TECHNISCHE UNIVERSITÄT DRESDEN

THEORETICAL INVESTIGATION OF DIAMOND FILMS WITH NANOMETER THICKNESS

Pavel B. Sorokin

Technological Institute of Superhard and Novel Carbon Materials

Moscow, Russian Federation

ТИСНУМ

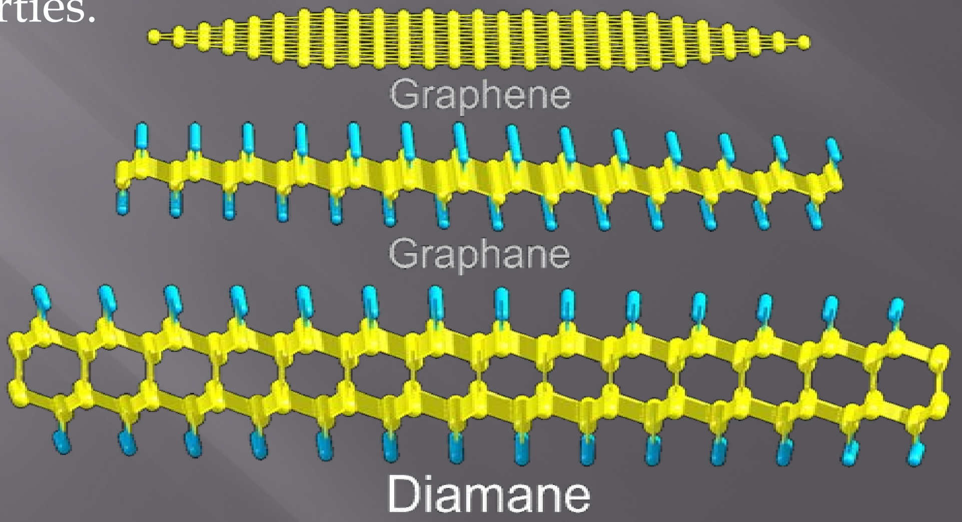
The work was supported by the Ministry of Education and Science of the Russian Federation (Contract No. 14.B37.21.1645) and the Russian Foundation for Basic Research (project no. 12-02-31261)

Outline of talk

- Motivation
- The features of the atomic structure of the *sp*^{3}-hybridized carbon films.
- Electronic and transport properties of the hydrogenated films
- Elastic properties
- Methods of fabrication. Chemically induced phase transition.
- Influence of arrangement of adatoms and attached molecular groups to the structure and properties of *sp*^{3}-hybridized films

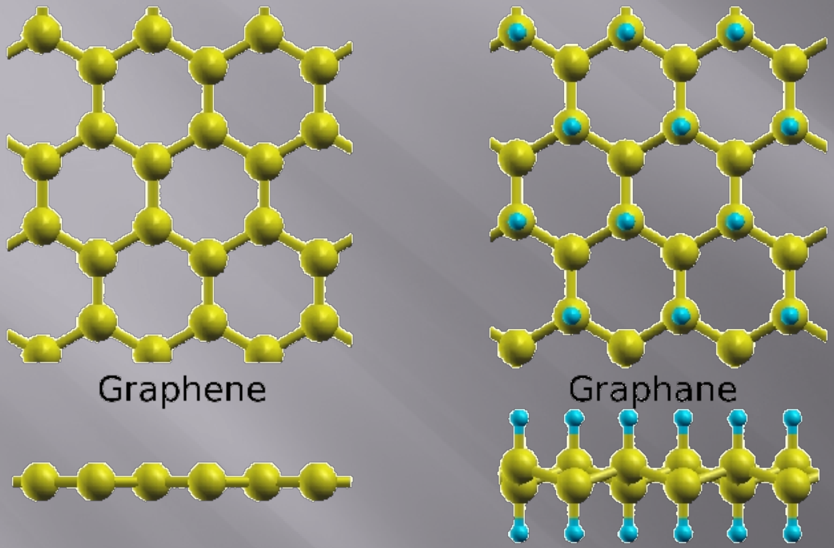
Motivation

- Hydrogenation of graphene enlarges its potential application in nanoelectronics. Regular adsorption of hydrogen atoms changes graphene electronic structure and opens the band gap depending upon the distance between hydrogen regions. Total hydrogenation of graphene changes the nature of electronic states due to changing of sp^2 hybridization of C-C bonds to sp^3 one and opens the dielectric band gap. Such two-dimensional insulator was called as graphane. The theoretical prediction was generally confirmed experimentally by Elias *et. al* [1].
- Graphane is an offspring of graphene along with graphene nanoribbons and carbon nanotubes. The other type of carbon bonding opens a new way for developing of two-dimensional carbon based materials.
- Graphane is the first member in a series of sp^3 bonded diamond films consist of a number of adjusted oriented layers which display unique physical properties.

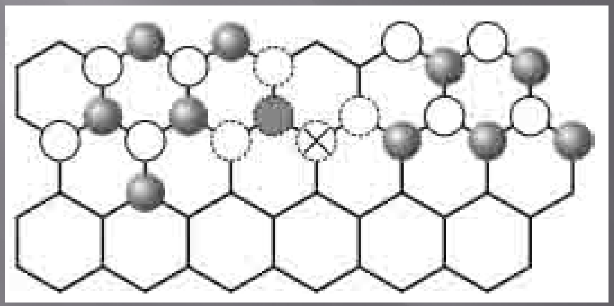


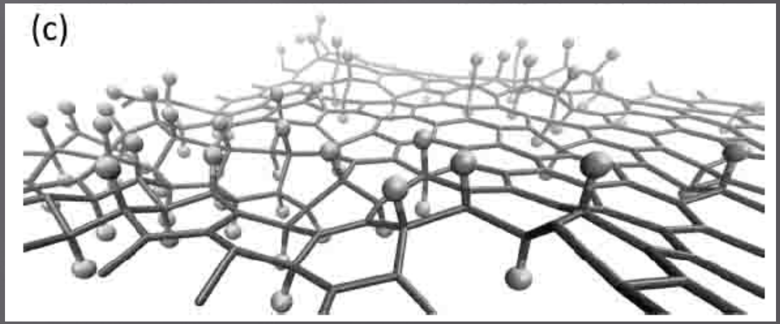
Motivation

- Total hydrogenation of graphene changes the nature of electronic states due to changing of sp^2 hybridization of C-C bonds to sp^3 one. Such two-dimensional insulator was called as graphane and can be considered as a thinnest possible diamond film



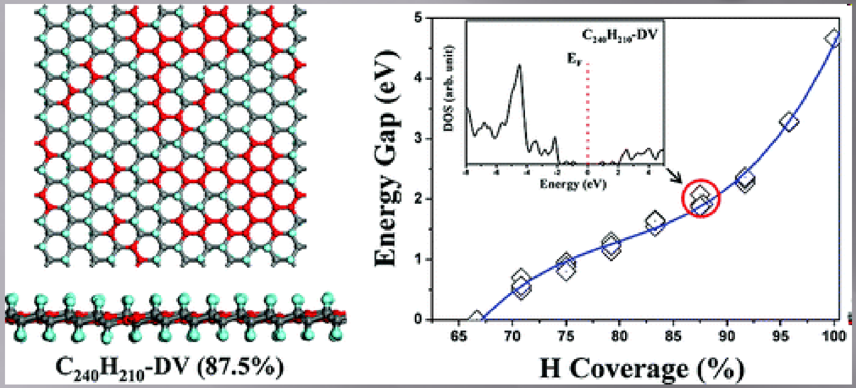
But irregular adsorption of the hydrogen atoms doesn't allow to consider graphane as a two-dimensional single crystal





Nanotechnology **20** (46): 465704, (2009)

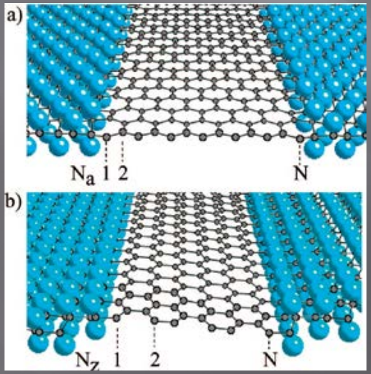
The impact of the irregular adsorption of the hydrogen to the electronic properties of the graphane

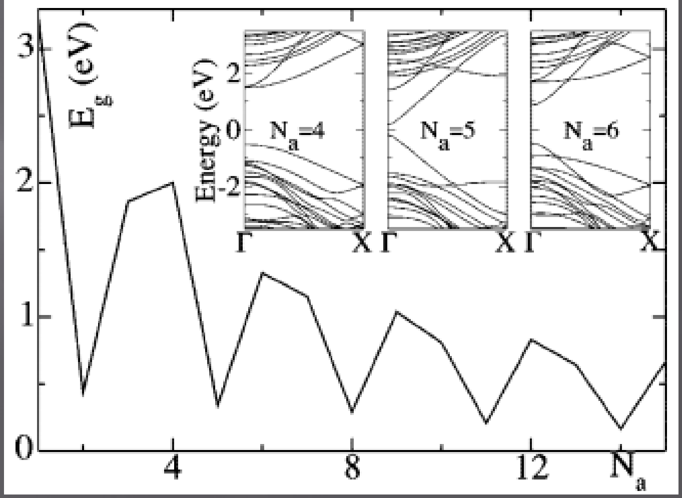


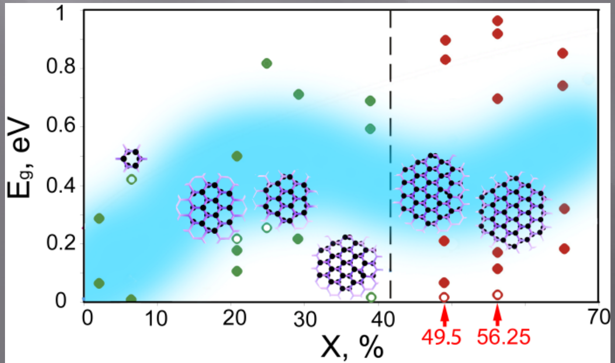
H. Gao, L. Wang, J. Zhao, F. Ding, L. Jianping, J. Phys. Chem. C 115, 3236 (2011)

A.K.Singh, B.I. Yakobson, Nano Lett. 9, 1540 (2009)

M.A. Ribas, A.K. Singh, P.B. Sorokin, B.I. Yakobson, Nano Research 4, 1, 143-152 (2011)



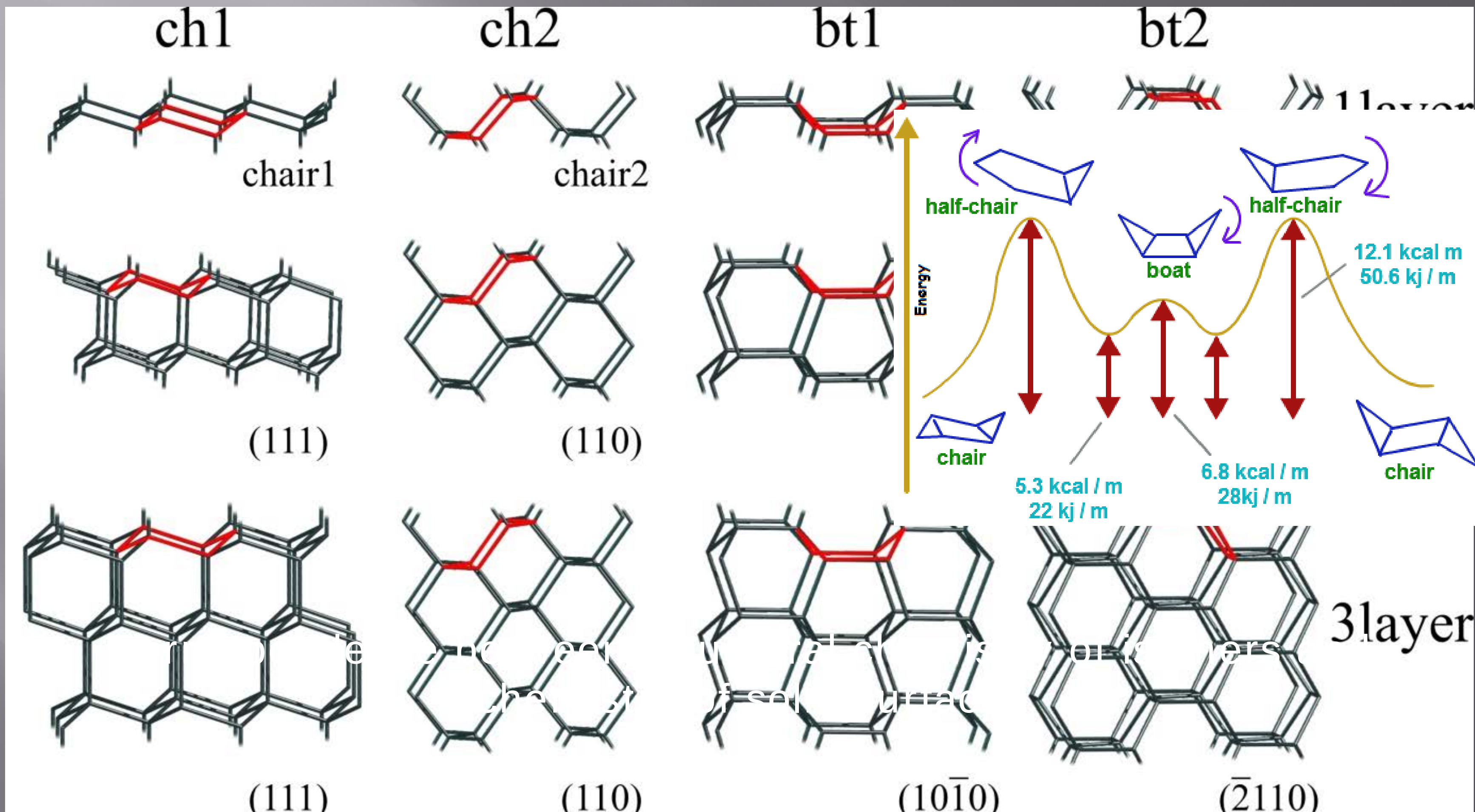




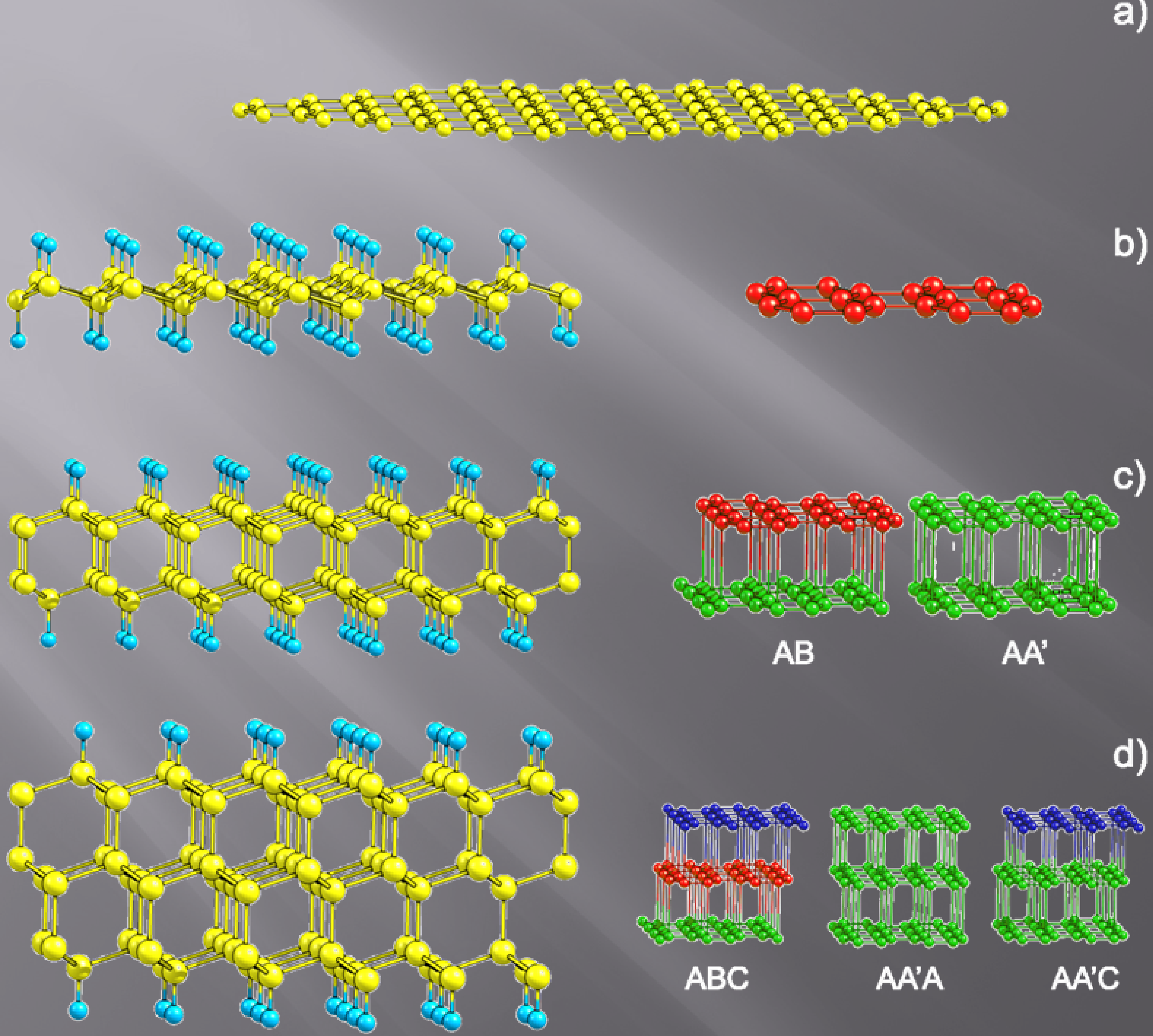
L.A. Chernozatonskii, D.G. Kvashnin, P.B. Sorokin, A.G. Kvashnin, J.W. Brüning, J. Phys. Chem. C (in press, 2012)

The features of the atomic structure of the *sp^3*-hybridized carbon films.

Atomic structure



Polytypes of ch1 type films



Graphene

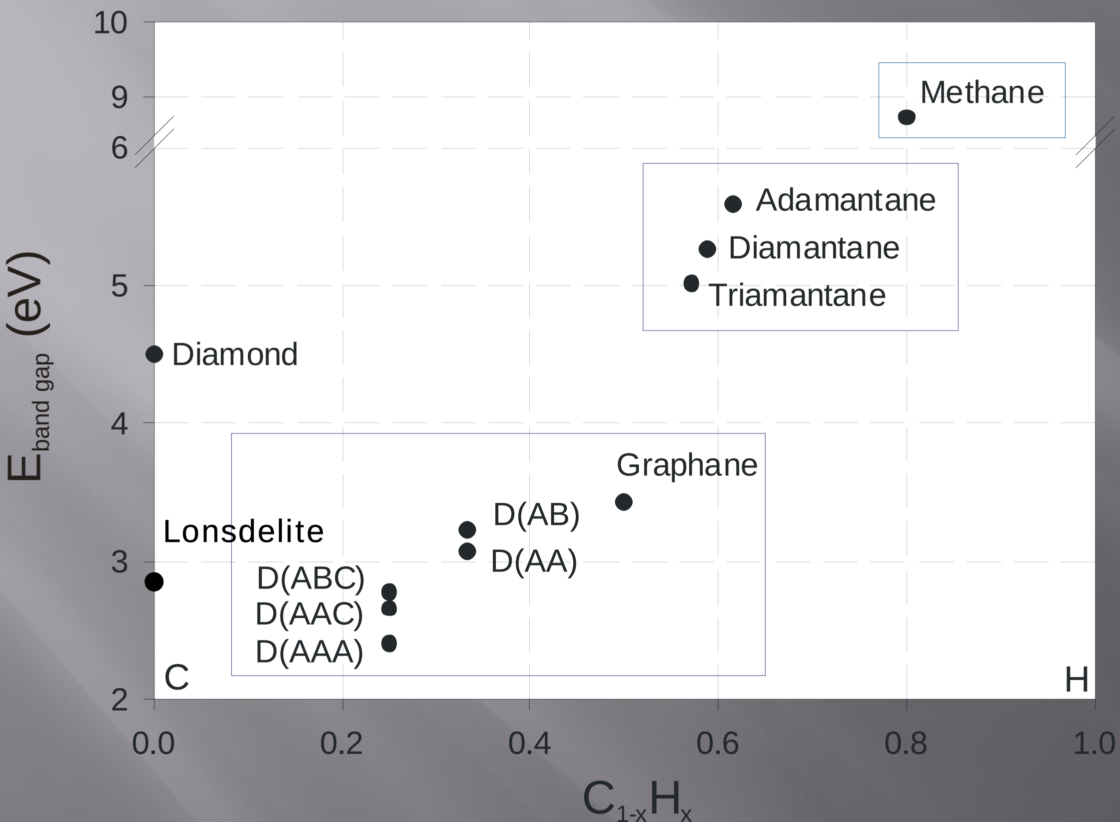
Graphane - A

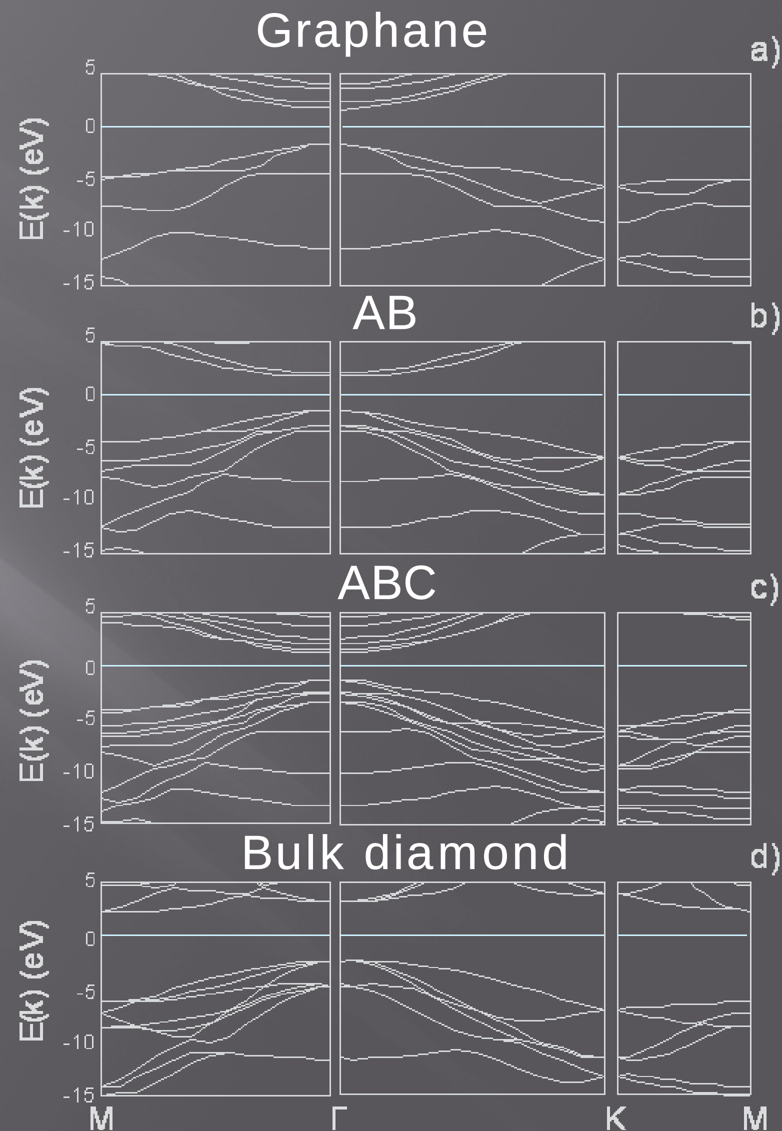
AB, AA′

ABC, AA′A AA′C

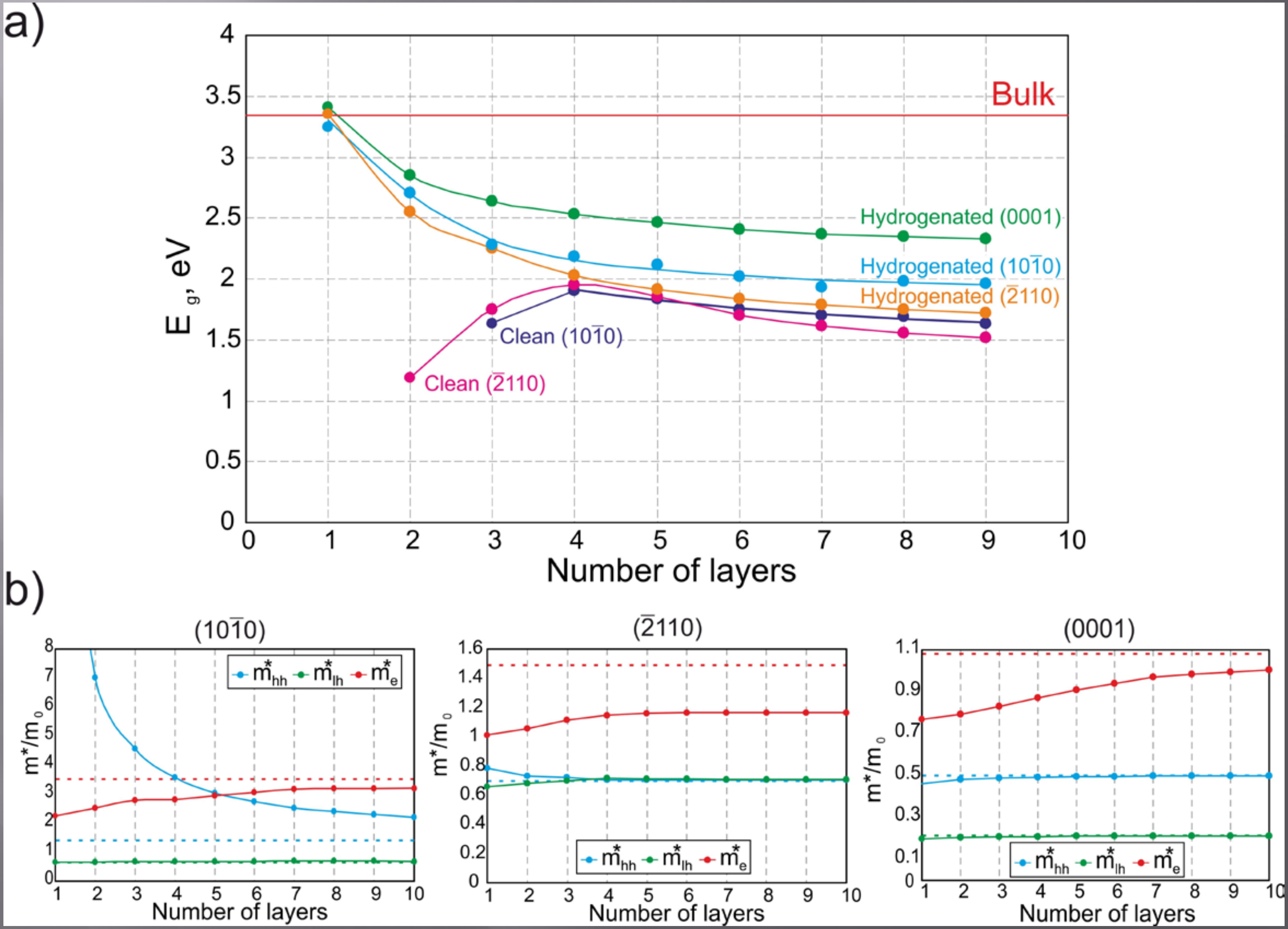
Electronic and transport properties of the hydrogenated films

Electronic properties of ch1 films





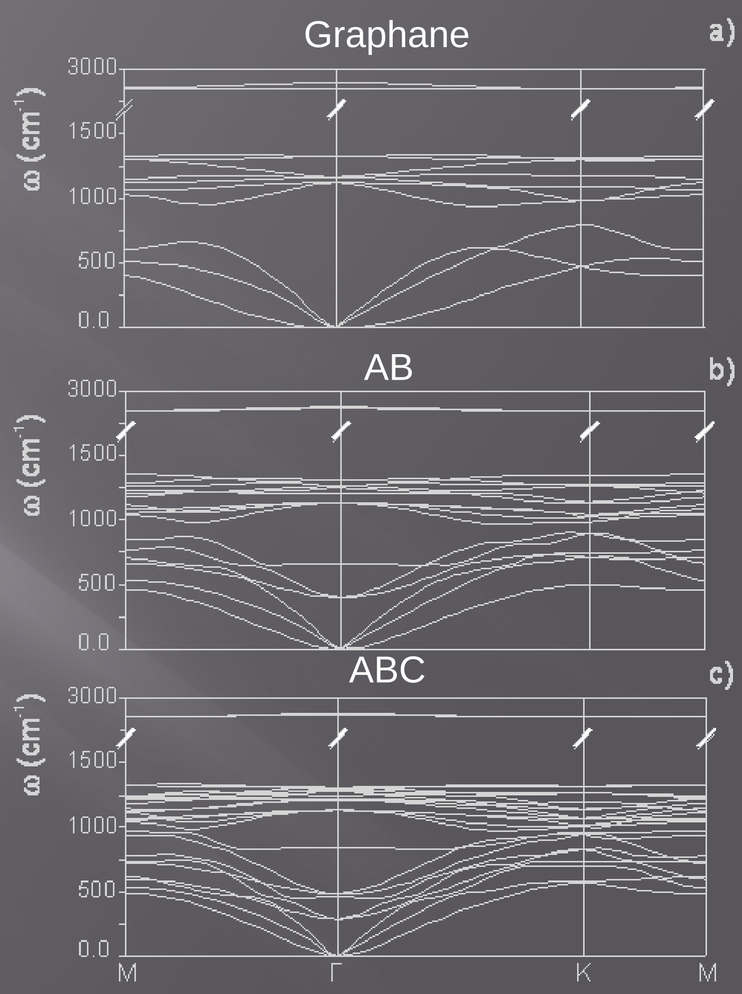
Electronic properties of lonsdaleite-type films



Elastic properties of the hydrogenated films

Elastic properties of ch1 films

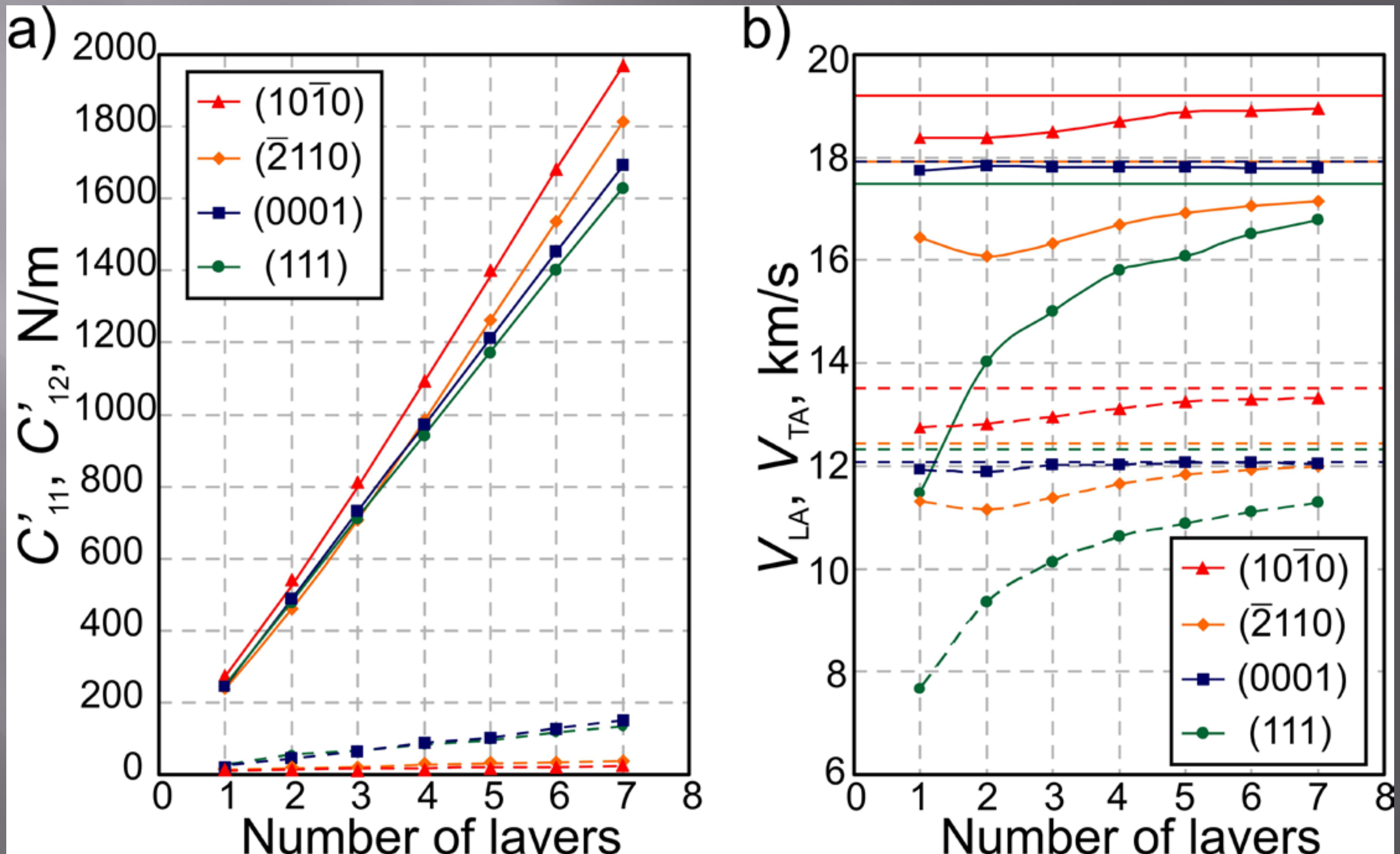
	v_{TA}, (10^3 m/s)	v_{LA}, (10^3 m/s)
Graphane	12.0	17.7
D(AB)	12.1	17.8
D(ABC)	12.2	18.0
Bulk diamond (experiment)	12.4	18.3



L.A. Chernozatonskii, P.B. Sorokin et al. JPCC **115**, *1*, 132-136 (2011)

Elastic properties of lonsdaleite-type films

	(10-10) bt1	(-2110) bt2	(0001) ch1
C_{11}'	C_{33}	C_{11}	C_{11}
C_{12}'	C_{13}	C_{13}	C_{12}
C_{11} = 1222.5 GPa, C_{12} = 106.8 GPa, C_{13} = 47.5 GPa, C_{33} = 1326.3 GPa, C_{44} = 459.4 GPa			



Indentation of the films

Strain energy is defined as following:

$$U = \frac{1}{2}\pi\sigma^{2D}\delta^2 + \frac{E^{2D}q^3}{4r^2}\delta^4,$$

where q=1.02 is is a dimensionless constant related to the Poisson's ratio, r is a membrane radius, σ^{2D} is the pretension in the film, E^{2D} is the elastic constant.

Our calculation results was approximated by the 4th order polynomial curve:

$$U = ax^2 + bx^4,$$

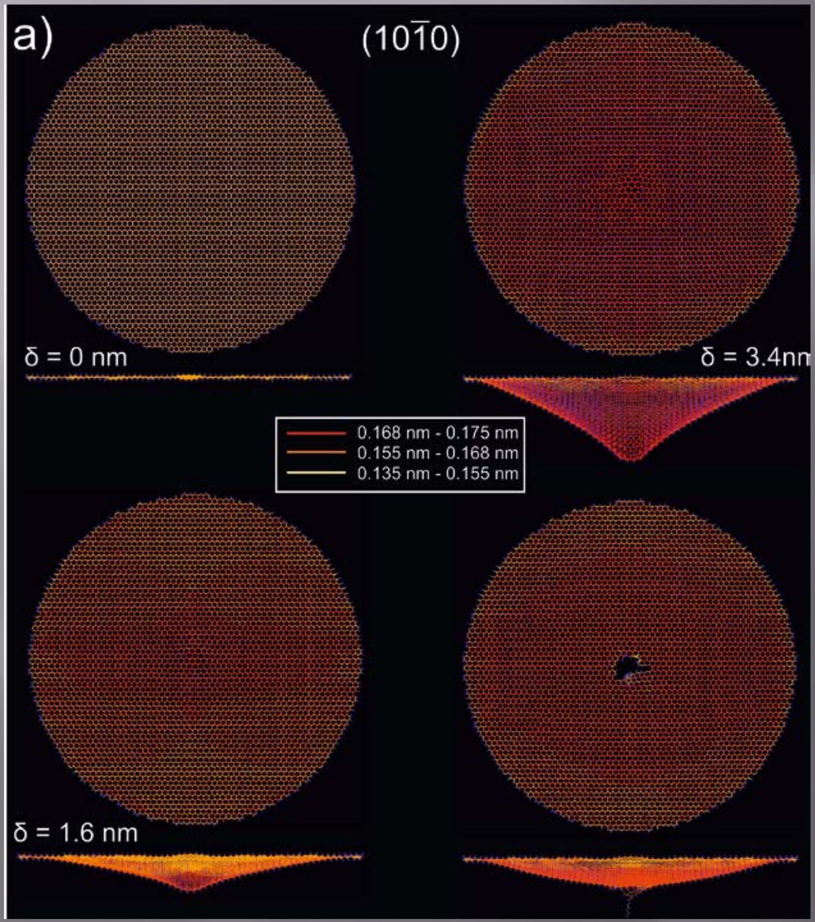
where coefficients a and b are defined as:

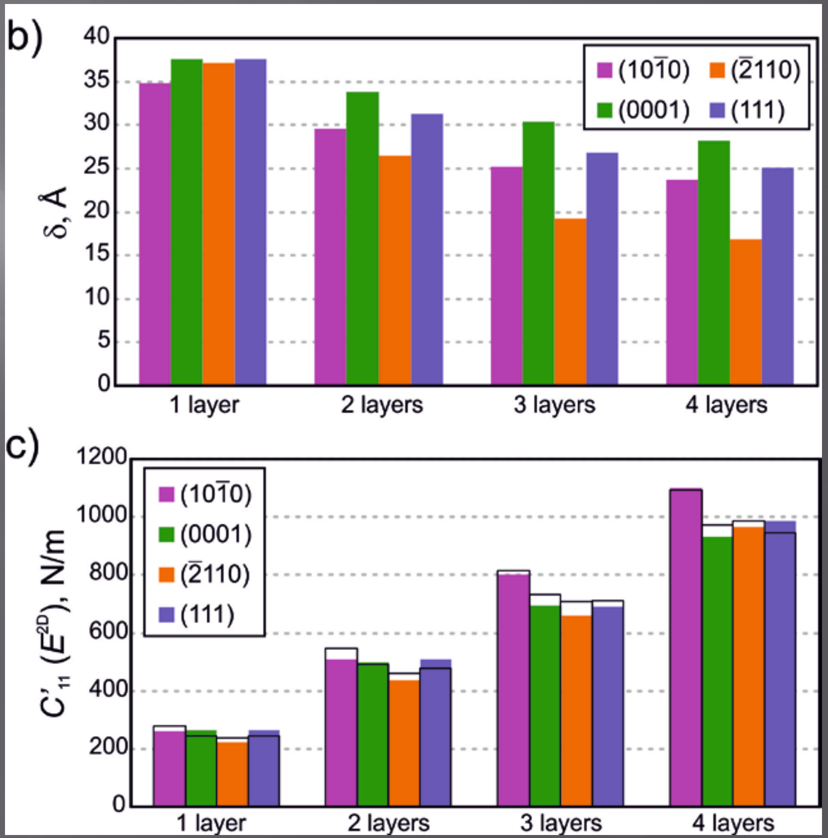
$$a = \frac{\sigma^{2D}\pi}{2}; b = \frac{E^{2D}q^3}{4r^2} \Rightarrow E^{2D} = \frac{4r^2 b}{q^3}$$

$$Y = \frac{E^{2D}}{h}$$

where h is a thickness of the film

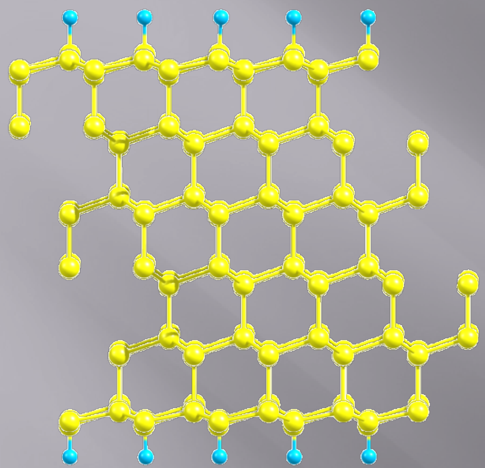
Indentation of the films





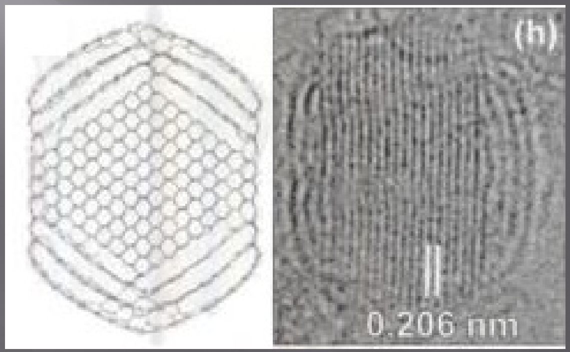
Methods of fabrication. Chemically induced phase transition.

The problem of stability of sp^3-hybridized nanostructures

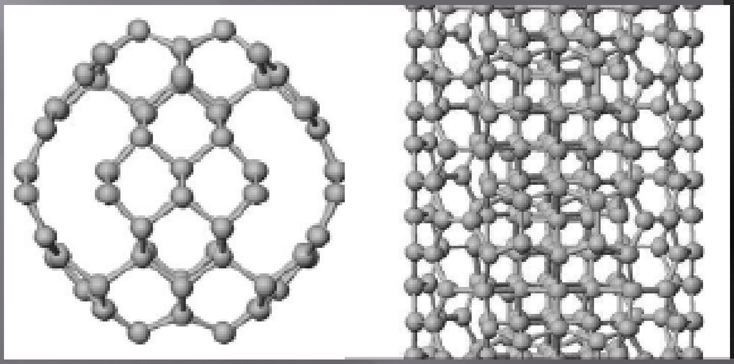


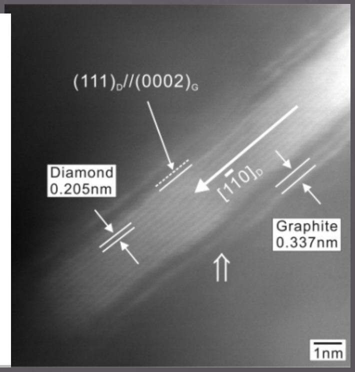
- Carbon diamond nanoclusters display graphitization effect due to more energy favorable of graphene against to diamond.

This effect can dramatically impact to the stability of the considered ultrathin diamond films!



Kuznetsov et. al



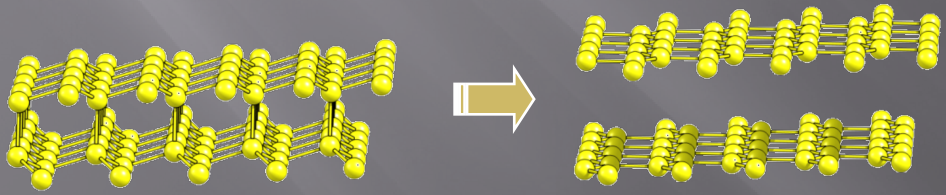


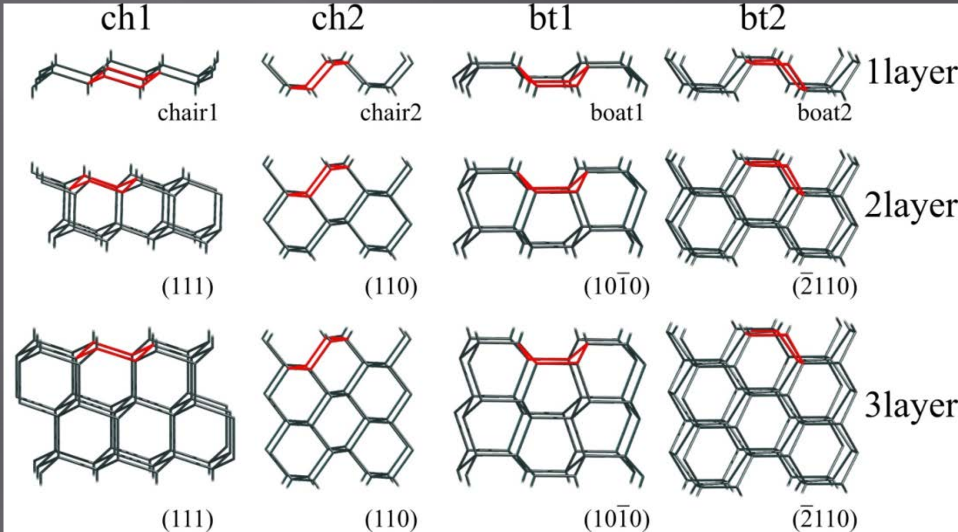
Barnard, Rev.Adv.Mater.Sci. 2004 Shang et. al, ACS Nano, 2009

The problem of stability of sp^3-hybridized films with nanometer thickness

- Diamond two- and three-layered ch1 films…
- Diamond three-layered ch2 films…
- Lonsdaleite two-layered bt1 films…
- Lonsdaleite two-, three-, four- and five-layered ch1 films…

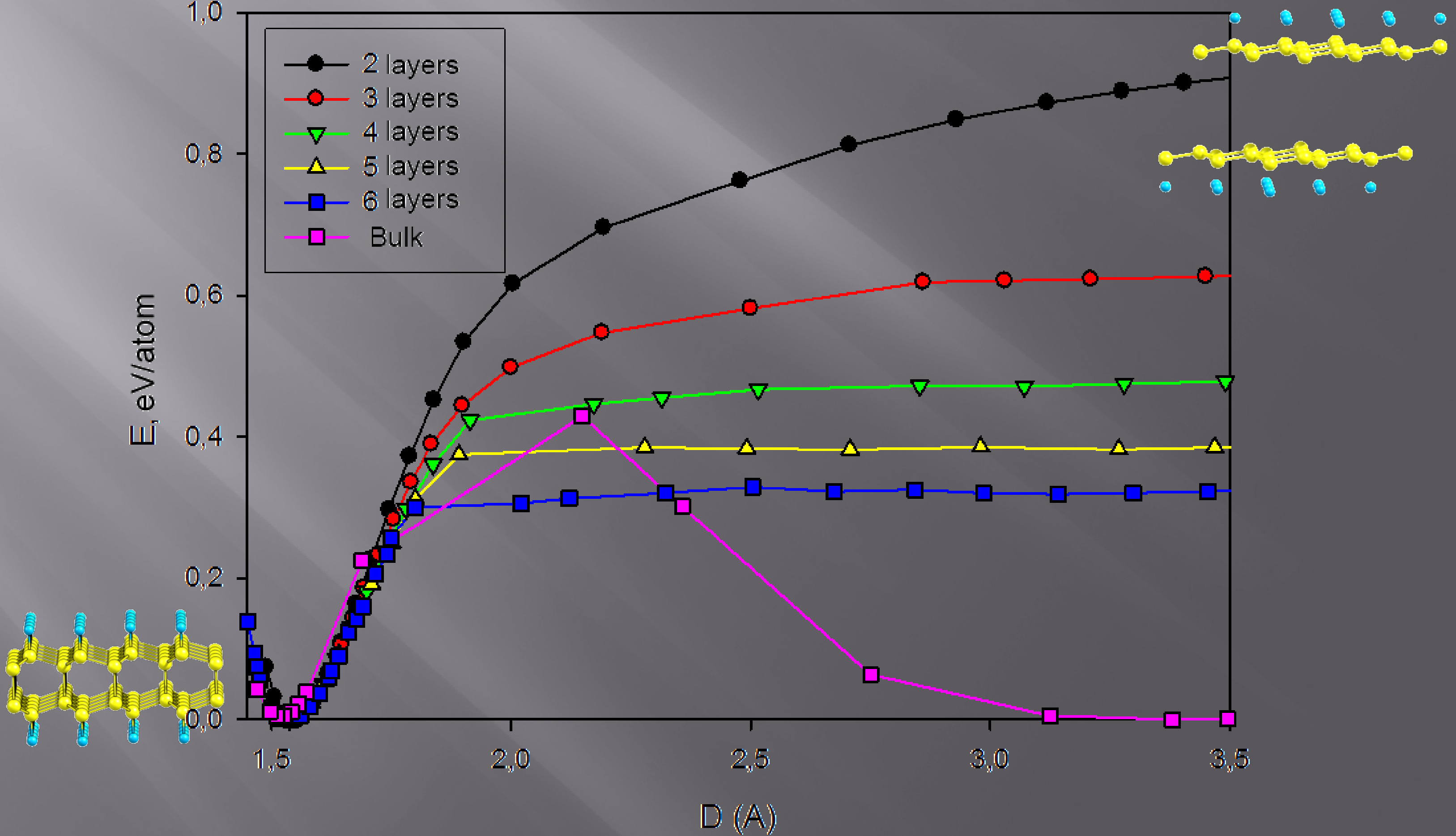
…without passivation are unstable and transform to corresponding multilayered layered graphene



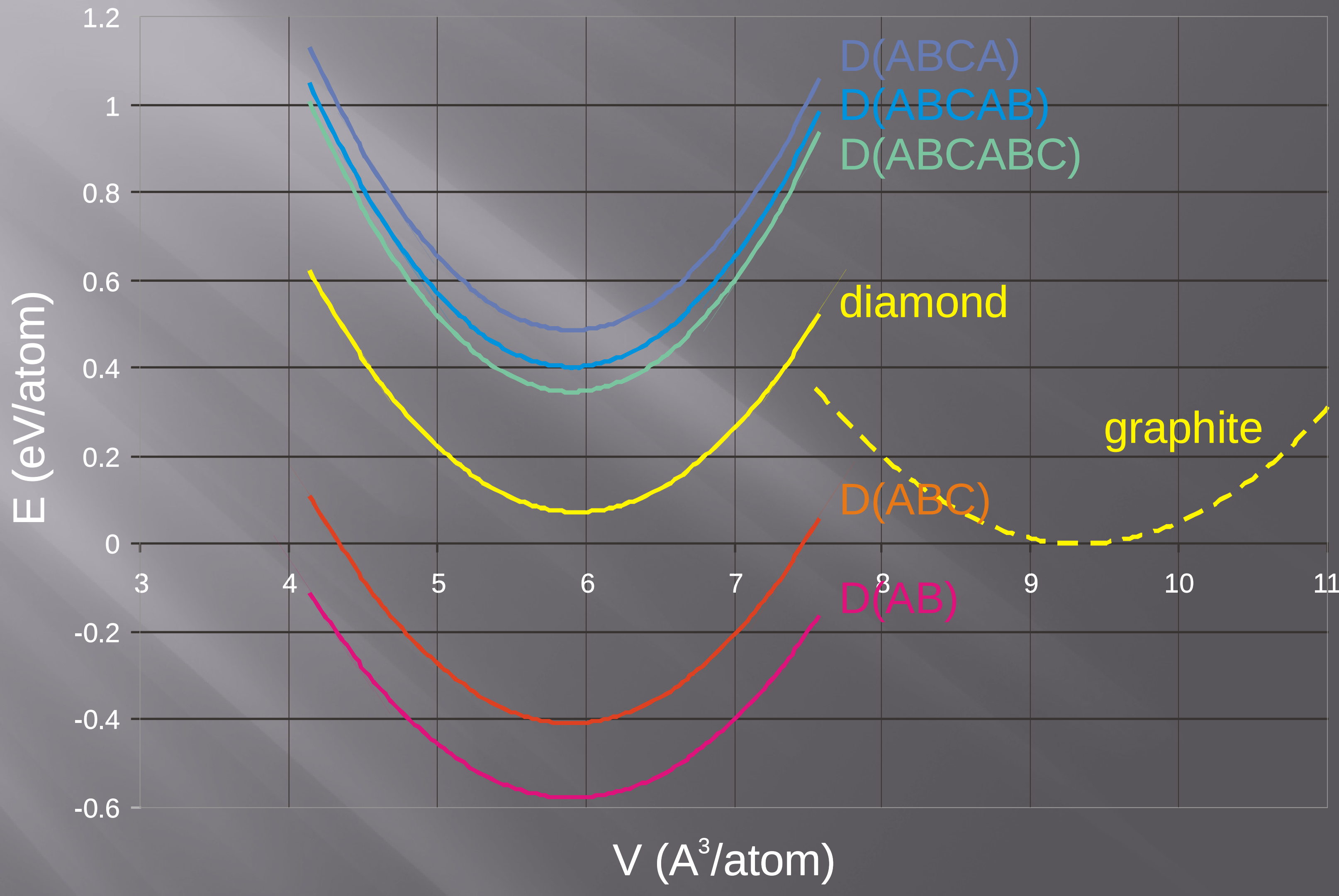


Chemically induced phase transition

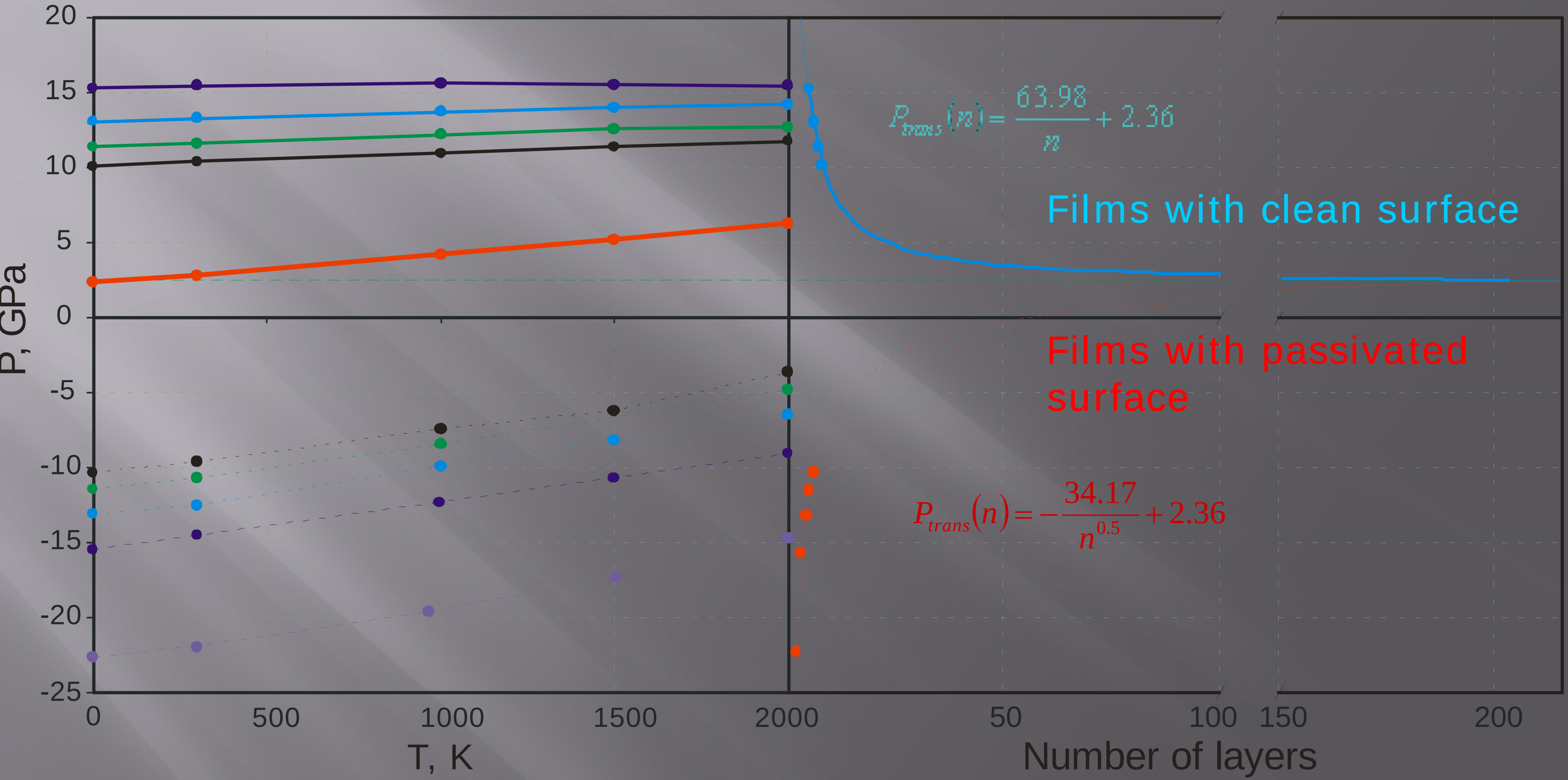
- From the other side, multilayered graphene with adsorbed adatoms on the outer surface transforms to *sp*^{3}-hybridized films without any activation barrier. We call this effect as **chemically induced phase transition**.



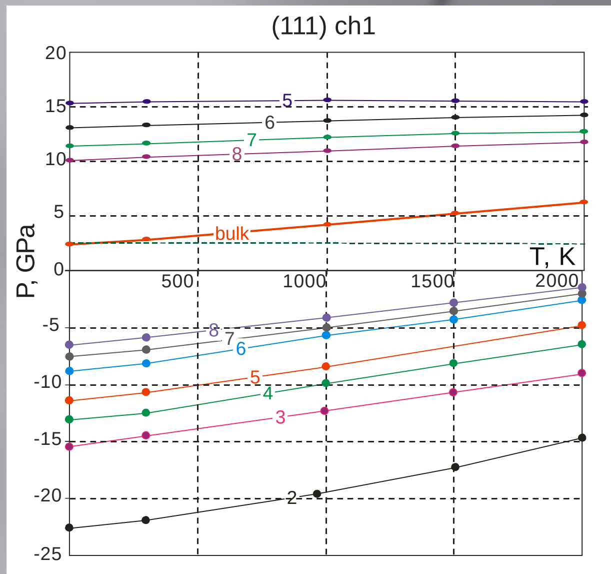
Energy diagram

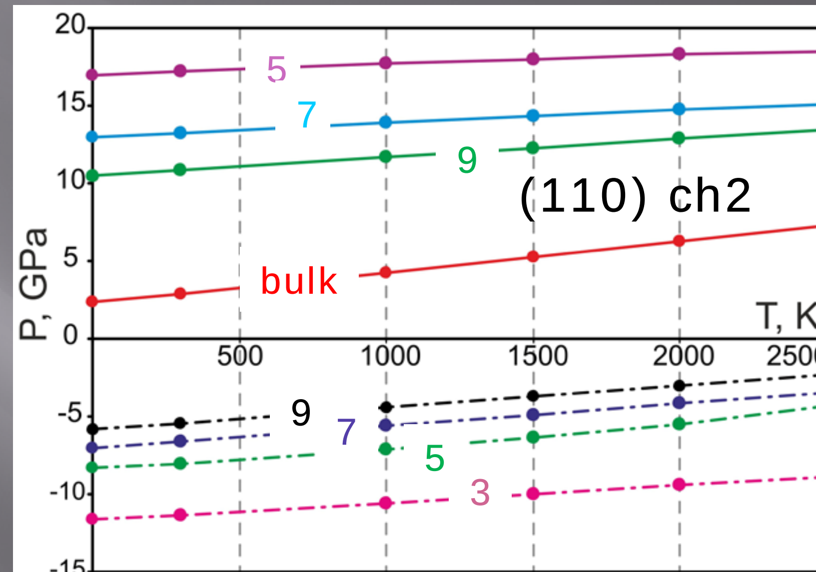


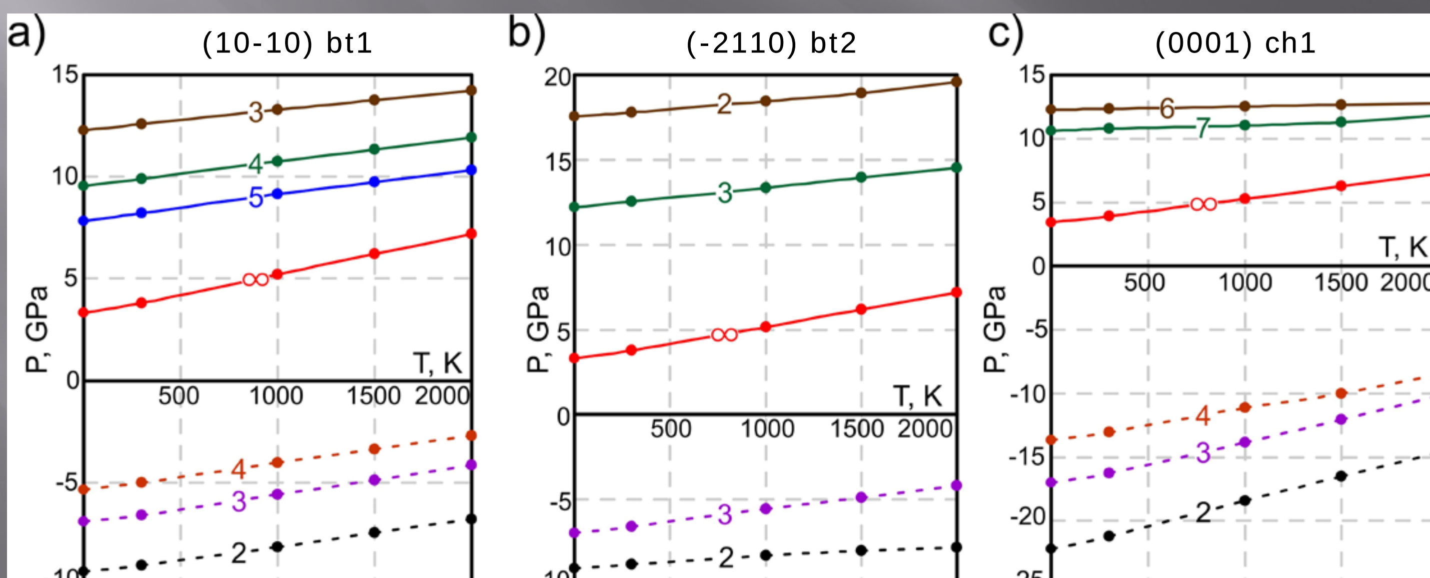
Phase diagram and dependence of the transition pressure (T=0) upon the ch1 diamond films thickness



Phase diagrams for studied sp^3-hybridized films







Influence of arrangement of adatoms and attached molecular groups to the structure and properties of sp^3-hybridized films

The evidence of experimental fabrication of *sp*^{3}-hybridized films

The bulk *sp*^{3}-hybridized fluorinated films was already obtained years ago by Japanese scientists in bulk graphite.

Z. anorg. allg. Chem. **544** (1987) 7—20 J. A. Barth, Leipzig

On the Structure of Graphite Fluoride

H. Touhara*, K. Kadono, Y. Fujii[1]), and N. Watanabe

Kyoto (Japan), Kyoto University, Faculty of Engineering, Department of Industrial Chemistry

Dedicated to Professor Paul Hagenmuller on his 65th Birthday

Abstract. The structure of graphite fluoride, $(C_2F)_n$ has been investigated by X-ray analyses, solid state ^{19}F-n.m.r., and electron microscopy for well characterized and crystallized samples obtained from natural graphite or HOPG (highly oriented pyrolytic graphite). On the basis of the present results and structural properties derived from previous works, $(C_2F)_n$ has a layered structure of stage-2 which belongs hexagonal to the system with C_{3h} symmetry. Detailed discussions on the symmetry both for $(CF)_n$ and $(C_2F)_n$ have led to possible stacking sequences each unit cell of graphite fluoride should require. The ideal structure of $(C_2F)_n$ is a hexagonal crystal lattice with a = b = 2.5 Å; c = 16.2 Å, and a plausible stacking sequence of AB/B'A'/ with I_c (identity period) = 8.09 Å. The layered structure of $(CF)_n$ is of stage-1 with A/A'/ stacking sequence.

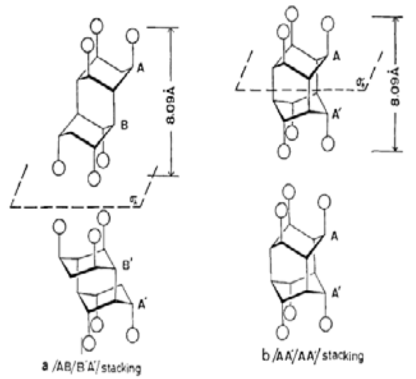
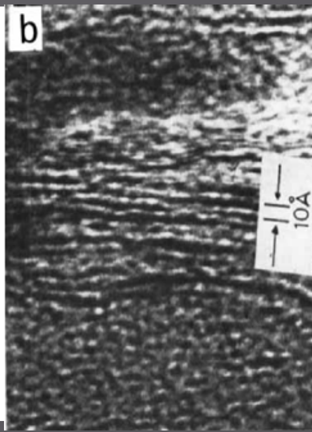


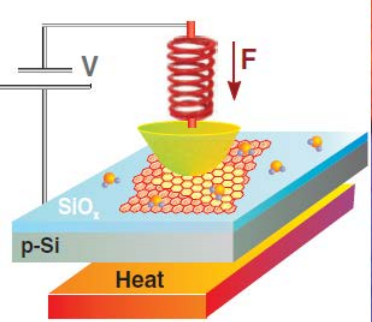
Fig. 4 Structure models of $(C_2F)_n$ showing stacking sequences a; AB/B'A'/ and b; A'/AA'/ (σ_h is a mirror plane.)

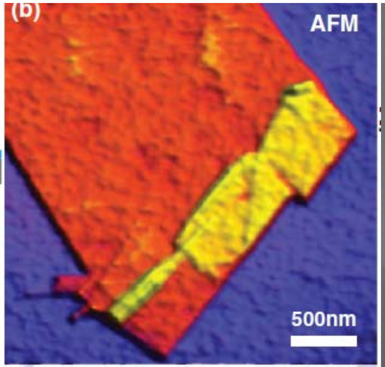


ADVANCED MATERIALS
www.advmat.de
Materials Views
www.MaterialsViews.com

Room-Temperature Compression-Induced Diamondization of Few-Layer Graphene

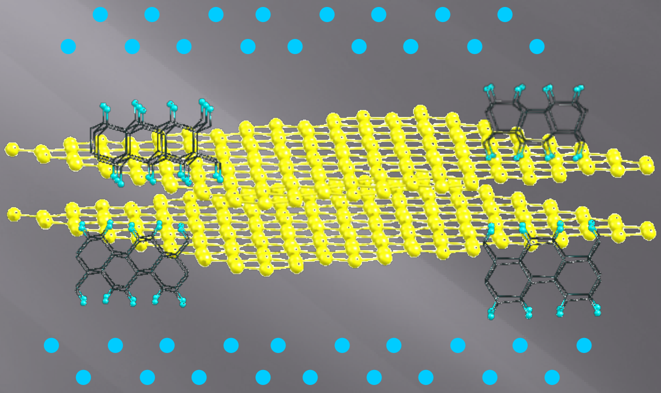
*Ana P. M. Barboza, Marcos H. D. Guimaraes, Daniel V. P. Massote, Leonardo C. Campos, Newton M. Barbosa Neto, Luiz G. Cancado, Rodrigo G. Lacerda, Helio Chacham, Mario S. C. Mazzoni, and Bernardo R. A. Neves**





The diamondization of few-layer graphene was observed after the applying of pressure by EPM tip in H_2O atmosphere ch1

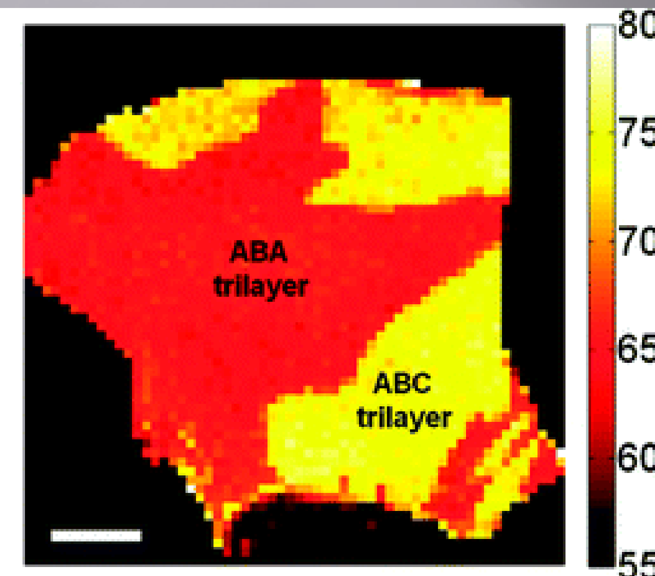
bt1



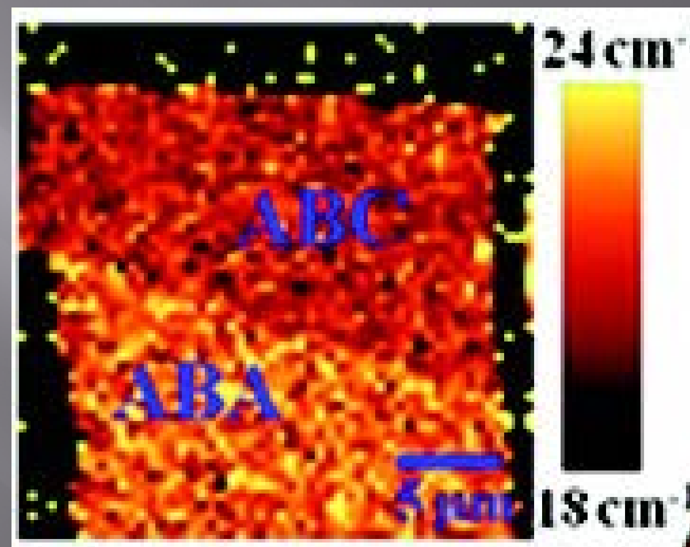
bt2

ch2

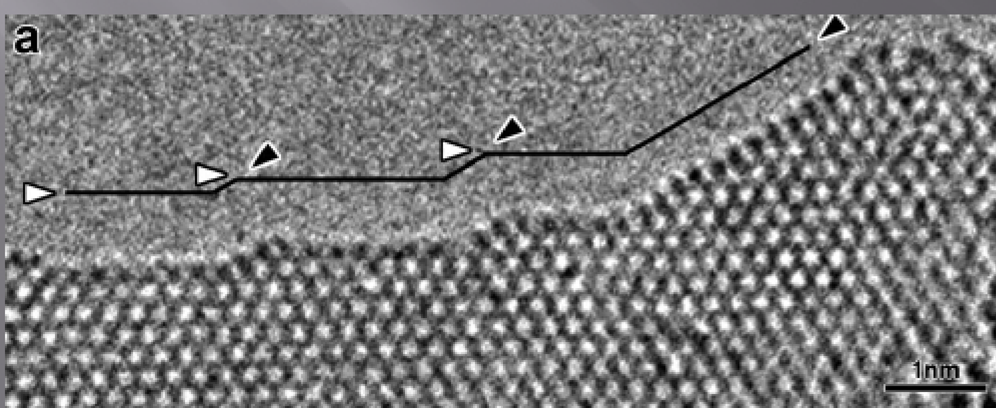
Evidence of different stacking of multilayered graphene



Lui et al. Nano Lett. 2010



Cong et al. ACS Nano. 2011



AA stacking,
Liu et al. Phys. Rev. Lett. 2009

Methodology

$$E_s = \frac{E_{tot} - n_{ad}E_{ad} - n_C E_C}{2S} - \frac{n_{ad}}{2S}\mu_{ad}(T,P)$$

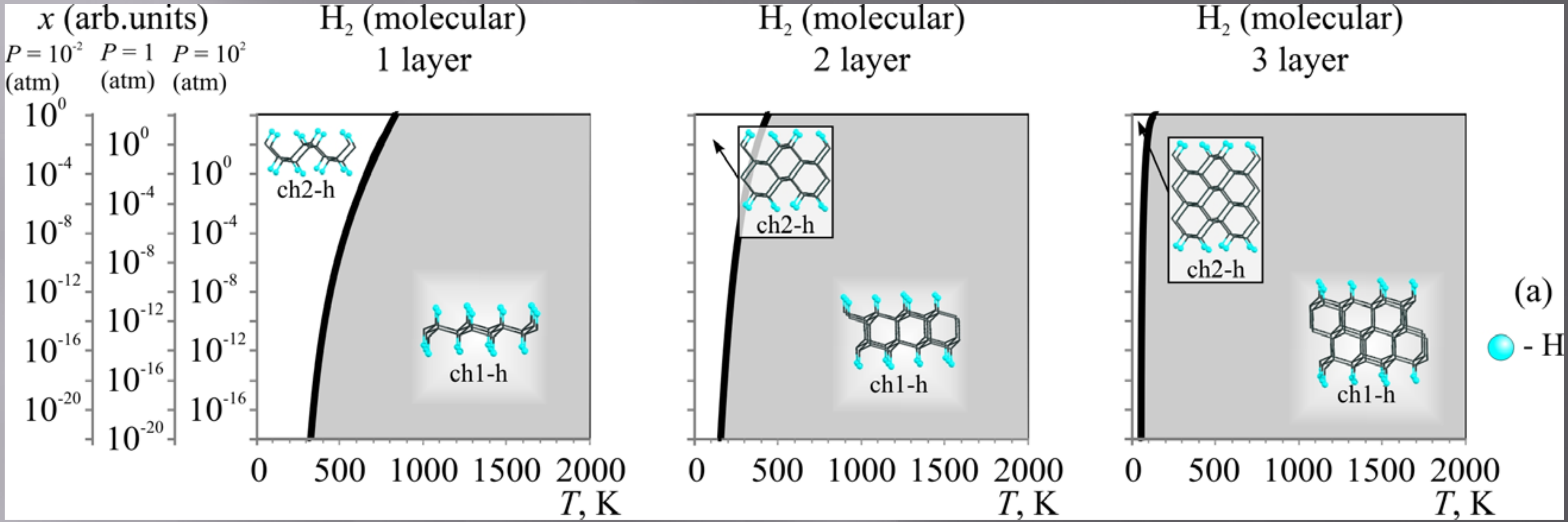
Here, the first part of the difference is the zero-temperature surface energy (per unit area); the last part is the chemical potential of the source of adatoms (or molecular groups) depending on the temperature, *T*, pressure, *P,* and implicitly on the adatoms (molecular groups) concentration

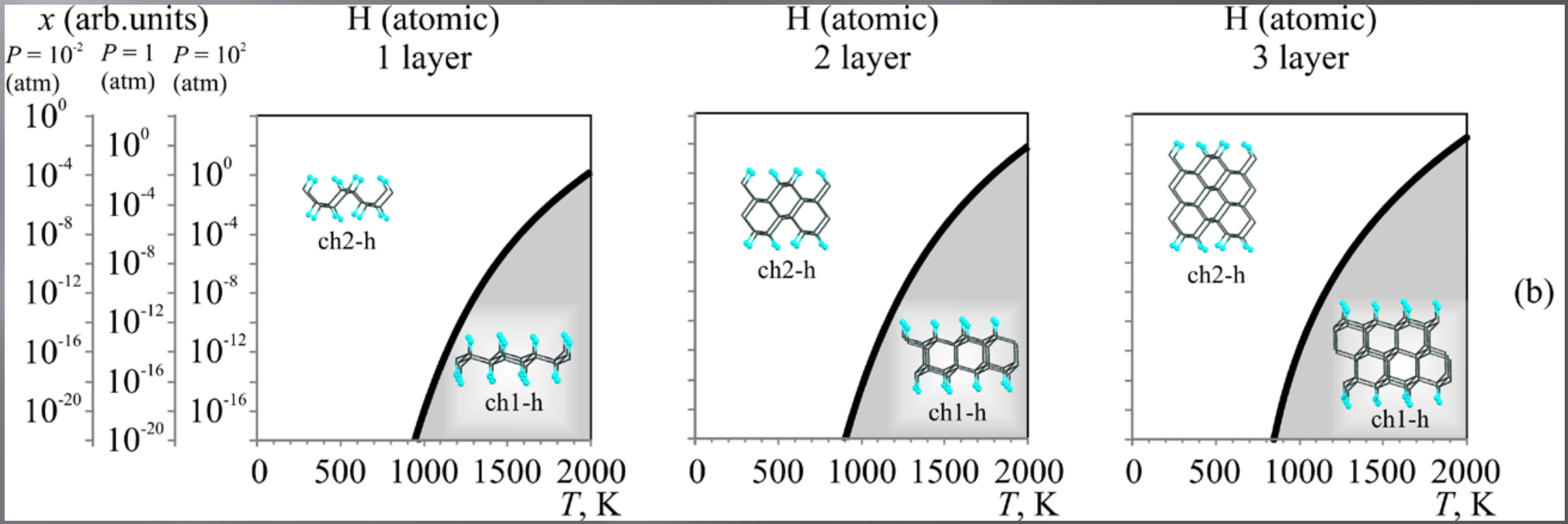
$$\mu_{ad}(T,P) = \Delta H - T\Delta S + kT\ln(x)$$

where ΔH and ΔS are the differences of enthalpy and entropy of the given temperature and the zero one, the values of which were obtained from the reference table, *x* is mole fraction, amount of the given constituent divided by the total amount of all constituents in a mixture

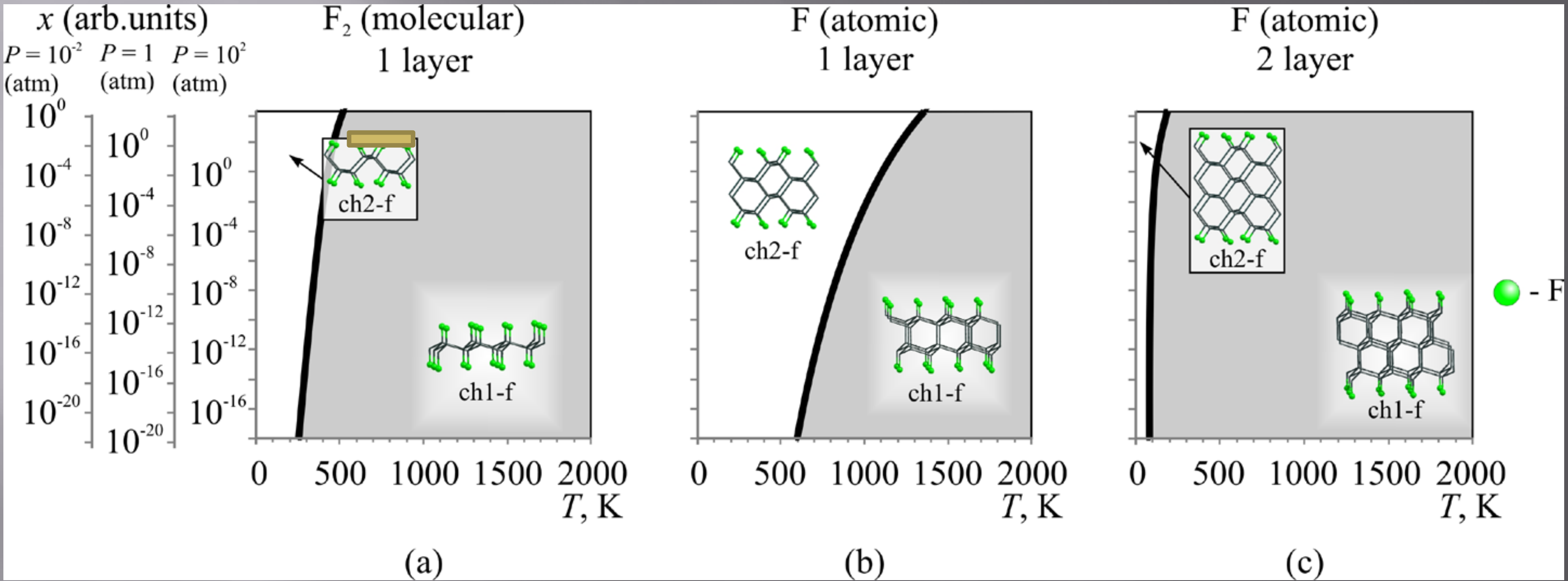
$$x = \frac{p^{o}}{P}$$

Hydrogen


x (arb.units)
P = 10^-2 (atm) P = 1 (atm) P = 10^2 (atm)
H2 (molecular) 1 layer
H2 (molecular) 2 layer
H2 (molecular) 3 layer
ch2-h
ch1-h
T, K
(a)
- H


x (arb.units)
P = 10^-2 (atm) P = 1 (atm) P = 10^2 (atm)
H (atomic) 1 layer
H (atomic) 2 layer
H (atomic) 3 layer
ch2-h
ch1-h
T, K
(b)

Fluorine

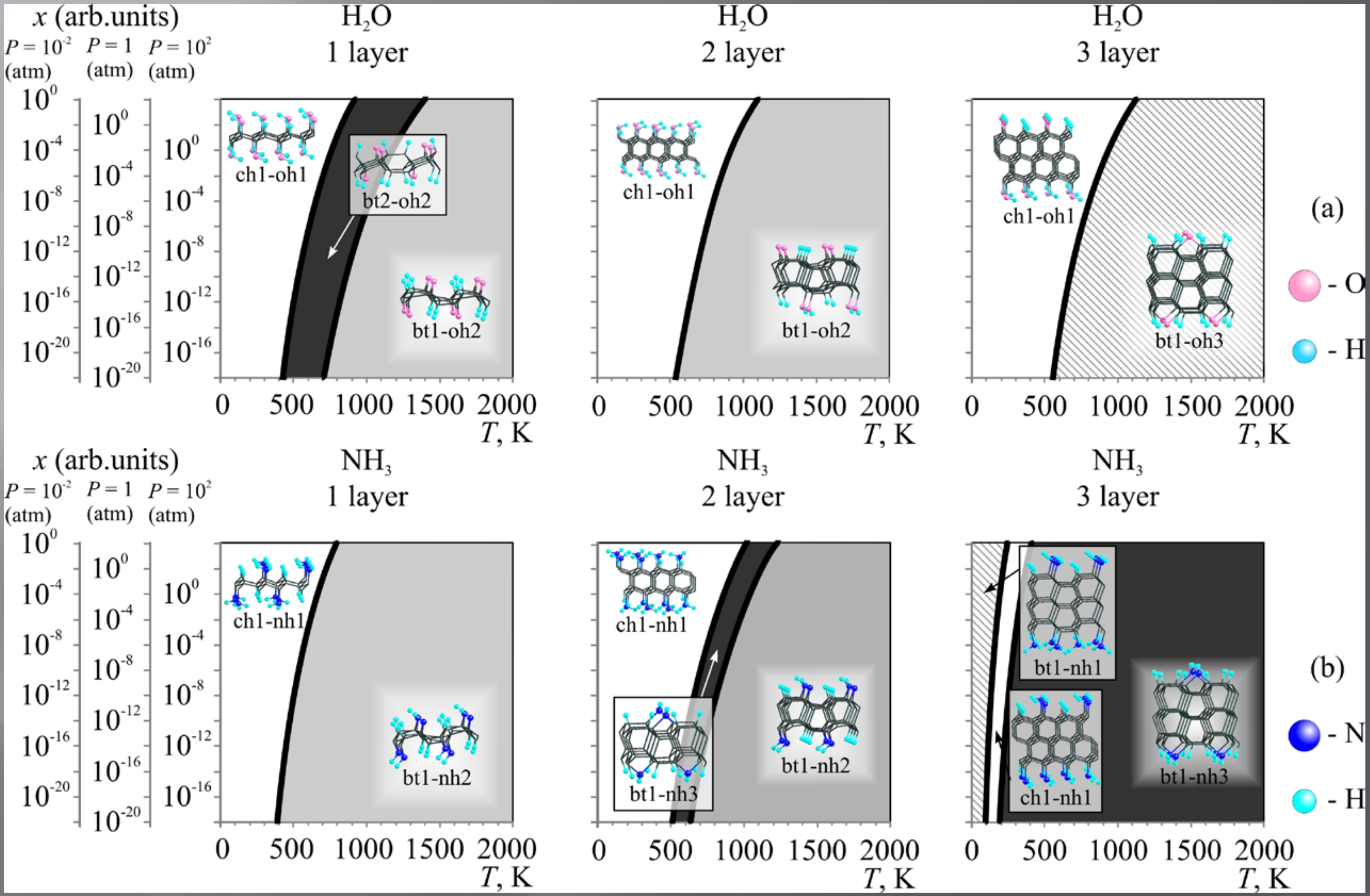


Yellow region: experiment

Kita, Y et al. *J. Am. Chem. Soc.* **1979**, *101*, 3832-3841.

Watanabe, N. *Solid State Ionics* **1980**, *1*, 87-110

Water and ammonia

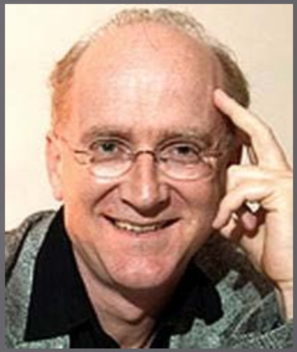


Electronic properties

Structure	Band gap, E_g, eV		
	Single layered film	Bi-layered film	Three-layered film
Hydrogen			
ch1-h	3.4	3.2	2.9
ch2-h	3.3	2.4	2.2
Fluorine			
ch1-f	3.1	4.0	*4.4*
ch2-f	3.5	4.3	*4.4*
Water			
ch1-oh1	4.4	4.1	3.9
bt1-oh2	*4.3*	*2.6*	*3.1*
bt1-oh3	*3.9*	*3.1*	*2.6*
bt2-oh2	*4.4*	*3.5*	*2.7*
Ammonia			
ch1-nh1	3.1	2.5	2.6
bt1-nh1	2.6	3.0	2.4
bt1-nh2	3.3	3.3	3.2
bt1-nh3	3.9	3.3	3.0

Acknowledgements

Prof. Leonid Chernozatonskii
Institute of Biochemical
Physics of RAS, Moscow, Russia



Prof. Boris Yakobson
Rice University,
Houston, USA

Dr. Lyubov Antipina

Alexander Kvashnin

Technological Institute for Superhard
and Novel Carbon Materials, Moscow, Russia