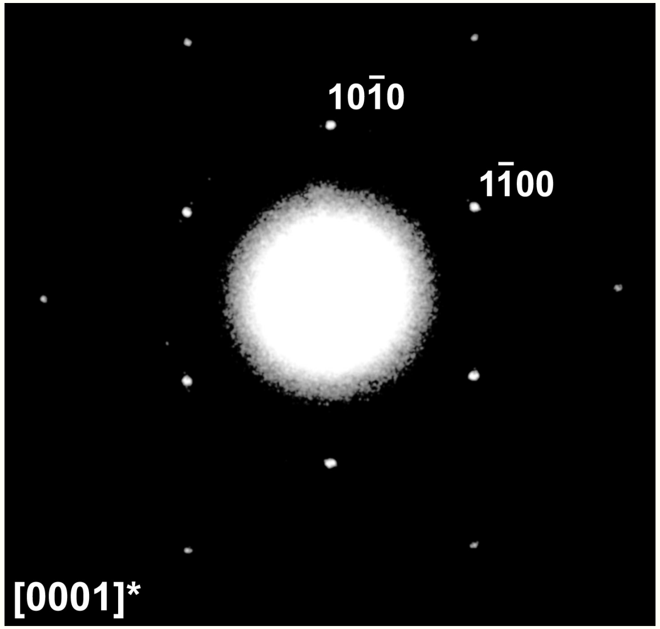


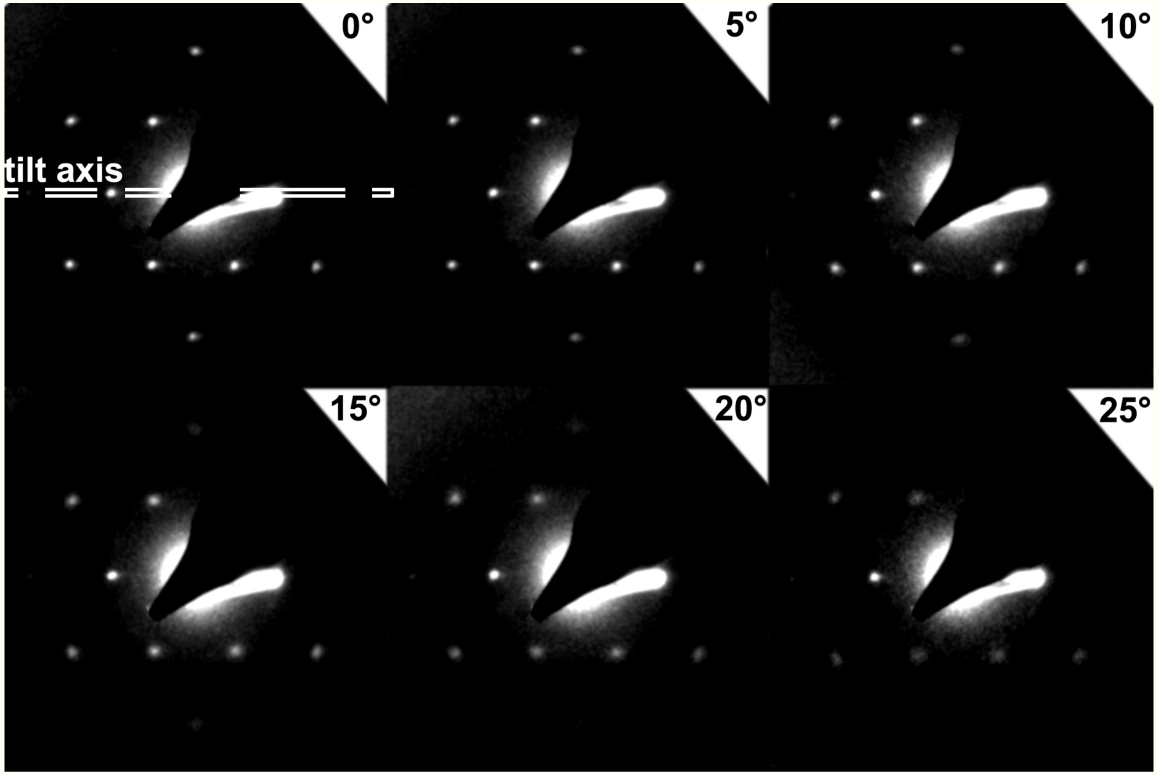


Дифракция электронов на слое оксида графена



Картина дифракции электронов на однослойной пленке оксида графена





The evidence for single layer structure of free standing GO films

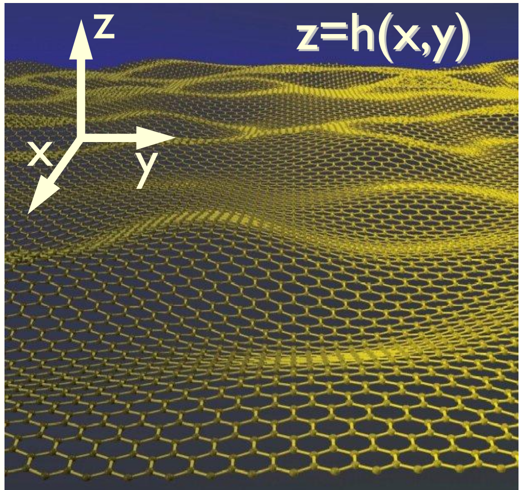
Волнистый рельеф свободной пленки оксида графена в обратном пространстве

$$F(u,v,w)=\iint_{XY} dydx\exp(2\pi i w h(x,y))\exp(2\pi i(ux+vy))$$

Expansion at small ***w***:

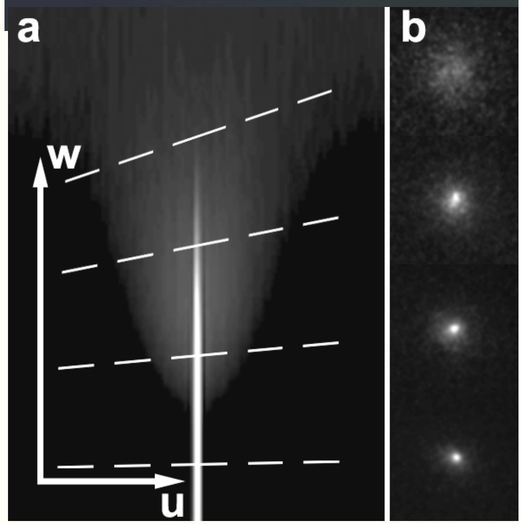
$$F(u,v,w)\approx\delta(u,v)\times(1-2(\pi w)^2\overline{h}^2)+2\pi i w h_q(u,v)$$

$$I=I_0\exp(-(2\pi w)^2\overline{h}^2)$$



Uncorrelated ripples:

$$\ln I \;\; vs \;\; w^2\propto\overline{h}^2$$



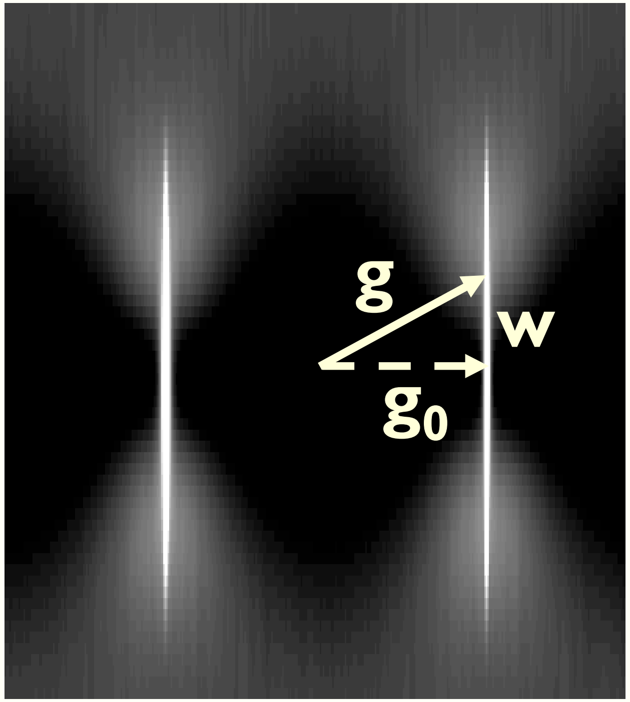
Spot’s broadening:

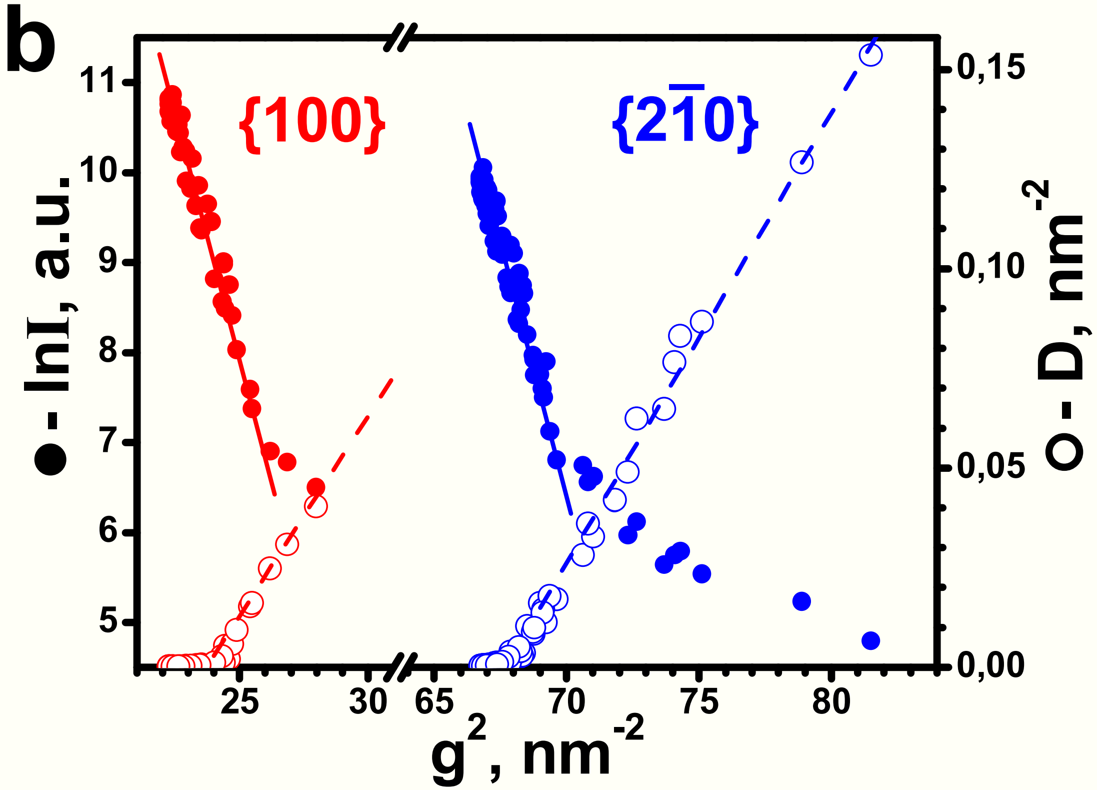
$$D=w^2\,|\nabla h|^2$$

Additionally:

$$\frac{|\nabla h|^2}{\overline{h}^2}=|\vec{q}\,|^2$$

Рельеф, оценка высоты и масштаба



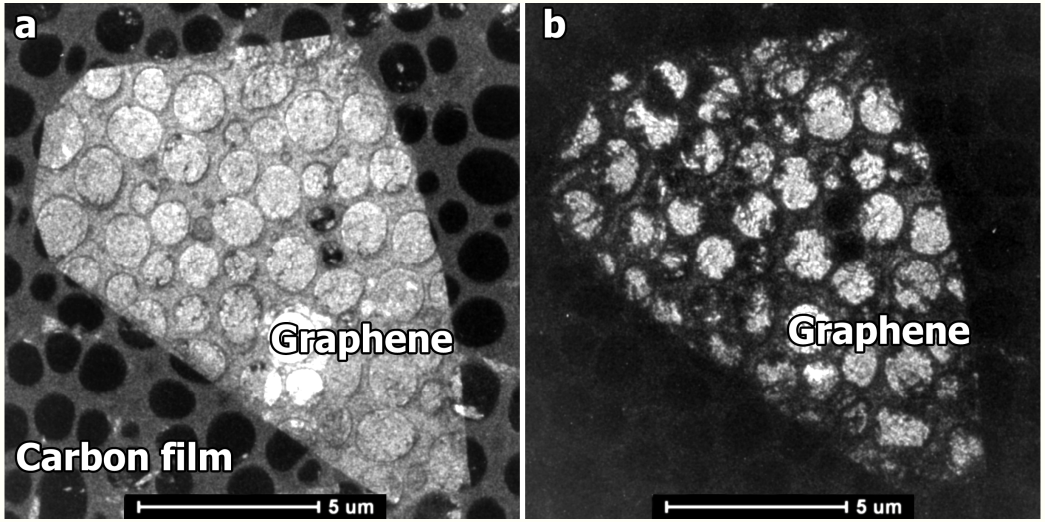


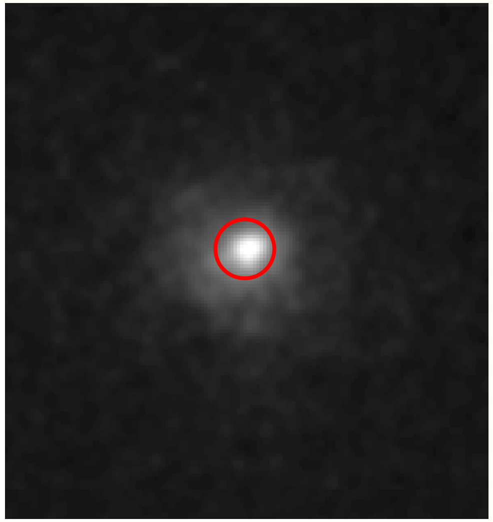
α≈4° h≈0,3nm l≈12nm

Graphene attached to a substrate

Suspended≈0,3nm

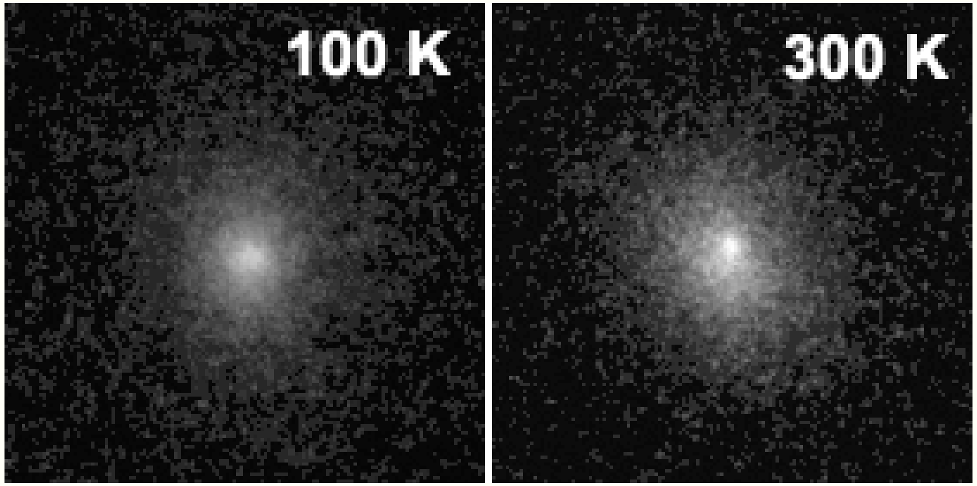
Attached≈0,4nm



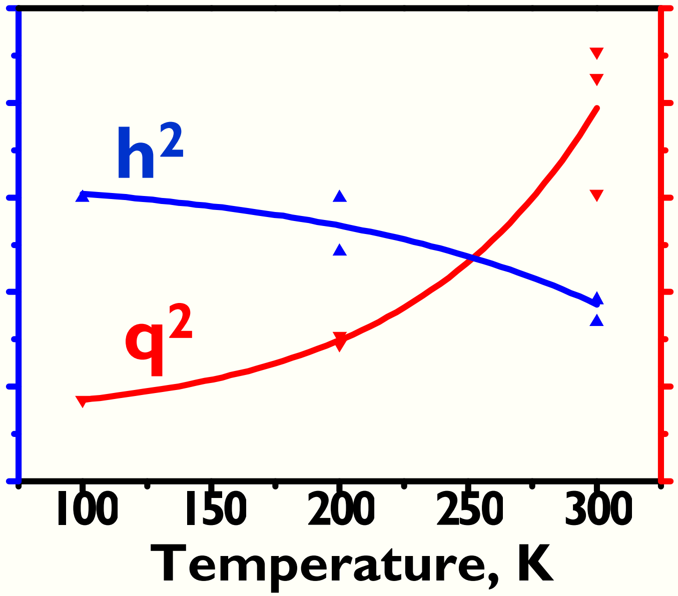


Suspended graphene is more flat than attached to the film

Temperature dependence of ripple spectrum



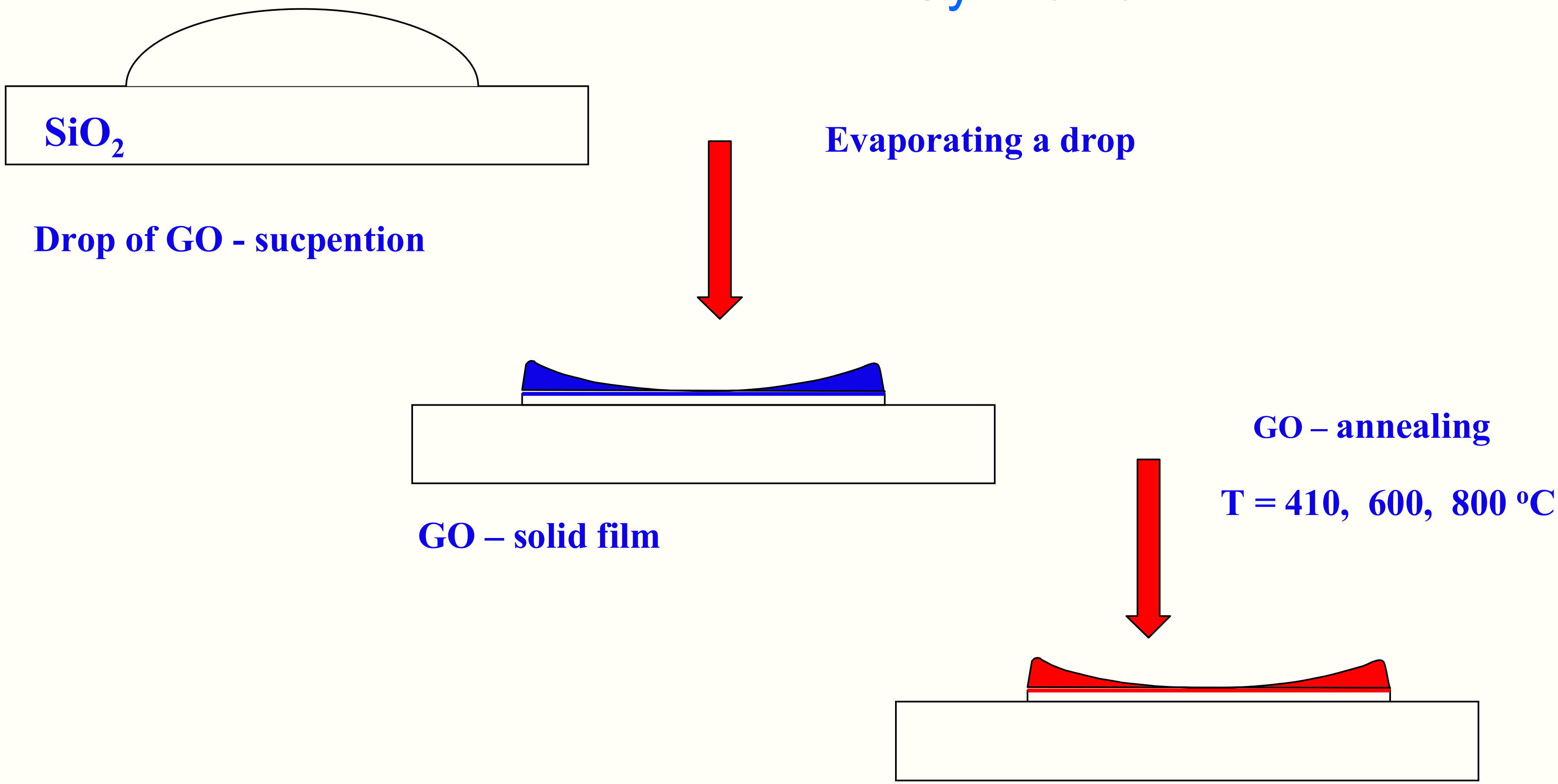
w≈0,1g



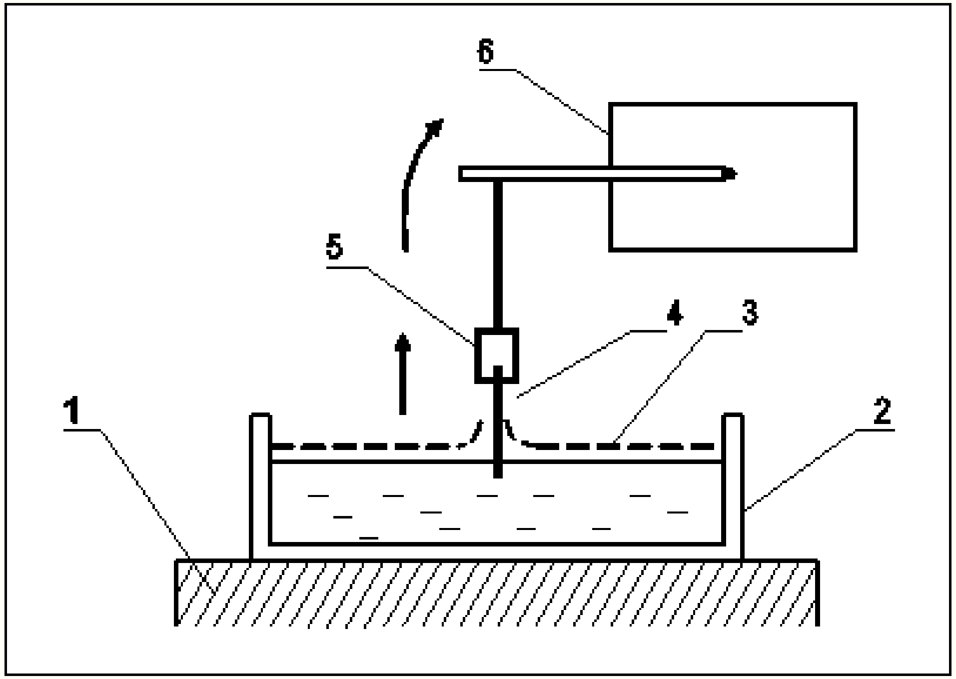
Average wavevector qualitatively follows the theoretical predictions, but roughness decreases with temperature in this temperature range

Получение пленок ОГ на твердых подложках

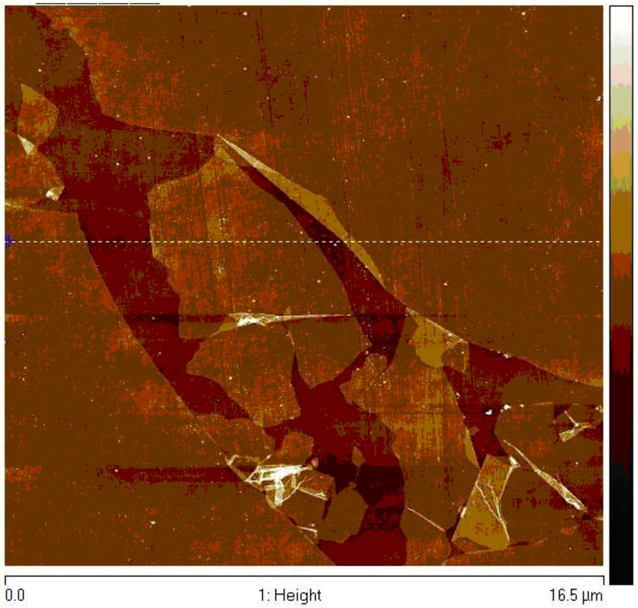
Сушка капли

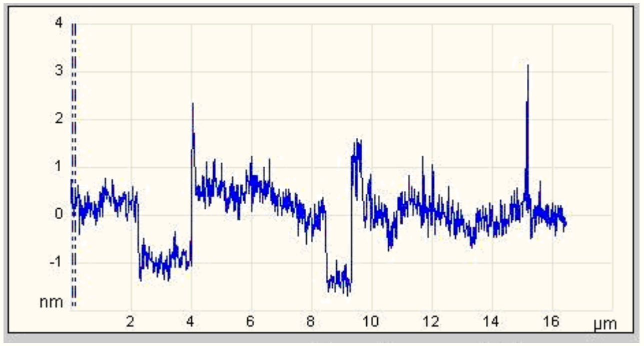


Получение однослойных гладких пленок ОГ на кремниевых подложках методом Ленгмюра-Блоджет



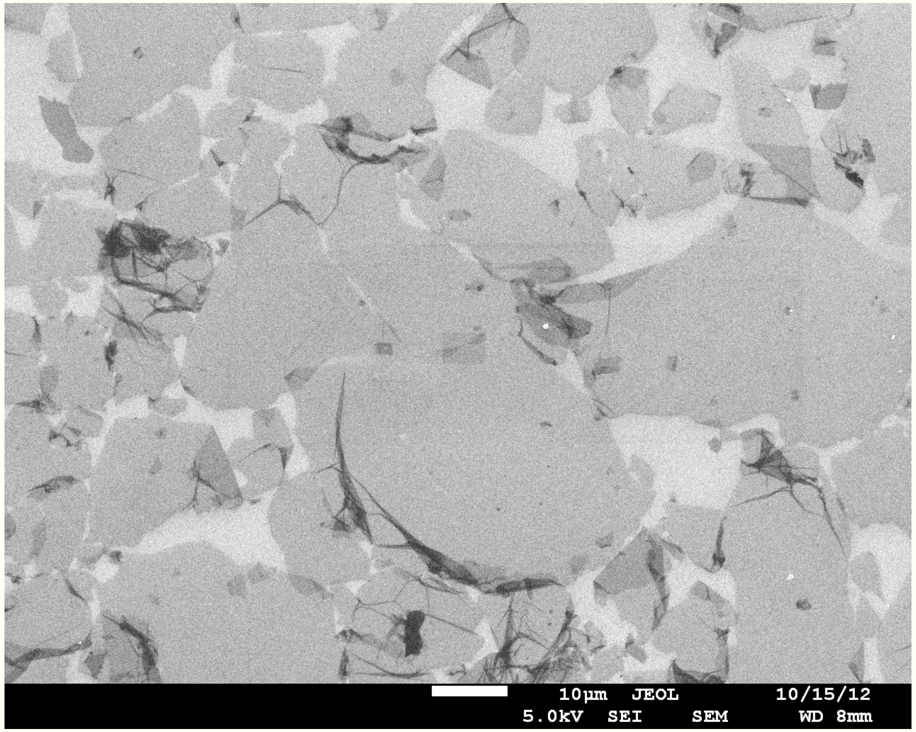
1.Base; 2. Cup, 3.Film on the water surface,
4.Substrate, 5.Holder, 6.Lifting gear.

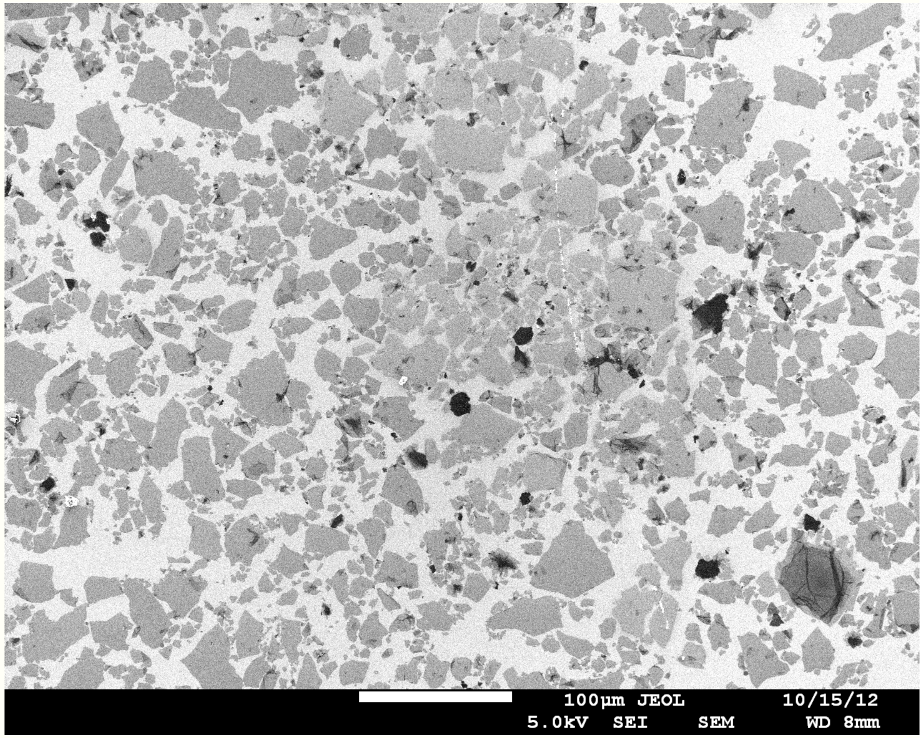




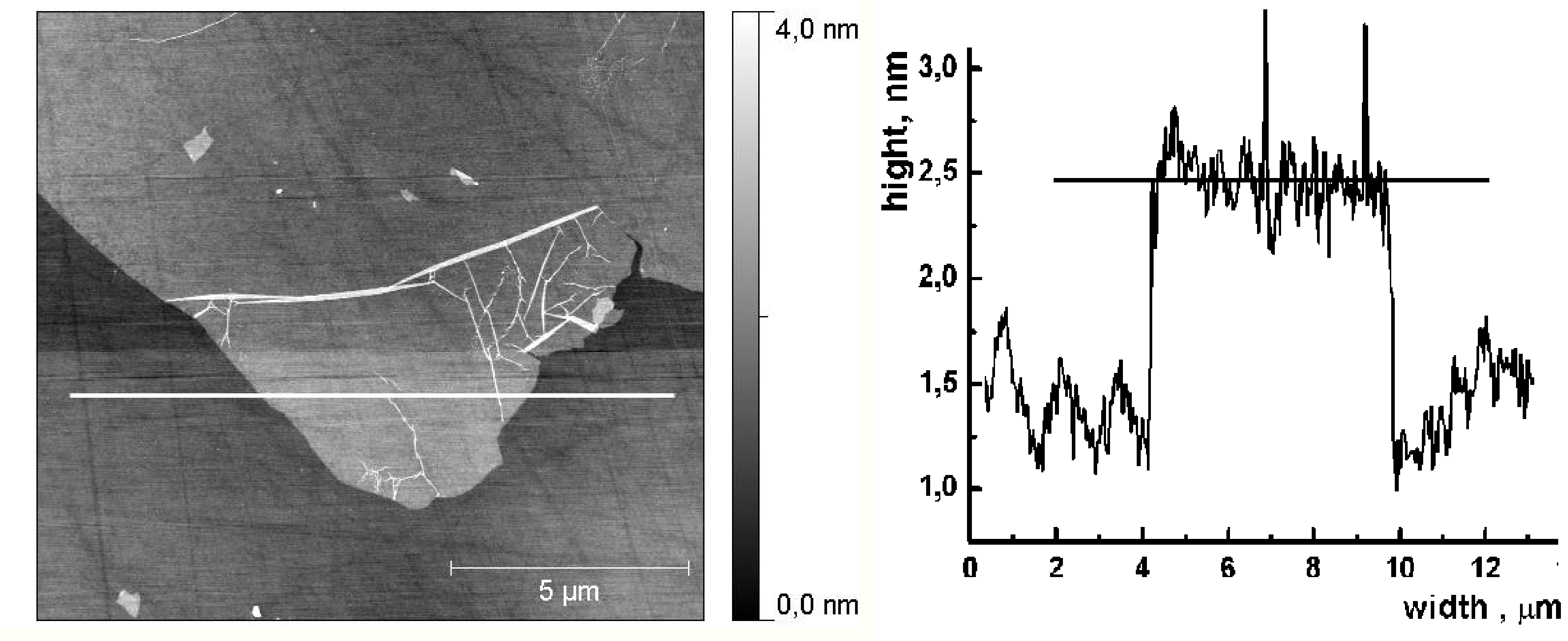
AFM image of single layer graphene film

SEM изображения однослойный пленок ОГ на кремнии

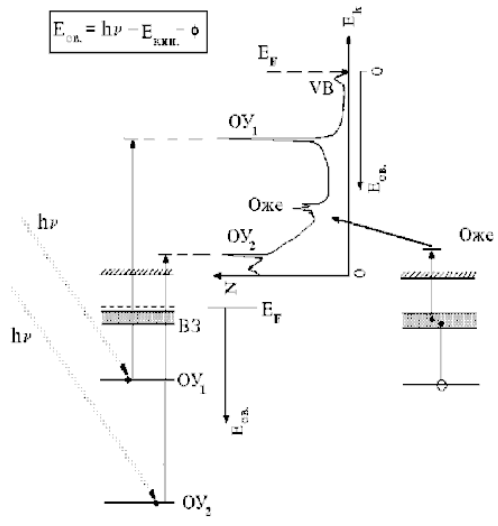


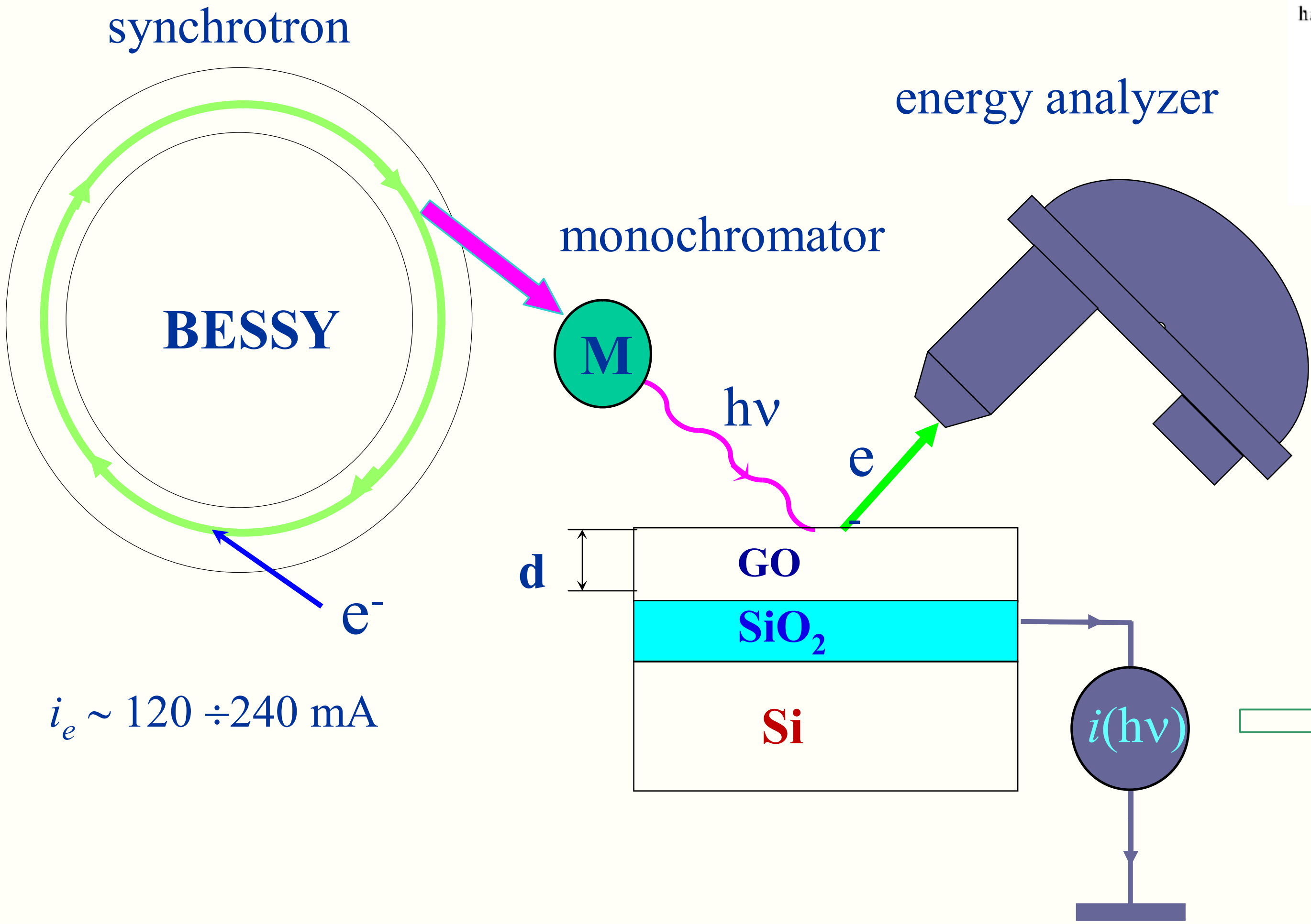


AFM изображение и профиль высот однородных фрагментов ОГ на кремнии



Рентгеновская фотоэлектронная спектроскопия ОГ на кремниевых подложках





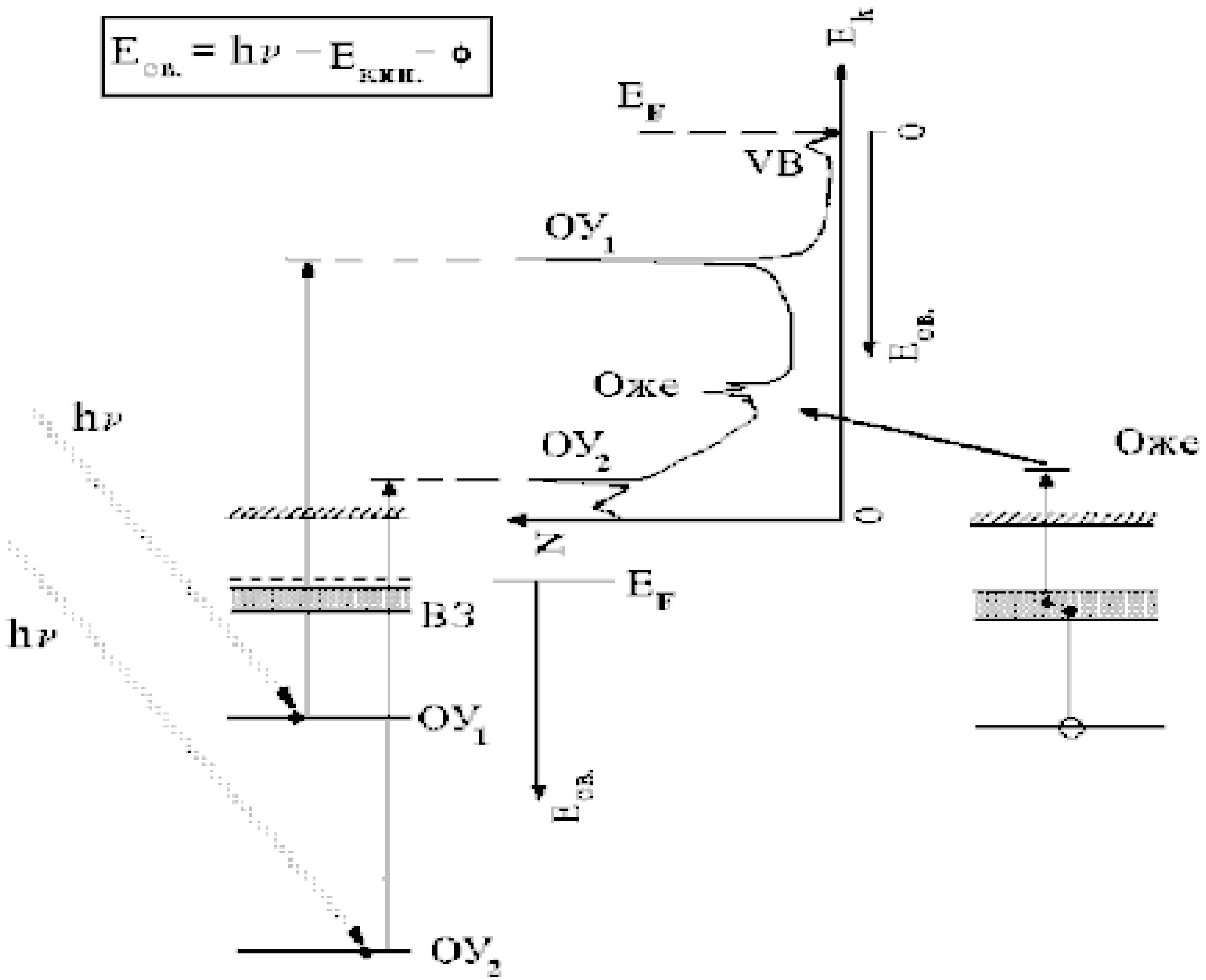
XPS :
information depth
~ **1÷2 nm**

P < 2*10^{-10} Torr

NEXAFS :
information depth
~ **10÷20 nm**

Основы фотоэлектронной спектроскопии твердого тела

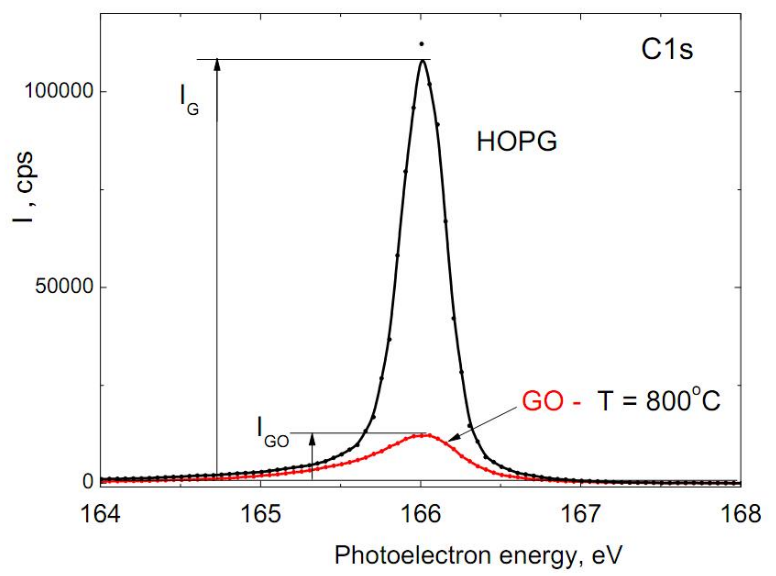
$$E_{св.} = h\nu - E_{кин.} - \phi$$



Оценка толщины пленок ОГ по спектрам C1s

$$l = \lambda_{GO} \ln\left(1 - \frac{I_{GO}/\lambda_{GO}}{I_G/\lambda_G}\right)^{-1},$$

- where λ_{GO} and λ_G are the mean free paths of C1s photoelectrons in GO and HOPG, respectively.



at $E_K \sim 160$ eV $\lambda_G = 2.5$ SL

[1] Seah M.P., Dench W.A. // Surf. Interface Anal., 1979. V. 1. P. 2.

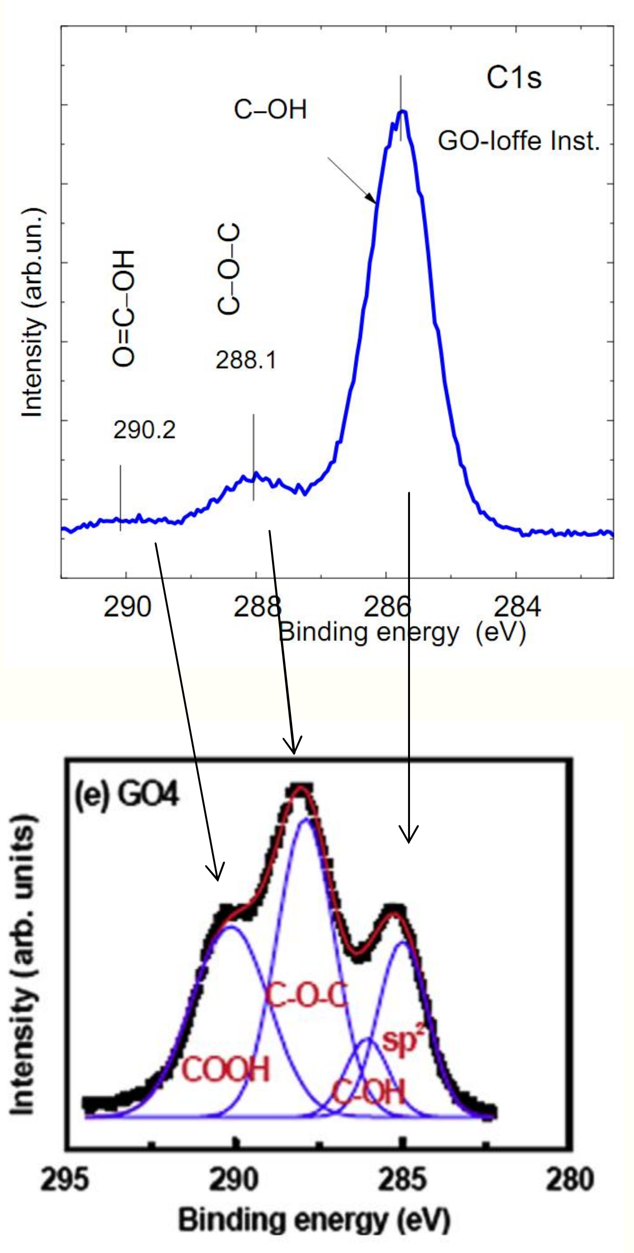
The distance between Single Layers is 3.5 Å

Fig. 1. C1s photoelectron spectra of HOPG and GO film (T = 800°C). Primary X-ray photon energy, hν = 450 eV.

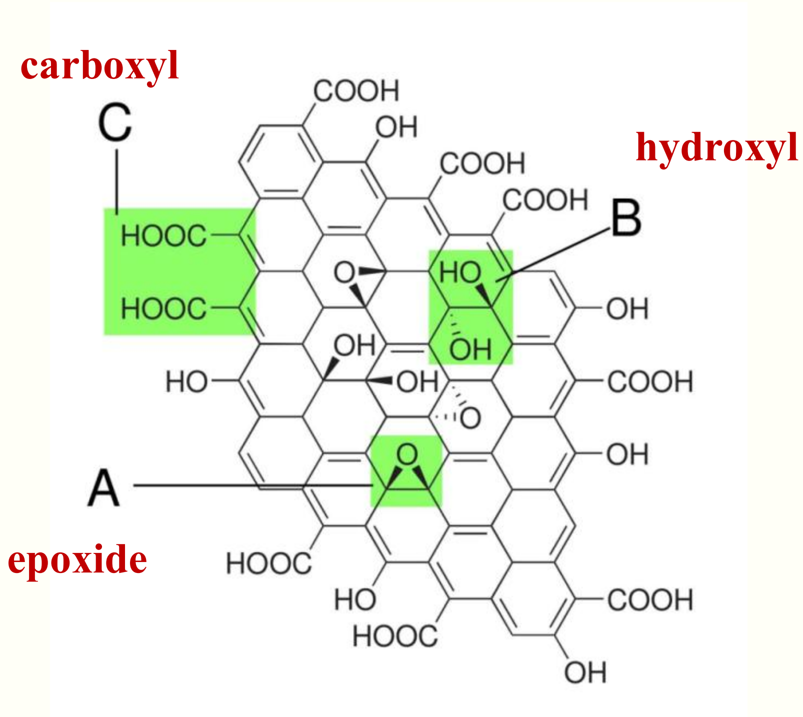
GO films with an average thickness of $l \sim 2$ SL were studied.

•

Химический состав пленок ОГ



Typical photoelectron spectra of C1s core level for GO films. The photon energy is hν = 450 eV.

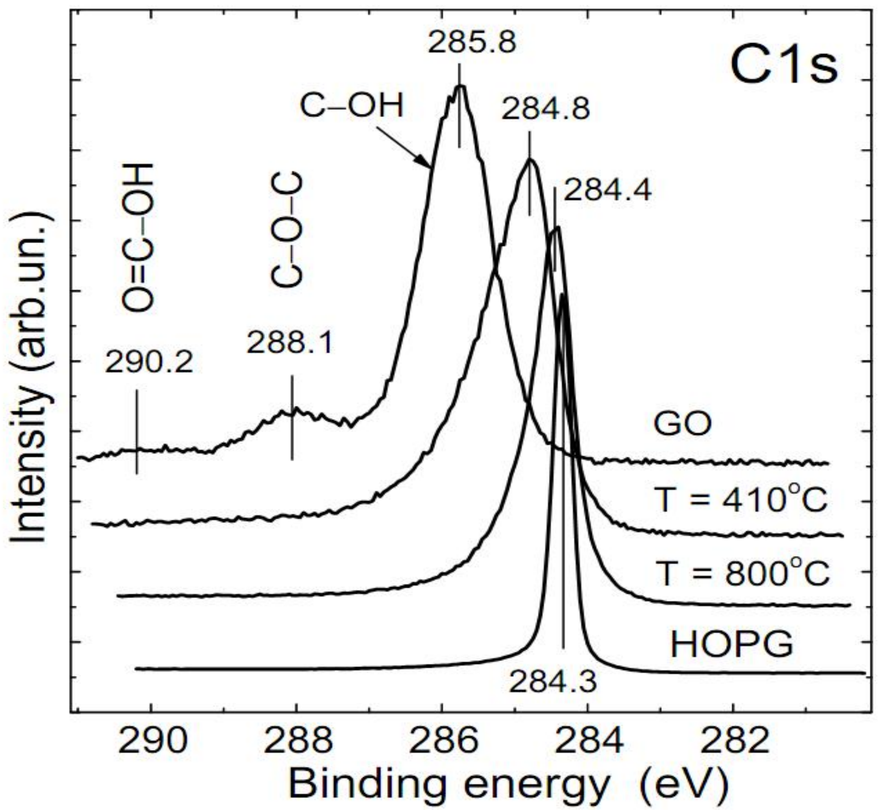


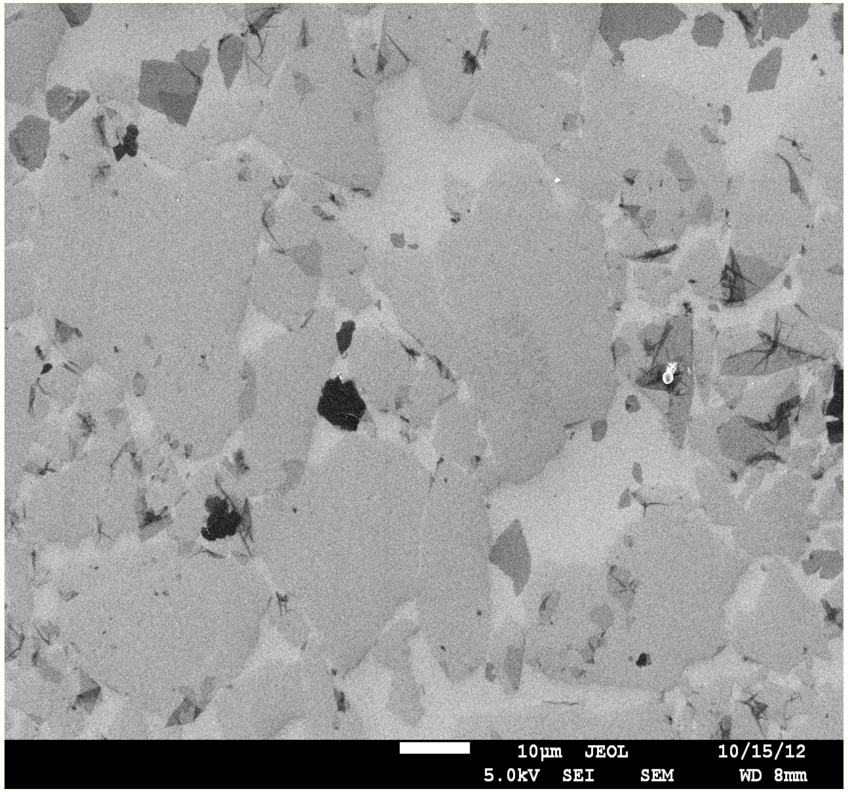
Since carboxil group is localized predominantly at the edges of GO flakes, it may be concluded that the flakes studied here are rather large.

H-K. Jeong at al., Chem. Phys. Letters **460,** 499 (2008).

Однослойный графен из однослойного ОГ, получаемый термическим восстановлением в водороде

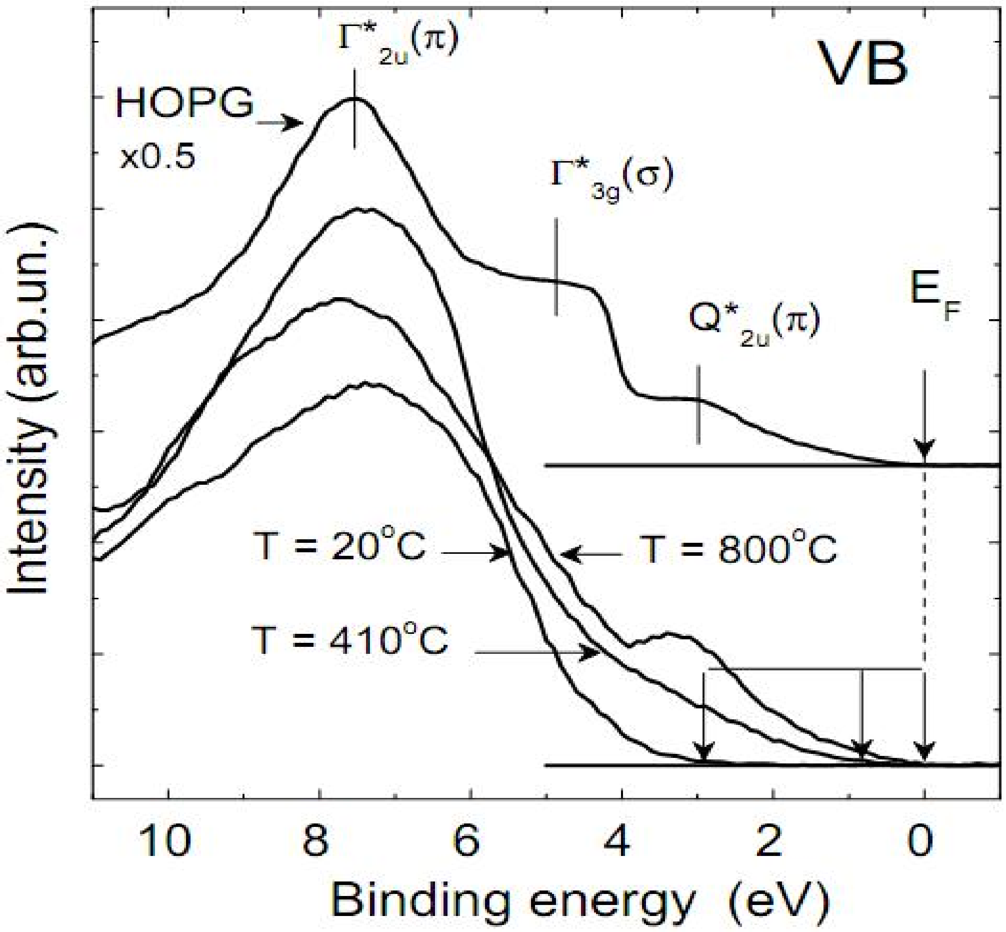
C1s photoelectron spectra of GO, HOPG and reduced GO in hydrogen



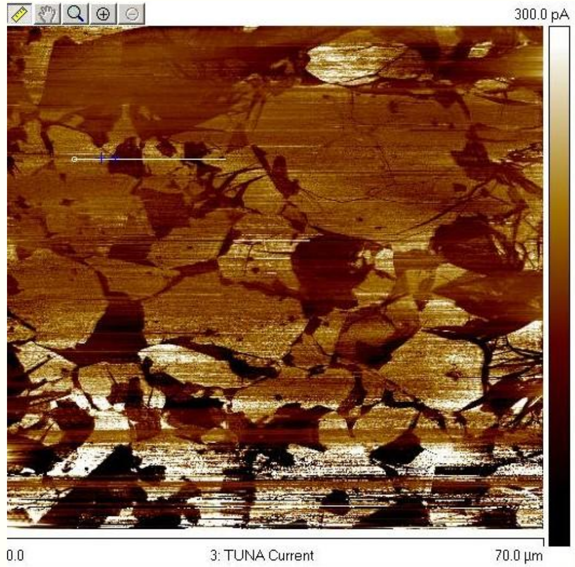


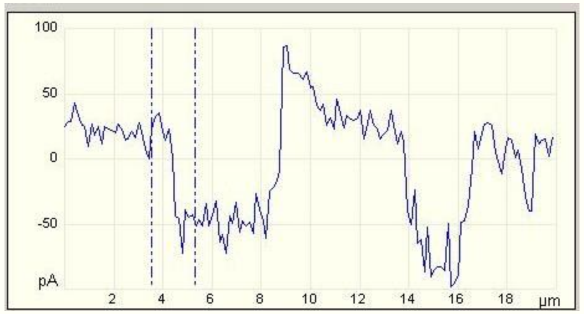
Изменение ширины запрещенной зоны в ОГ термообработкой в водороде при различных температурах

VB photoelectron spectra of GO, HOPG and reduced GO in hydrogen Photon energy 130eV

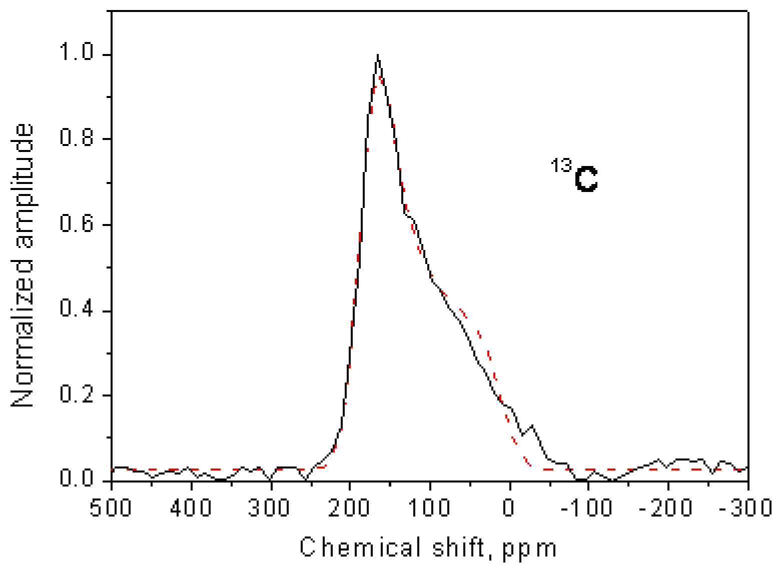


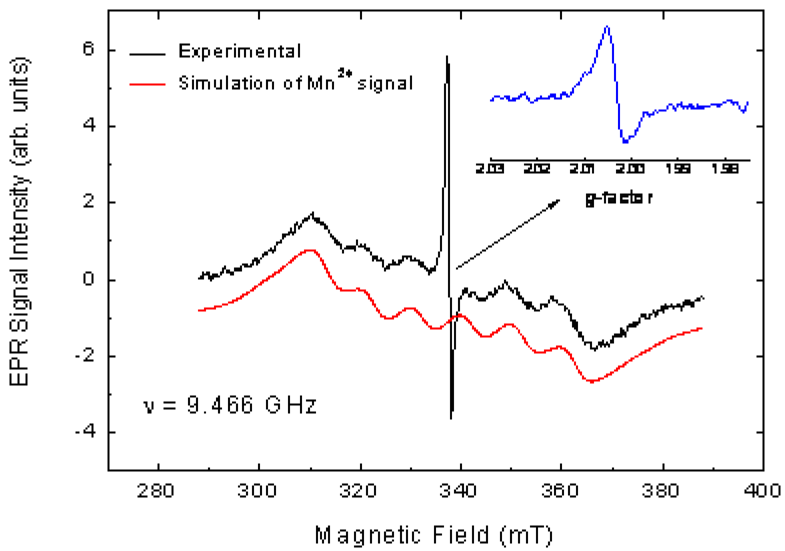
The conductance of reduced GO film by probe scanning technique





ЯМР и ЭПР спектры восстановленного ОГ





The evidence of presence of Mn^{2+} complexes with concentration 10^{-4} ат% in the graphene films reduced from graphite oxide

Валентная зона и запрещенная зона легированного ОГ

GO is known to be a wide-bandgap n-type semiconductor.

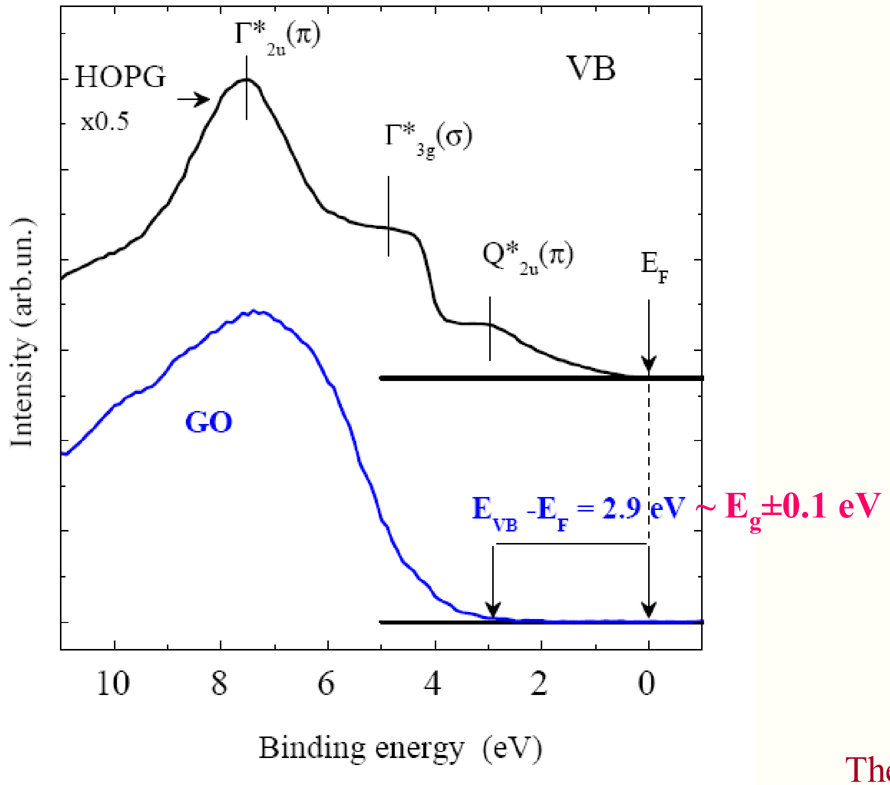
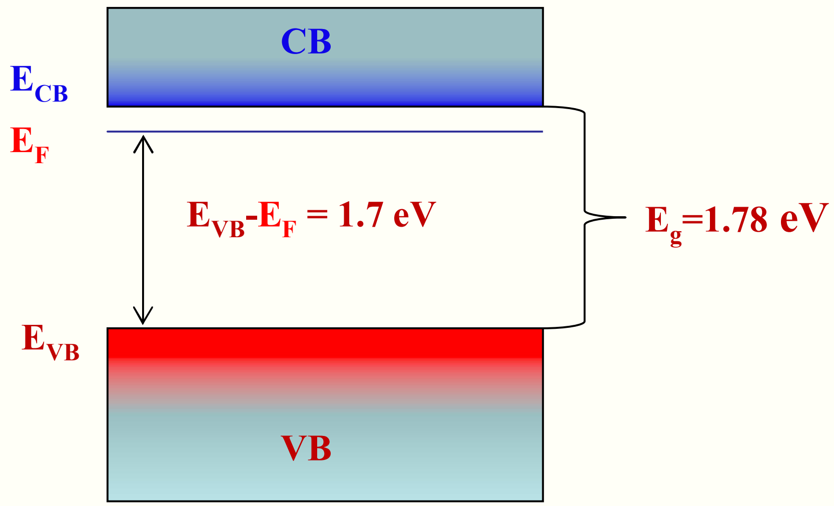


Fig. 1. Photoelectron spectra of GO Valence-band for HOPG and initial GO film. X-ray photon energy, hν = 130 eV.

Comparison of the photoelectron and optical absorption spectroscopy data showed that the Fermi-level in GO is very close to the conduction band edge.

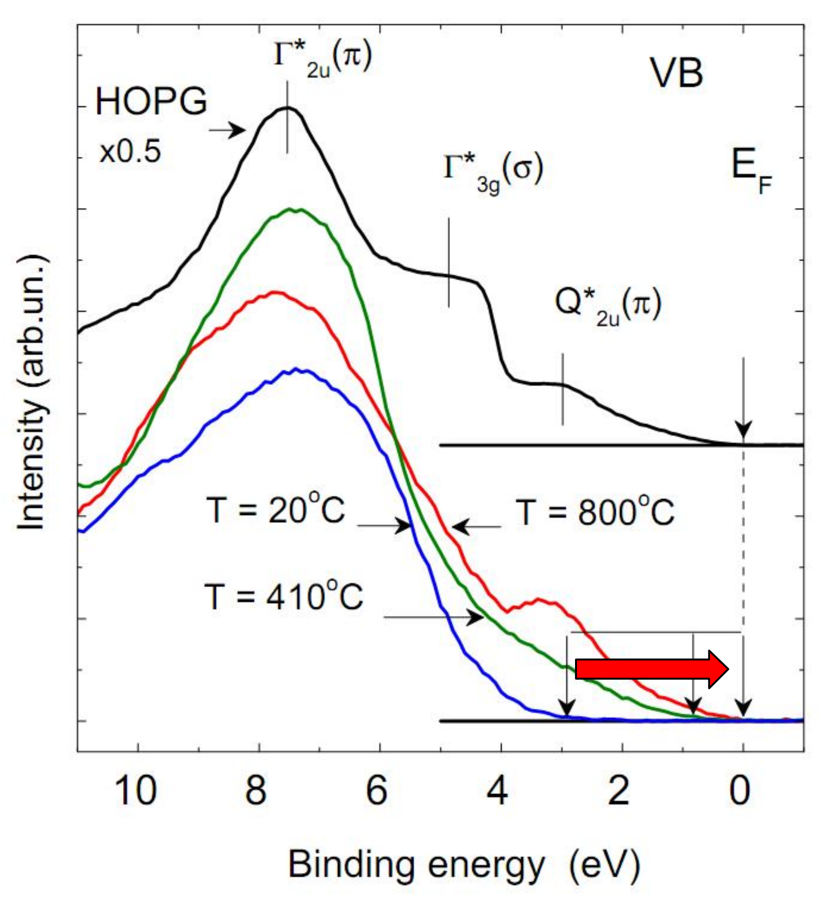
H.-K. Jeong et al., Europhys. Lett. 92, 37 005 (2010).



Therefore, the photoelectron spectroscopy provedes estimation of the GO bandgap with the accuracy better than 0.05 eV.

The bandgap reaches 3 eV in studied GO films.
This gap almost doubly exceeds those reported previously.

Трансформация валентной зоны в пленкх ОГ при термообработке



Increase in the annealing temperature leads to narrowing of the bandgap.

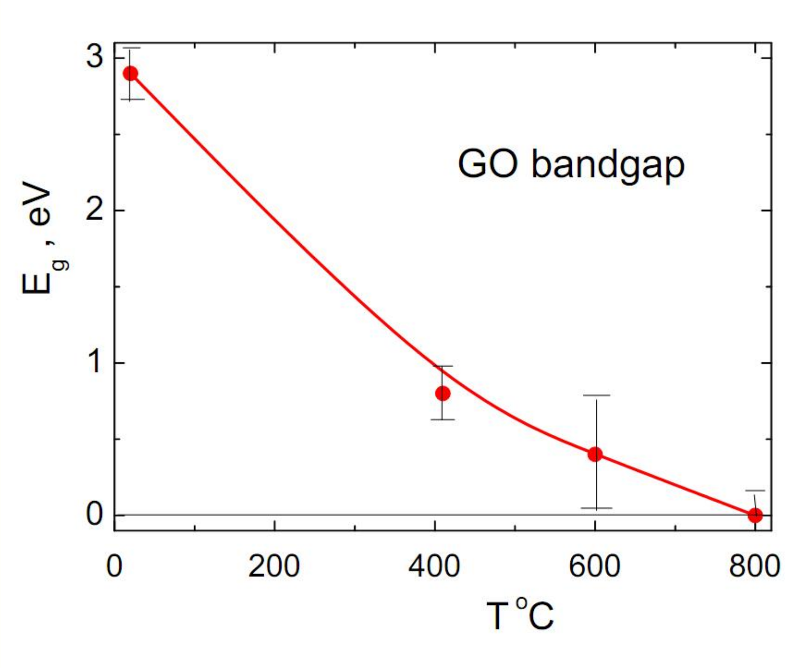
After treatment at T = 800°C, the edge of the valence band attains the Fermi level.

The high-temperature annealing leads to restoration of the DOS of graphite, primarily of the π- states.

This is a result of the rupture of chemical bonds to the oxygen functional groups and recovery of the π-electron sub-system.

Fig. 1. Valence-band photoelectron spectra of HOPG, initial GO film, and the films annealed at different temperatures. X-ray photon energy, hν = 130 eV.

Управление шириной запрещенной зоны ОГ отжигом при различных температурах



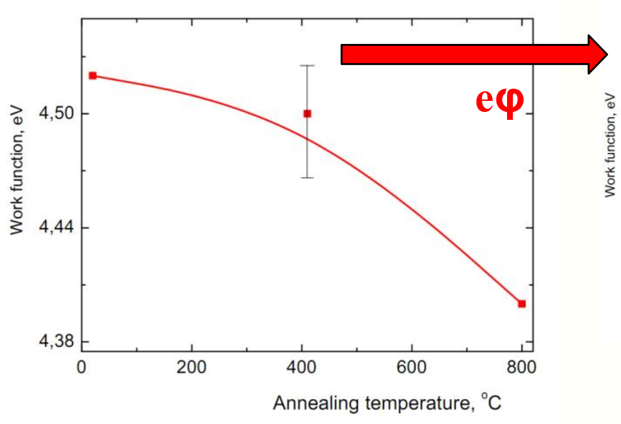
Dependence of the GO bandgap width on the annealing temperature.

One can see that GO bandgap can be controlled by varying the temperature of the heat treatment.

By this means, the GO nanolayers can be modified from dielectric to conductor through semiconductors with the bandgap smoothly passing over the entire optical spectrum:

E_g = 3 ÷ 0 eV.

Работа выхода не изменяется



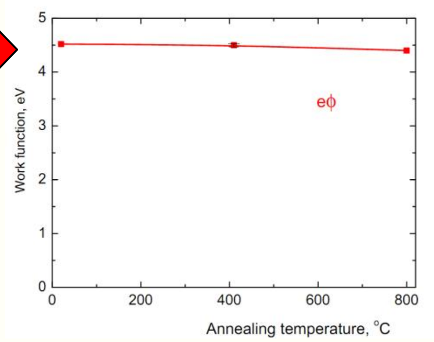


Fig. 2. Dependence of the GO work function on the annealing temperature.

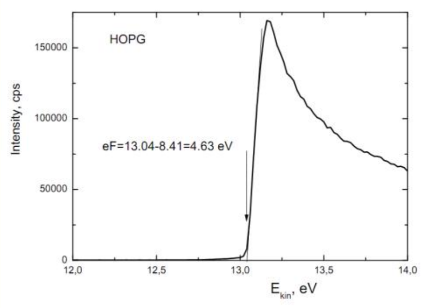
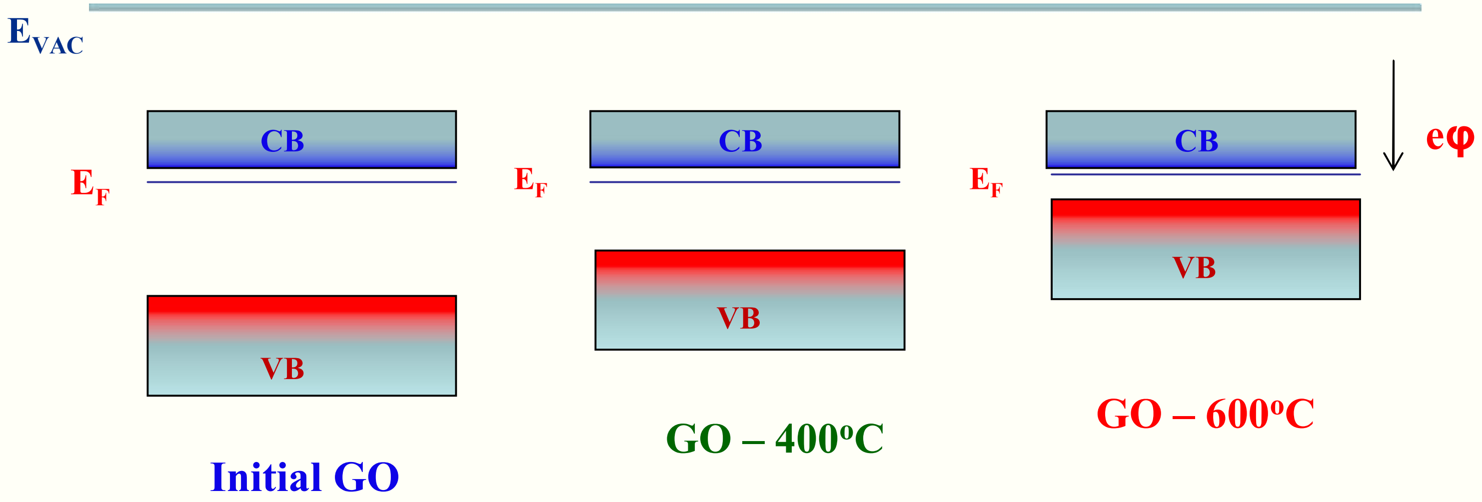
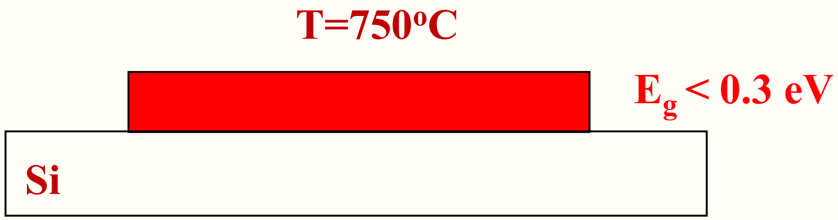


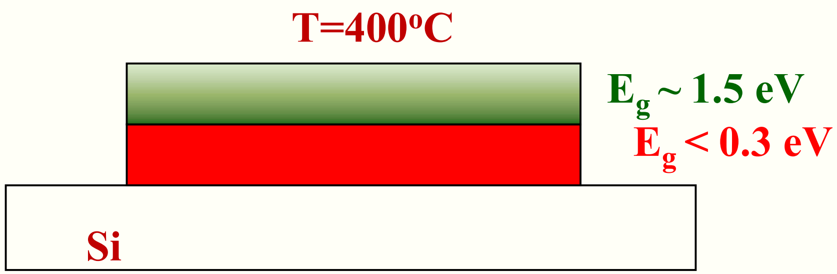
Fig. 1. The cut-curve for work function determination.

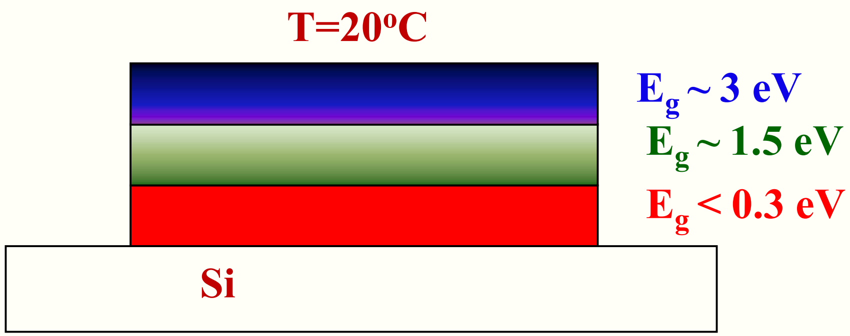
Трансформация электронной структуры ОГ при отжиге



Возможная технология последовательного формирования пленочных гетероструктур для солнечных элементов на основе ОГ

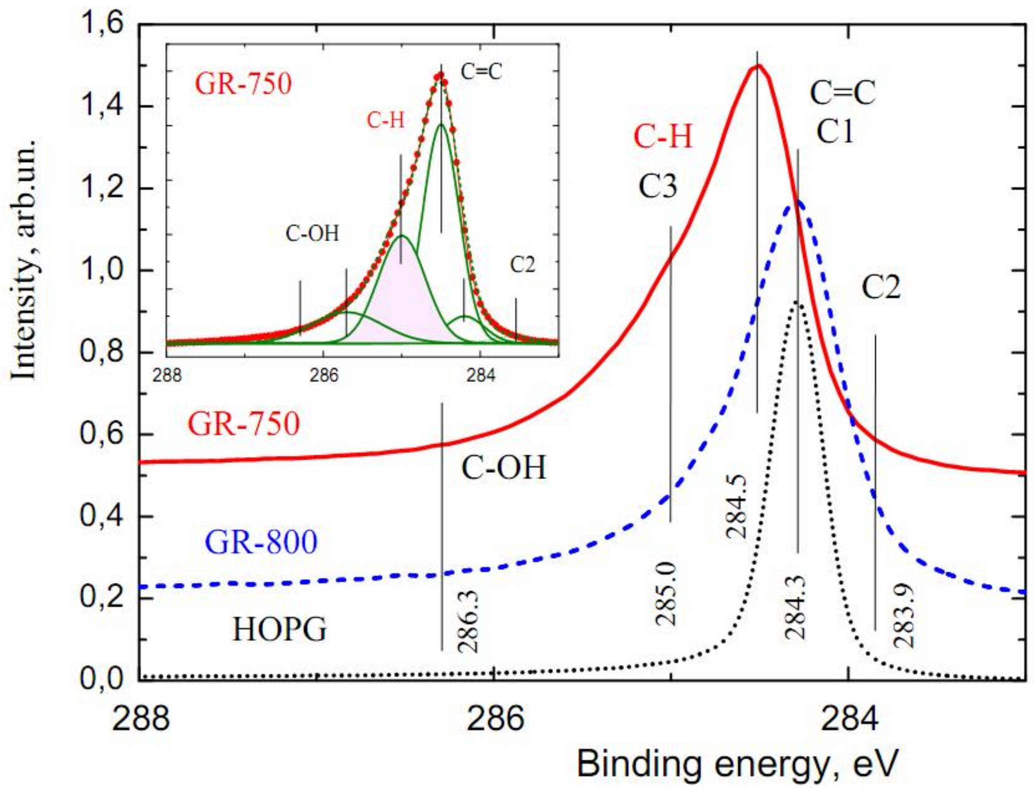






The sequence of the layers is convenient for photovoltaic: the narrow bandgap layers treated at high temperature first are placed below, and the wide bandgap layers treated at low temperatures are placed above.

Формирование связей C-H на поверхности ОГ при отжиге в водороде по данным XPS

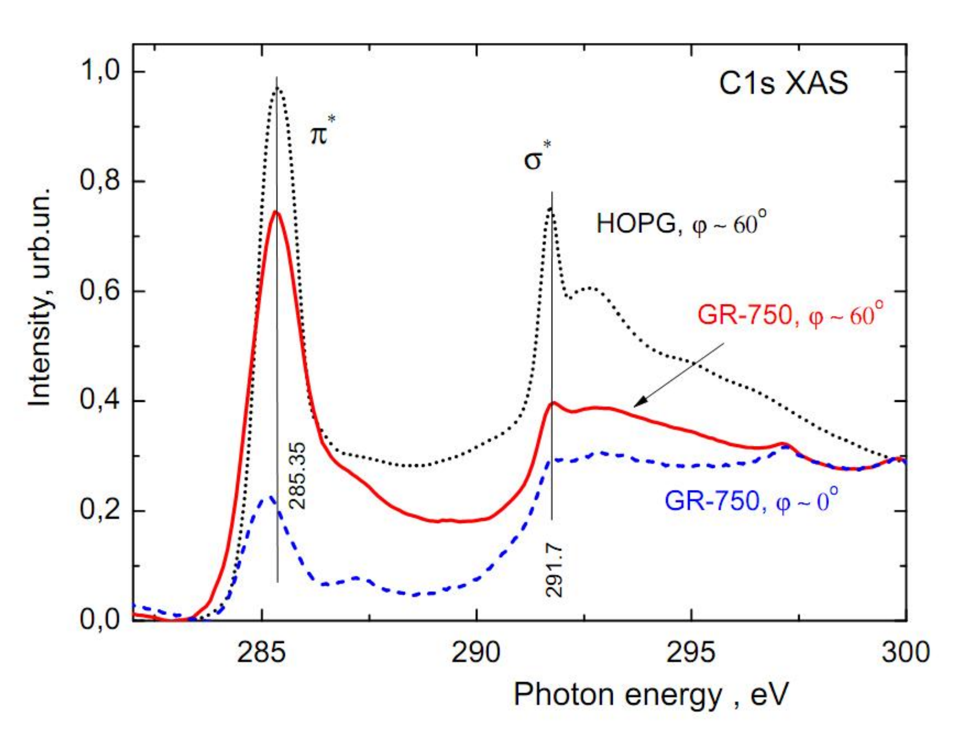


C1s photoelectron spectra of HOPG and the films annealed in hydrogen at different temperatures: T = 800°C and T = 750°C.

The insert shows decomposed spectrum of the GR750 film.

H-coverage strongly depends on the temperature and reaches the value H/C ~ 40 at % .

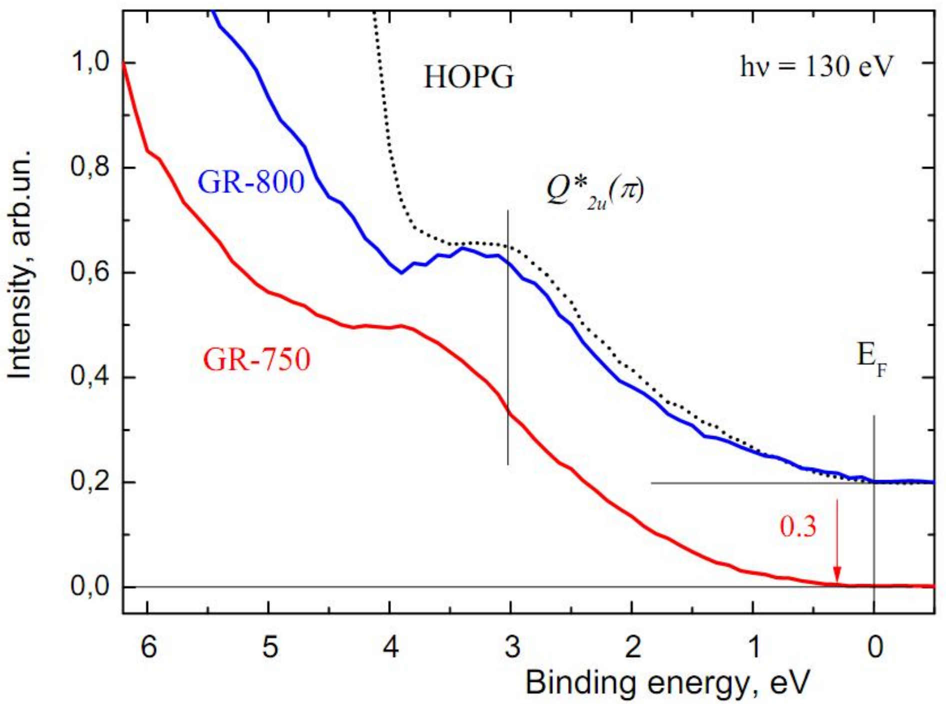
Гидрирование ОГ в спектрах NEXAFS



NEXAFS spectra for HOPG and GR750 film.

Decrease in the π* peak intensity as compared to that of PG is a result of hydrogen atoms attachment to graphene sheet and transformation of the corresponding part of π-bonds into C-H σ-bonds.

Изменение запрещенной зоны и гидрирование ОГ при отжиге в водороде



Valence band spectra of HOPG and the films annealed in hydrogen at different temperatures: T = 800°C and T = 750°C.

The VB edge in the film annealed at higher temperature is very close to the Fermi level, indicating occurrence of metallic conductivity.

On the contrary, the VB edge in the film annealed at lower temperature shows the band gap opening.

The bandgap was estimated to be **0.3 eV.**

Диссоциация «горячих» молекул H_2 на поверхности графена

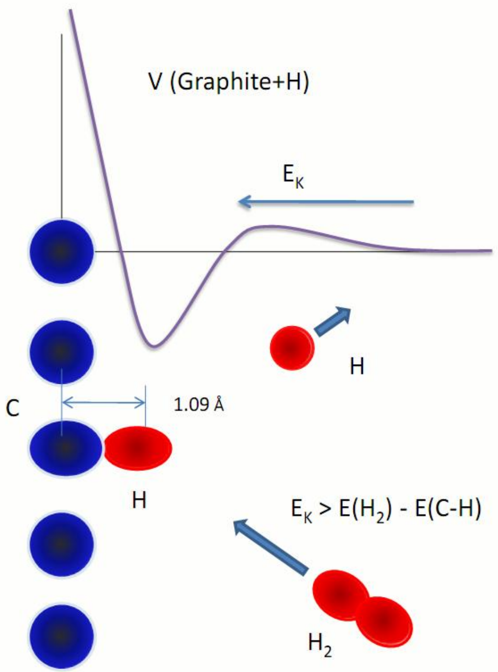


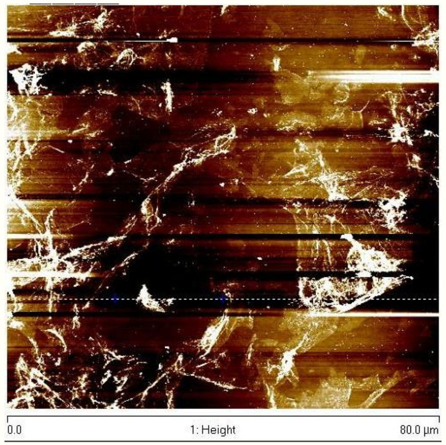
Fig. 1. Scheme of "H_2 – graphene" interaction.

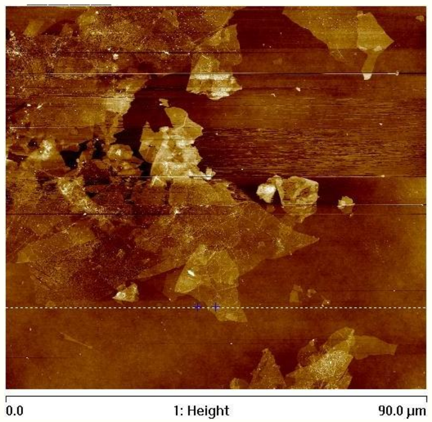
Hot H_2 molecule passes over the barrier in the C-H potential energy curve;

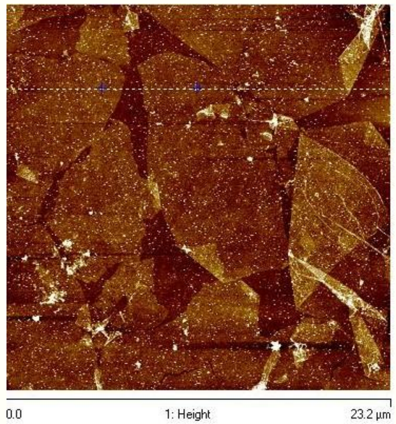
Hydrogen atom approaches carbon atom to the C-H bond length (0.109 nm);

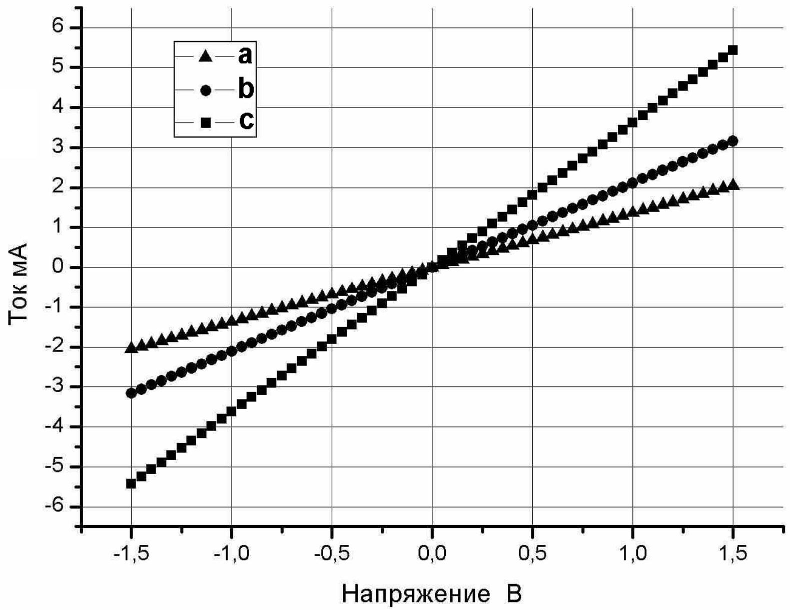
H_2 molecule decays due to excitation in collision and creates C-H bond.

Пленки, полученные восстановлением оксида гарфена и их вольт-амперные характеристики









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