Oddziaływanie grafenu z metalami

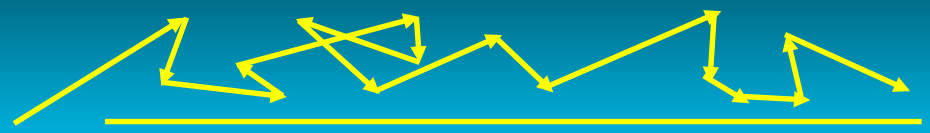
prof. dr hab.
Zbigniew Klusek

Grafen – dla czego intryguje ?

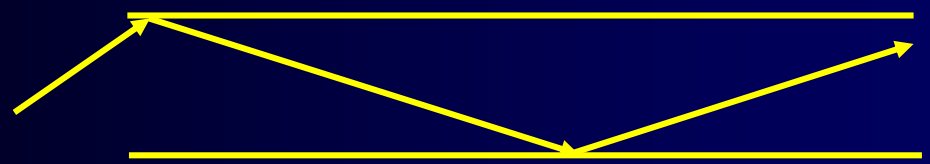
$$\mu = \frac{v}{E} \qquad E = \frac{U}{d}\left[\frac{V}{cm}\right] \qquad v = \frac{d}{t}\left[\frac{cm}{s}\right]$$

$$\sigma \approx en\mu$$

Transport dyfuzyjny

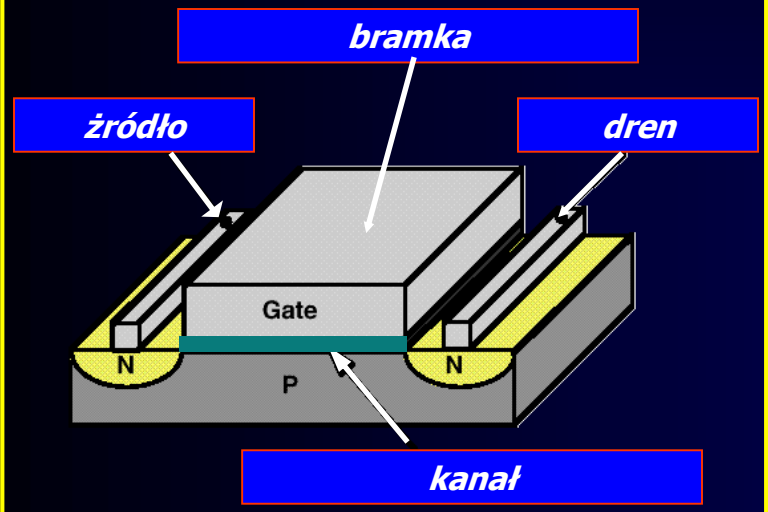


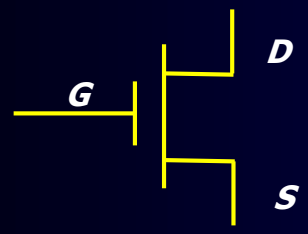
Transport kwantowy – balistyczny



Grafen – dlaczego intryguje ?

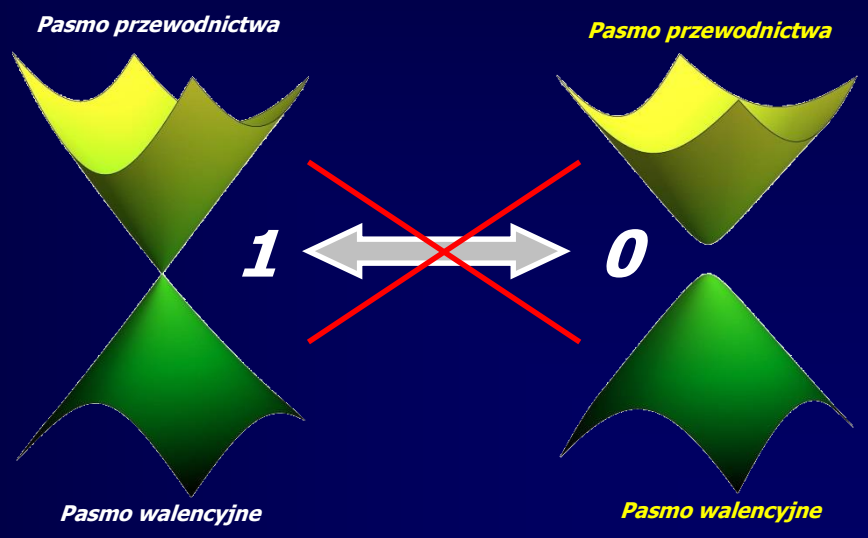
Tranzystor typu MOSFET





Nowa idea

kanał tranzystora wykonany z grafenu

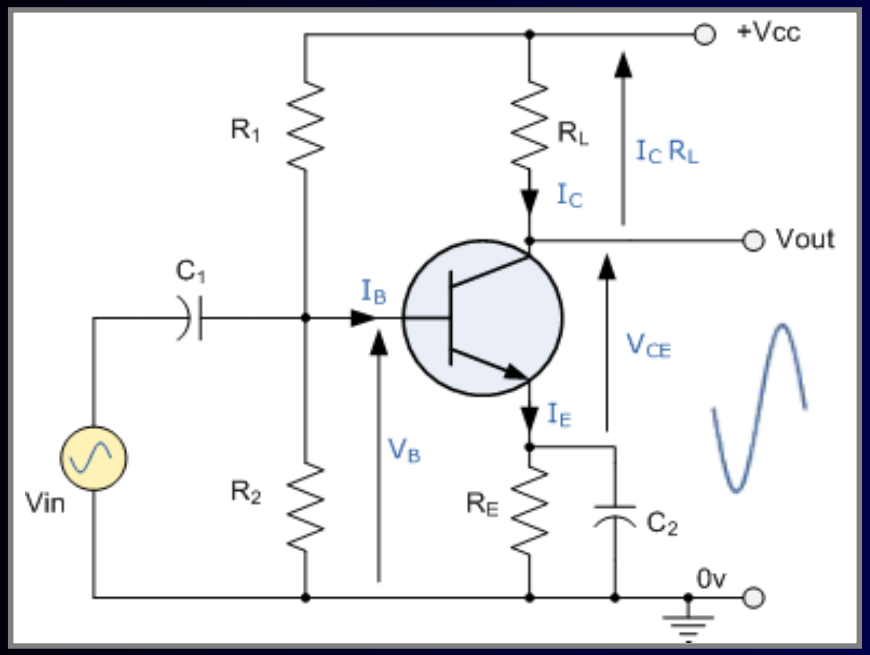


Wzmacniacze wysokiej częstości

Elektronika analogowa

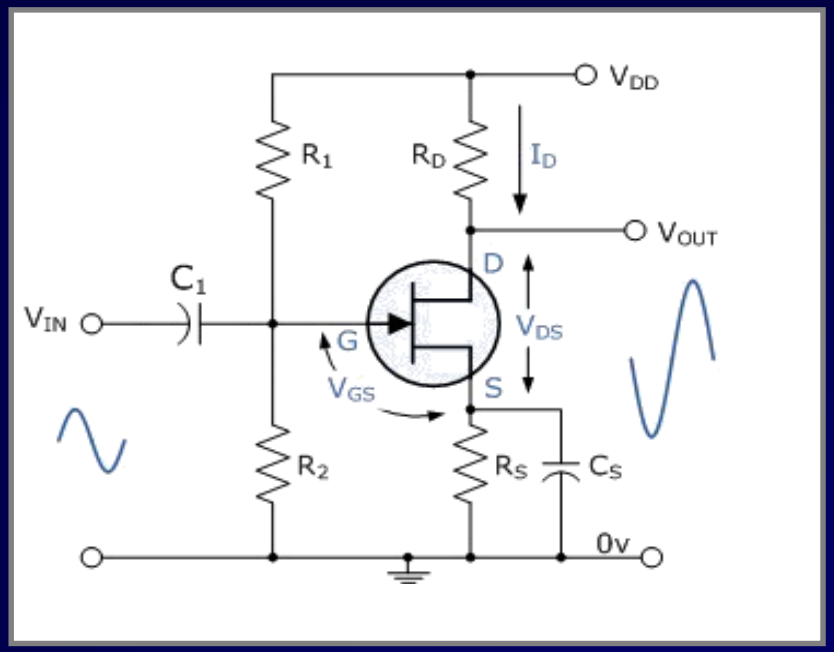
Tranzystory bipolarne

(n-p-n) or (p-n-p)

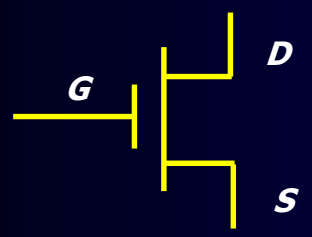


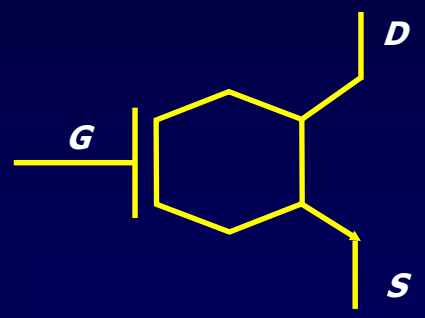
Tranzystory unipolarne

FET



Elektronika ambipolarna





FET → **GFET**

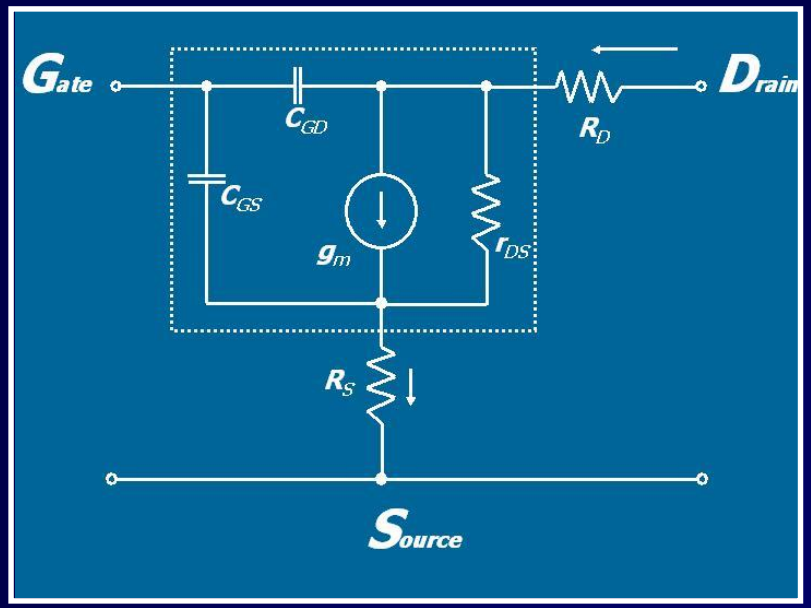
Częstotliwość odcięcia

Częstotliwość odcięcia to częstotliwość dla której wzmocnienie dąży do jedności

$$f_T \approx \frac{g_m}{2\pi} \frac{1}{(C_{GS}+C_{GD})\left[1+g_{ds}(R_S+R_D)+C_{GD}g_m(R_S+R_D)\right]}$$

f_T	częstotliwość odcięcia
g_m	wewnętrzna transkonduktancja
C_{GS}	pojemność bramka-źródło
C_{GD}	pojemność bramka-dren
g_{ds}	przewodność drenu
R_S	opór źródła
R_D	opór drenu

Wszystkie pojemności i oporności powinny być jak najmniejsze



Częstotliwość odcięcia

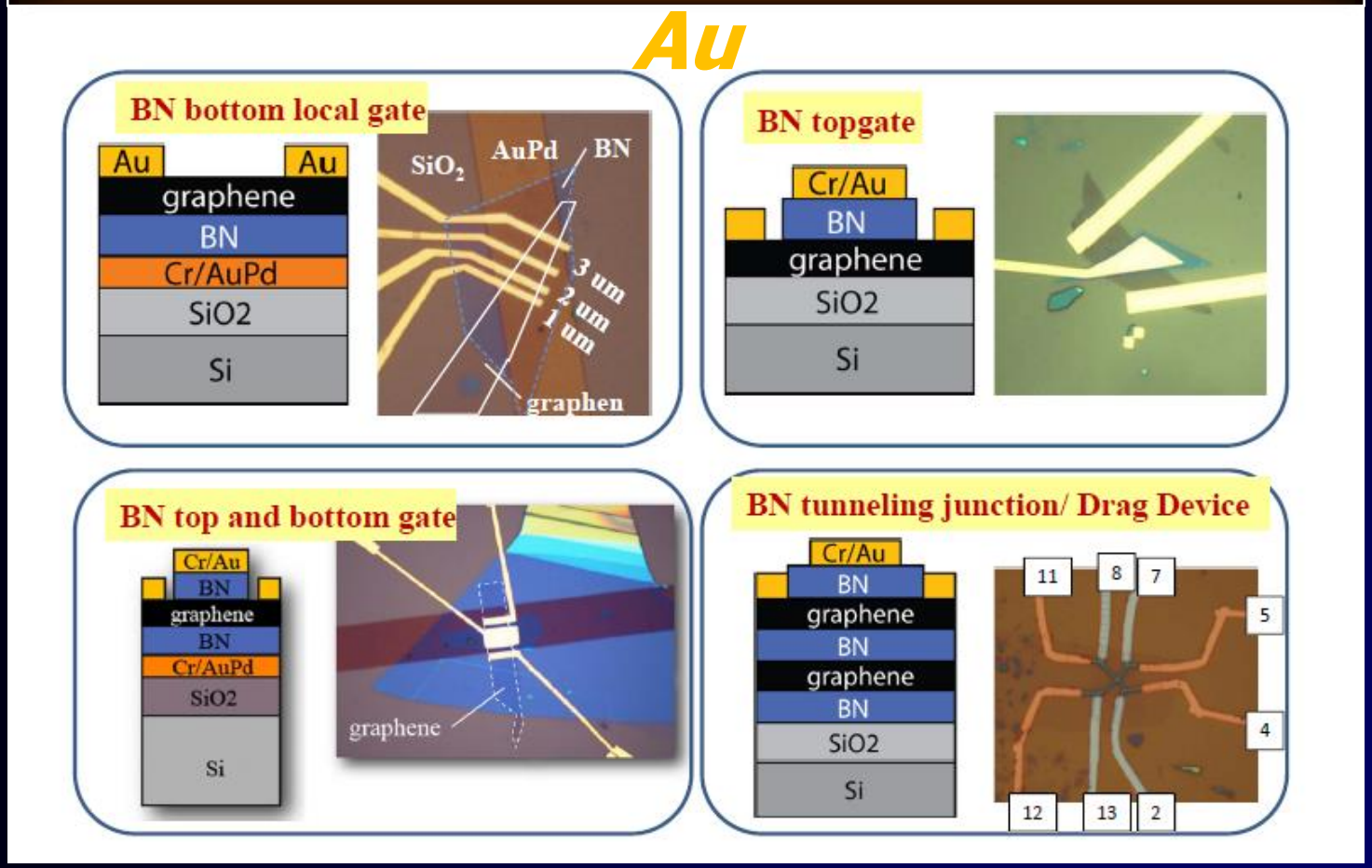
$$f_T \approx \frac{g_m}{2\pi} \frac{1}{(C_{GS} + C_{GD})\left[1 + g_{ds}(R_S + R_D) + C_{GD} g_m (R_S + R_D)\right]}$$

Częstotliwość odcięcia może być zmaksymalizowana

- **Wewnętrzna transkonduktancja jak największa**
- **Konduktancja drenu jak najmniejsza**
- **Pojemności jak najmniejsze**
- **Wszystkie rezystancje jak najmniejsze**

Przewodnictwo złącza grafen-metal

We wszystkich aplikacjach wymagany jest kontakt elektryczny



Przewodnictwo złącza grafen-metal

Rolf Landauer (1927-1999)

Formuła Landauera

$$G = \frac{2e^2}{h} \sum_{n=1}^{N} T_n$$

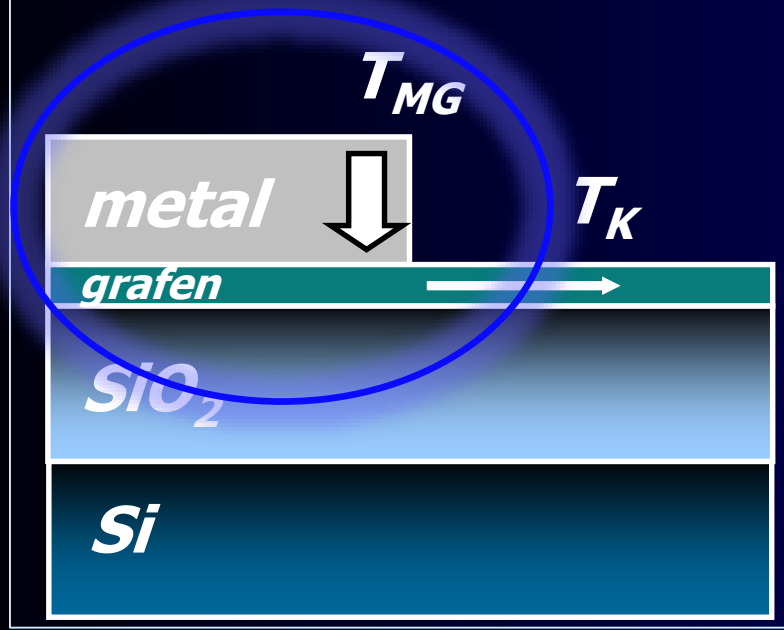
$$G = \frac{2e^2}{h} \sum_{n=1}^{N} M T_n$$

Przewodnictwo złącza grafen-metal

Formuła Landauera

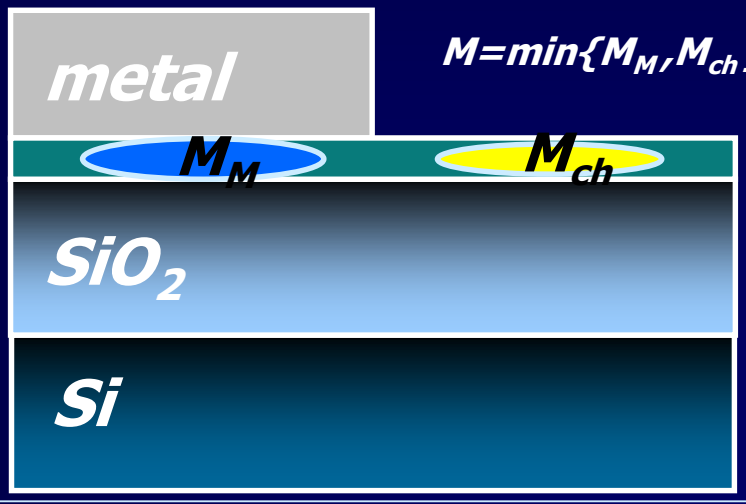
$$G = \frac{4e^2}{h} TM$$

T_{MG} współczynnik transmisji metal - grafen
T_K współczynnik transmisji w kanale



M_M liczba modów przewodnictwa
M_{ch} liczba modów przewodnictwa graf

$M=\min\{M_M, M_{ch}\}$



DFT – teoria funkcjonału gęstości

Rozpoczęliśmy badania od symulacji DFT

J. Slawinska, P. Dabrowski, I. Zasada
Phys. Rev. B 83 (2011)

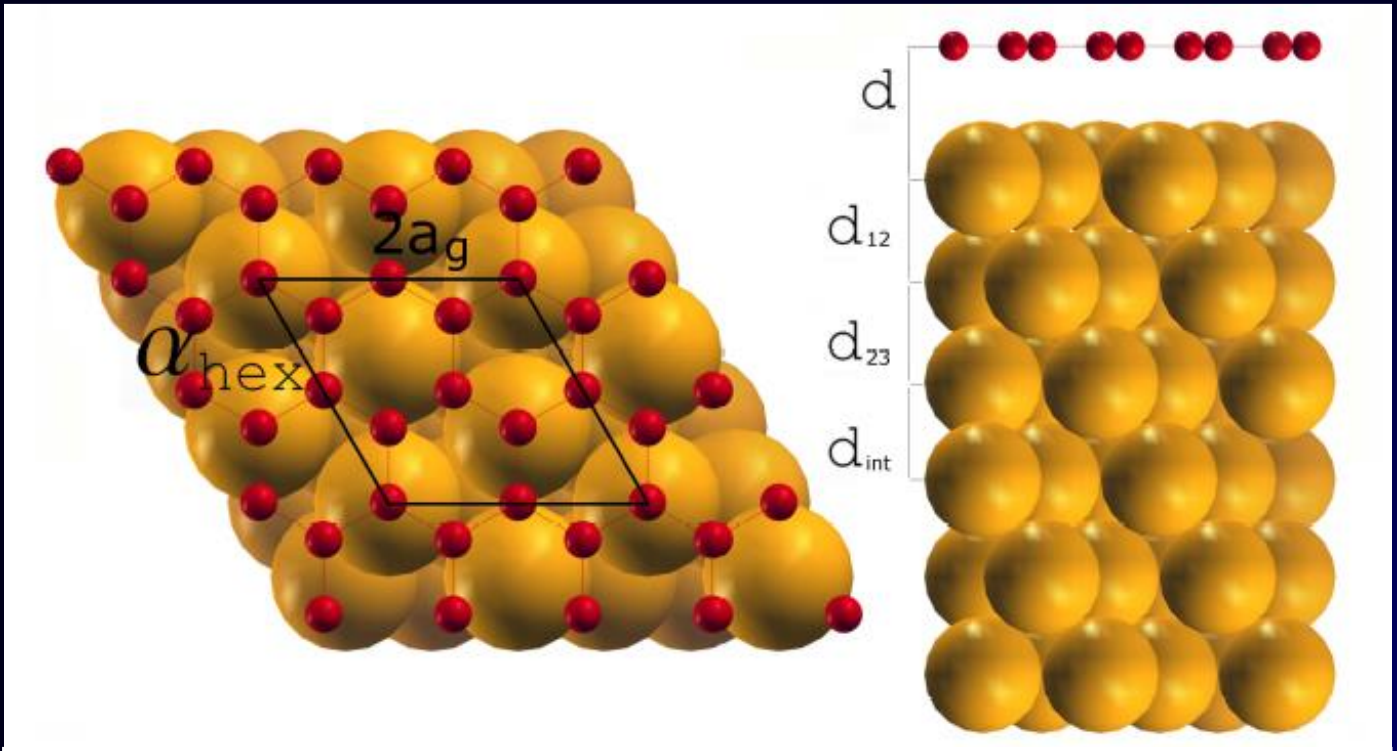
J. Slawinska, I. Wlasy, P. Dabrowski, Z. Klusek, I. Zasada
Phys. Rev. B 85 (2012)

I. Wlasy, P. Dabrowski, M. Rogala, P.J. Kowalczyk, I. Pastrnak, W. Strupinski, J.M. Baranowski and Z. Klusek
Appl. Phys. Lett. 102, 111601 (2013)

Physical Review B
condensed matter and materials physics

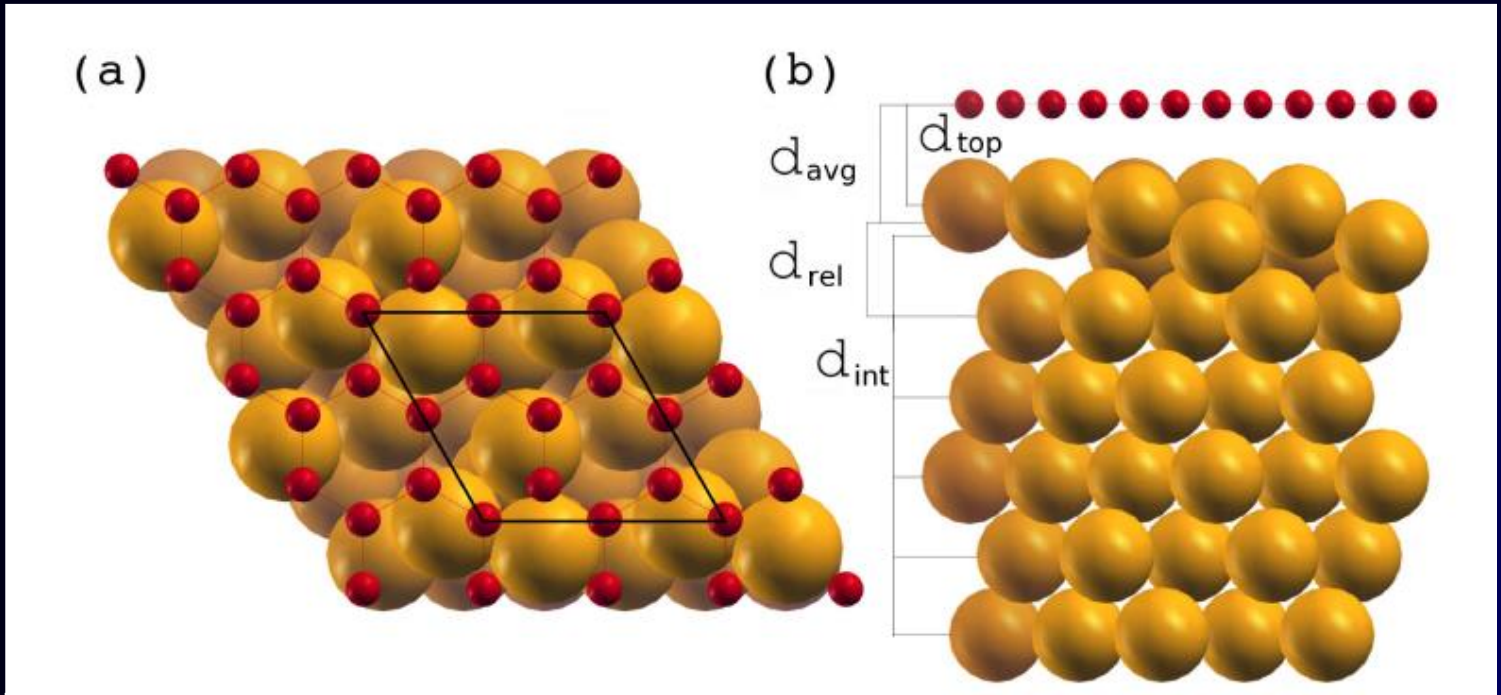
AIP Applied Physics Letters

DFT – grafen na Au(111)



Geometria adsorpcji grafen/Au(111) – widok z góry	Geometria adsorpcji grafen/Au(111) – widok z boku

DFT – grafen na Au(111) poli



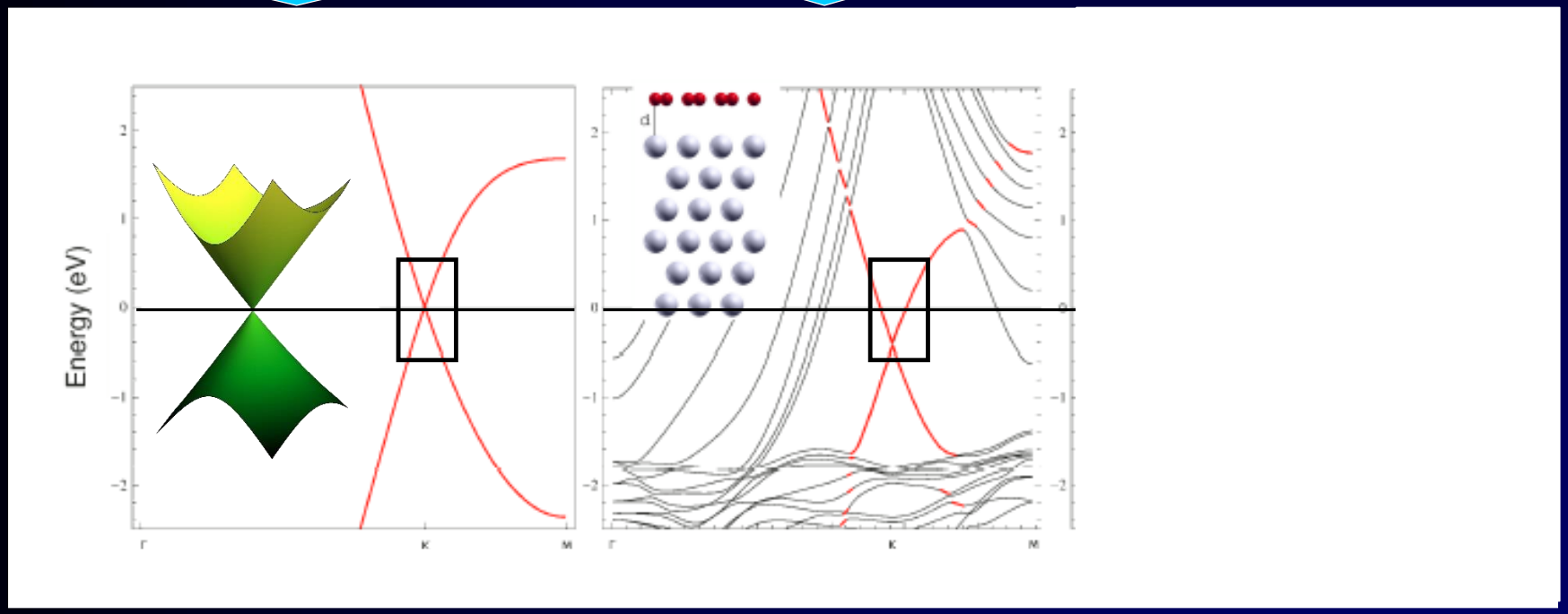
Geometria adsorpcji Grafen/Au(111) – widok z góry. Wprowadzono zaburzenia podłużne stałych sieci.

Geometria adsorpcji Grafen/Au(111) – widok z boku. Wprowadzono zaburzenia poprzeczne stałych sieci.

DFT: Oddziaływanie grafen-metal

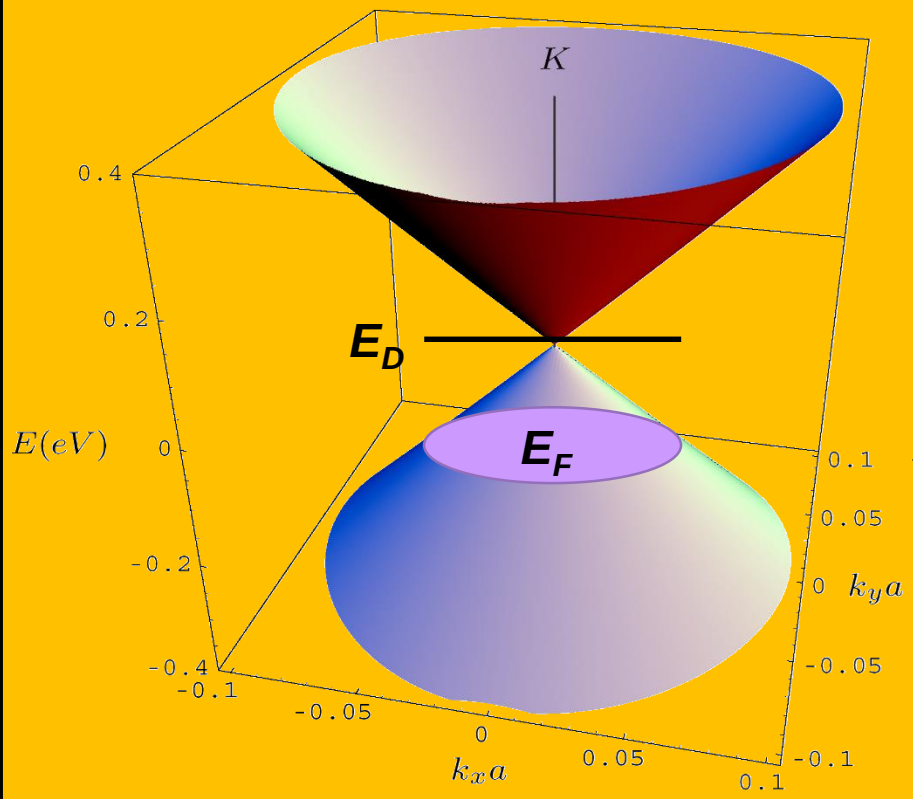
czysty grafen

fizysorpcja Cu(111)

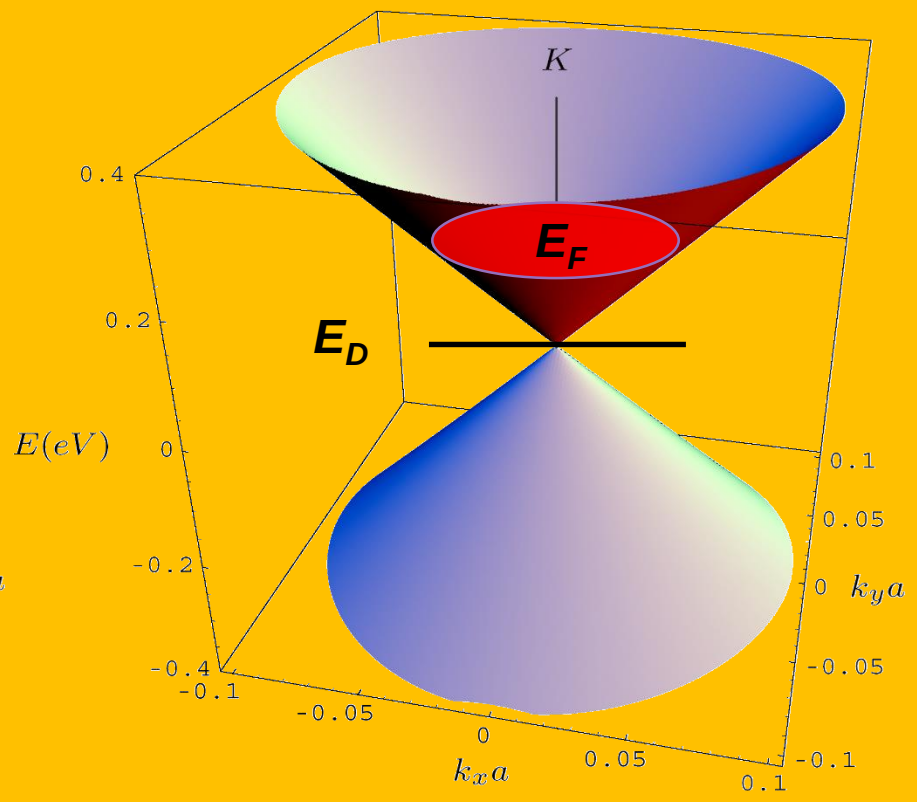


J. Sławińska, Rozprawa Doktorska Łódź 2012

DFT: Oddziaływanie grafen-metal



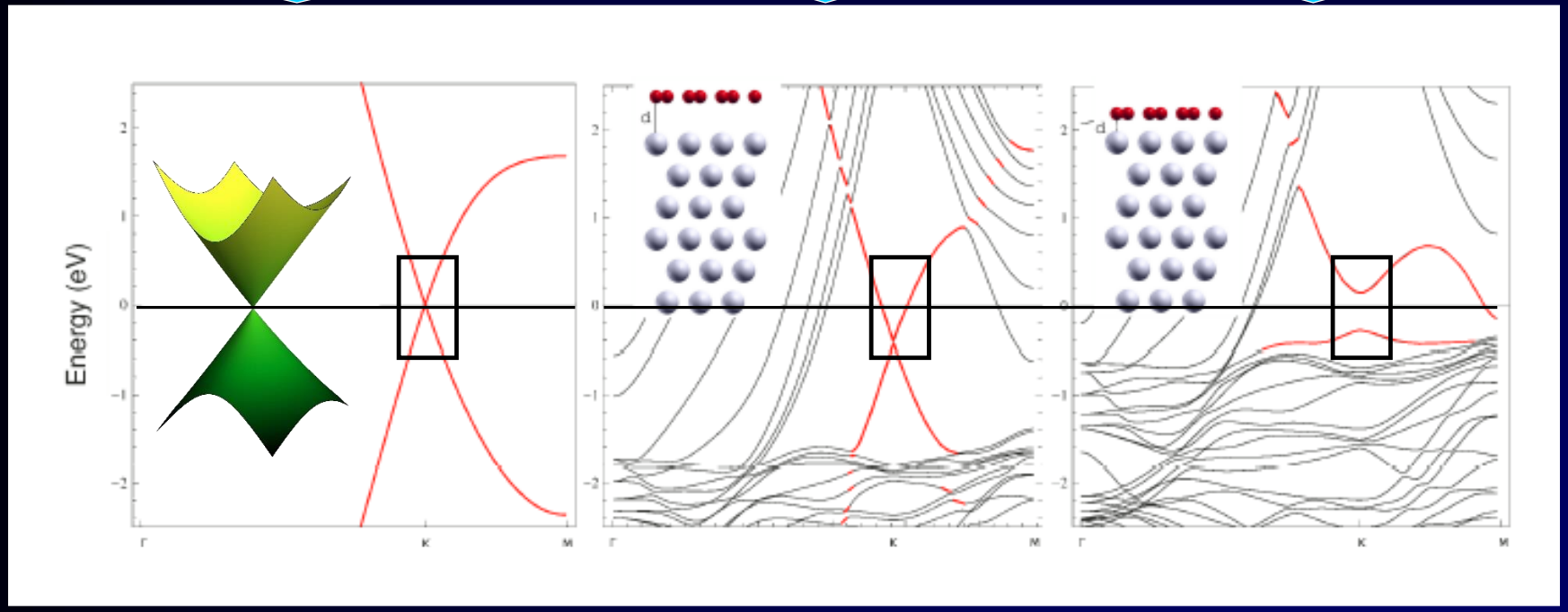
Domieszkowanie typu p



Domieszkowanie typu n

DFT: Oddziaływanie grafen-metal

czysty grafen	fizysorpcja Cu(111)	chemisorpcja Ni(111)



J. Sławińska, Rozprawa Doktorska Łódź 2012

DFT: Oddziaływanie grafen-metal

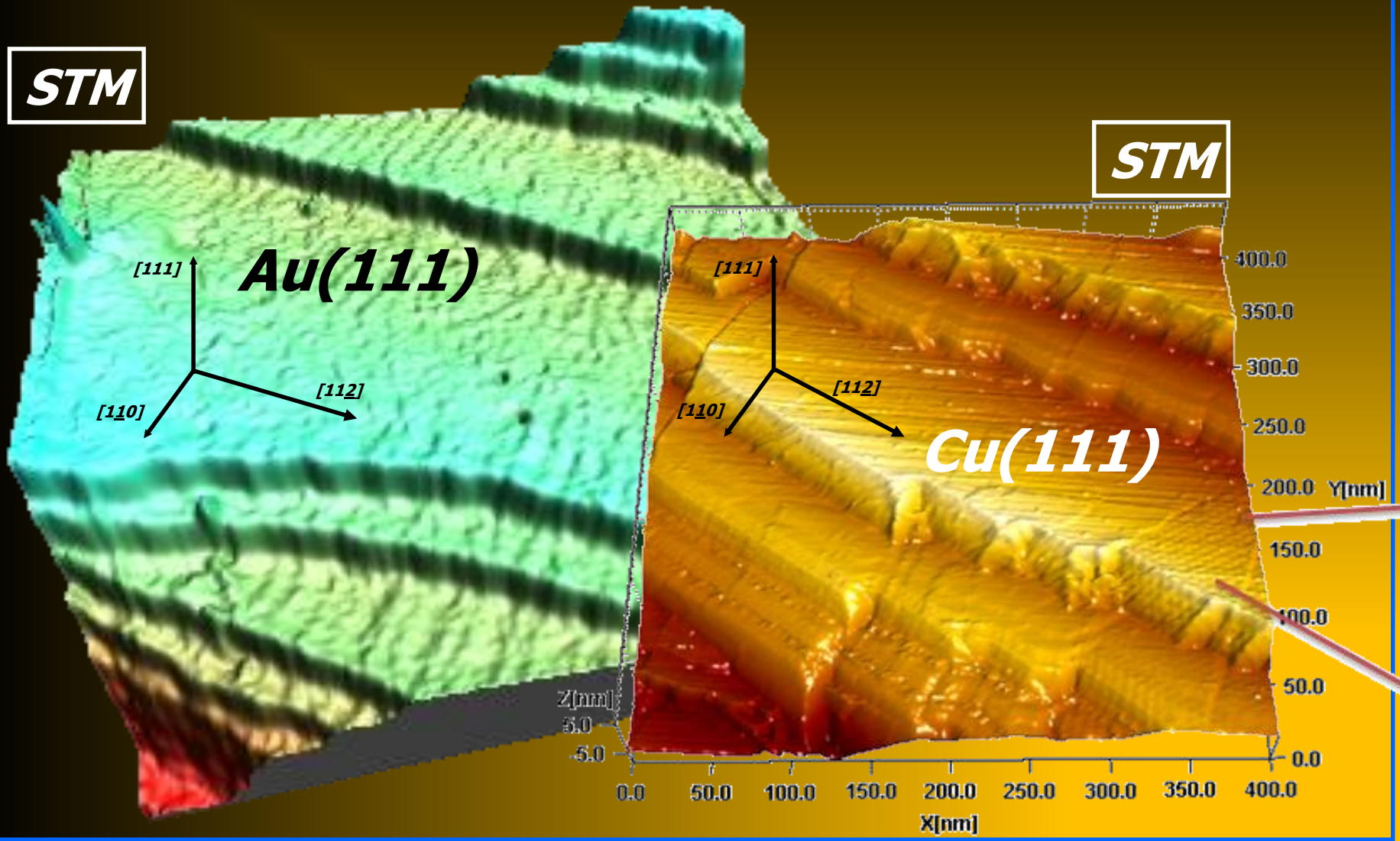
Własności elektronowe grafenu ulegają zmianie na skutek oddziaływania z metalami

Oddziaływanie grafen-metal silne/słabe

chemisorpcja	fizysorpcja
Co(111) Ni(111) Pd(111)	Al(111) Ag(111) Cu(111) Au(111) Pt(111)

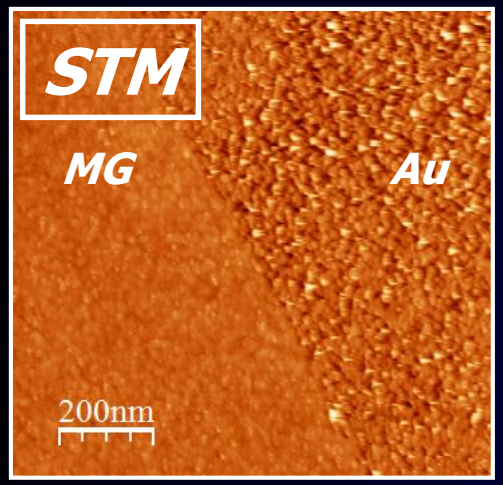
Czy DFT daje poprawne rezulataty ?

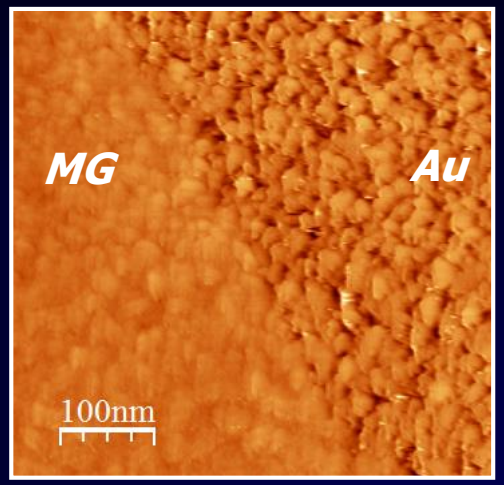
Oddziaływanie grafenu z metalami

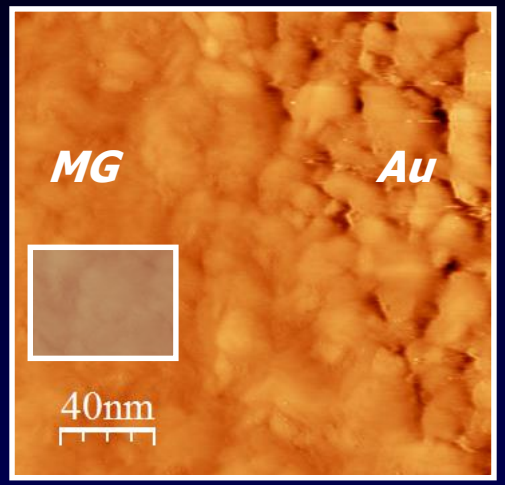


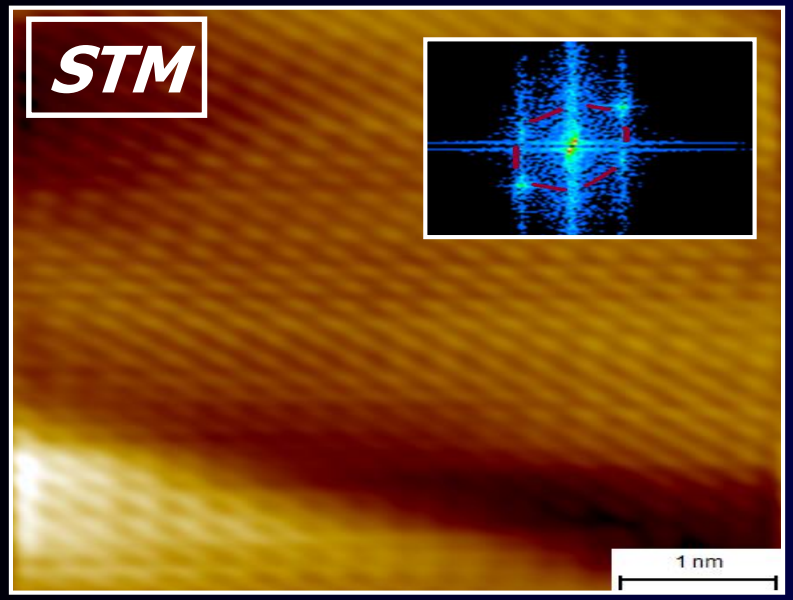
UNIWERSYTET ŁÓDZKI

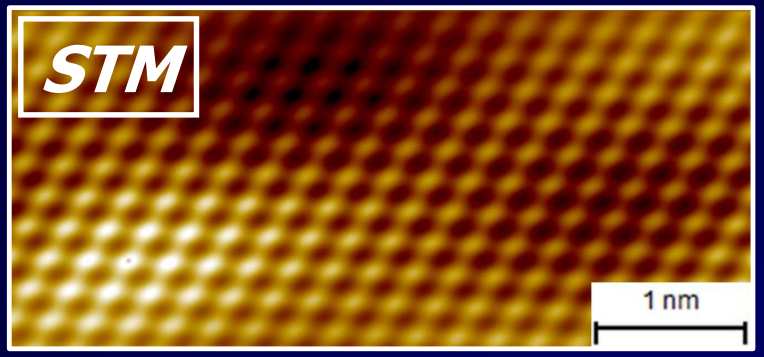
Oddziaływanie grafen - Au







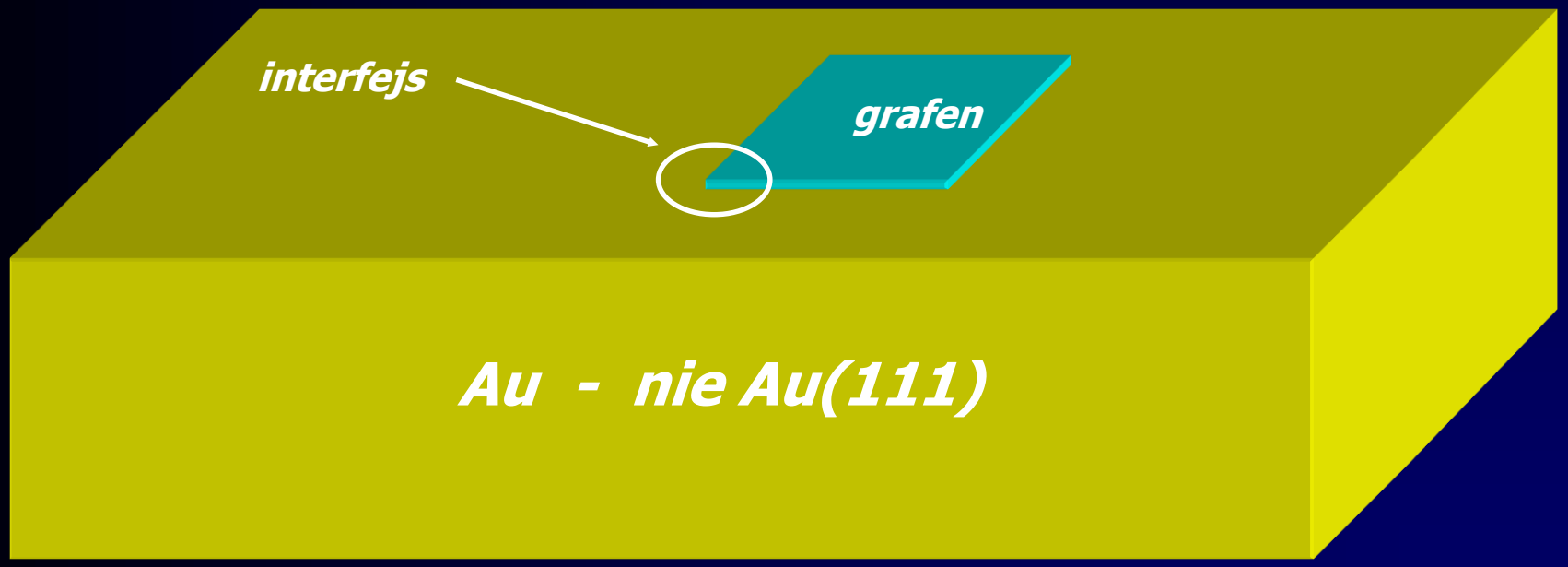




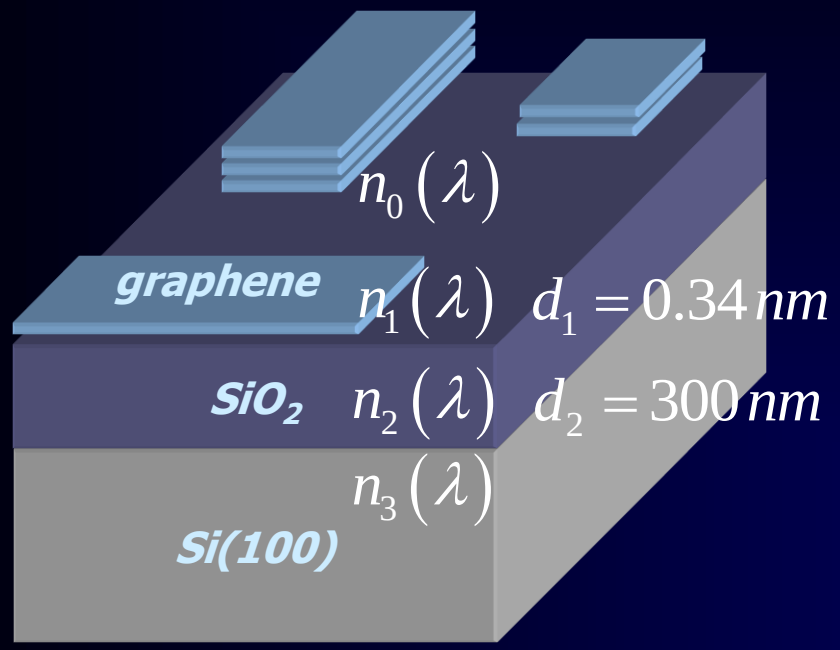
Oddziaływanie grafen-Au

Najprostsza wersja próbki do badań

Identyfikacja optyczna – nie możliwa
Spektroskopia Ramana - wpływ oddziaływań



Identyfikacja optyczna grafenu na SiO_2



grafen/SiO_2/Si

$$r_1 = \frac{n_0 - n_1}{n_0 + n_1}$$

$$r_2 = \frac{n_1 - n_2}{n_1 + n_2}$$

$$r_2 = \frac{n_2 - n_3}{n_2 + n_3}$$

$$\Phi_1 = \frac{2\pi n_1 d_1}{\lambda}$$

$$\Phi_2 = \frac{2\pi n_2 d_2}{\lambda}$$

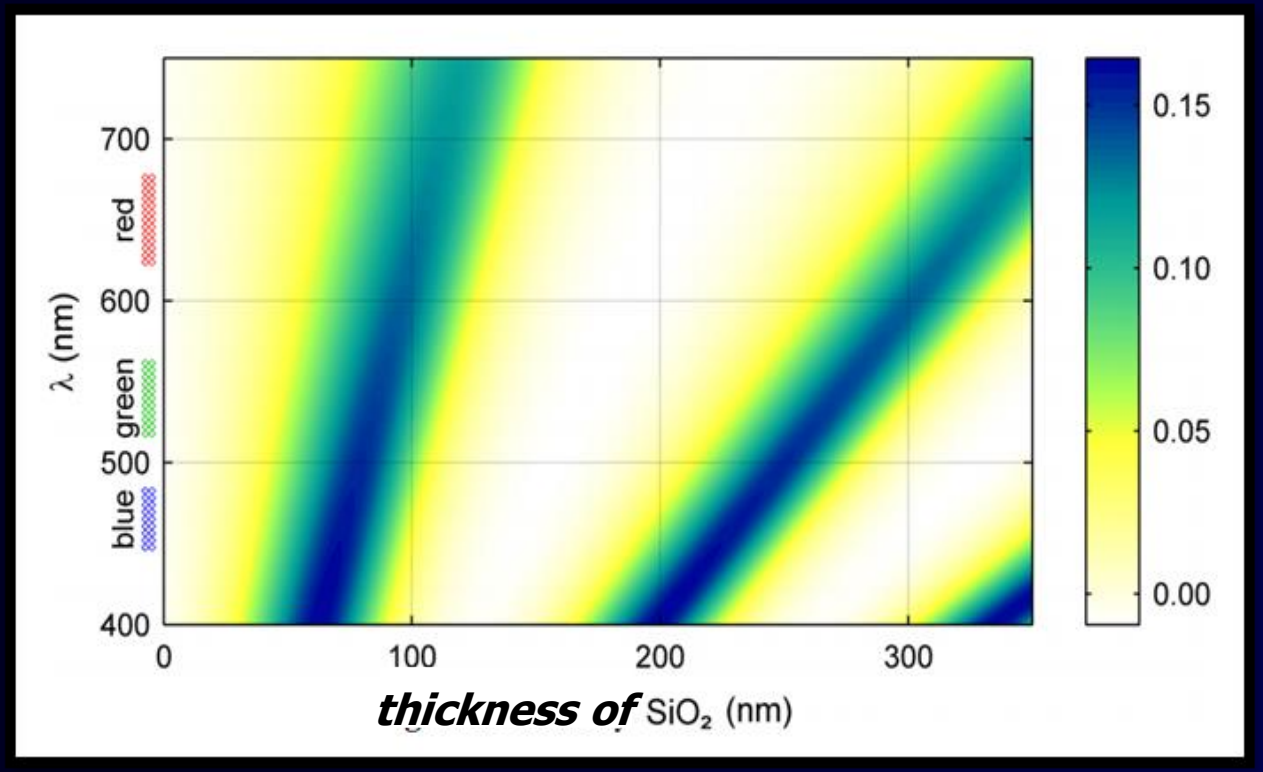
$$I(n_1) = \Big| \left(r_1 e^{i(\Phi_1+\Phi_2)} + r_2 e^{-i(\Phi_1-\Phi_2)} + r_3 e^{-i(\Phi_1+\Phi_2)} + r_1 r_2 r_3 e^{i(\Phi_1-\Phi_2)} \right)$$
$$\times \left(e^{i(\Phi_1+\Phi_2)} + r_1 r_2 e^{-i(\Phi_1-\Phi_2)} + r_1 r_3 e^{-i(\Phi_1-\Phi_2)} + r_2 r_3 e^{i(\Phi_1-\Phi_2)} \right)^{-1} \Big|^2$$

P. Blake, et al. Appl. Phys. Lett. 91, 063124 (2007).

Identyfikacja optyczna grafenu na SiO_2

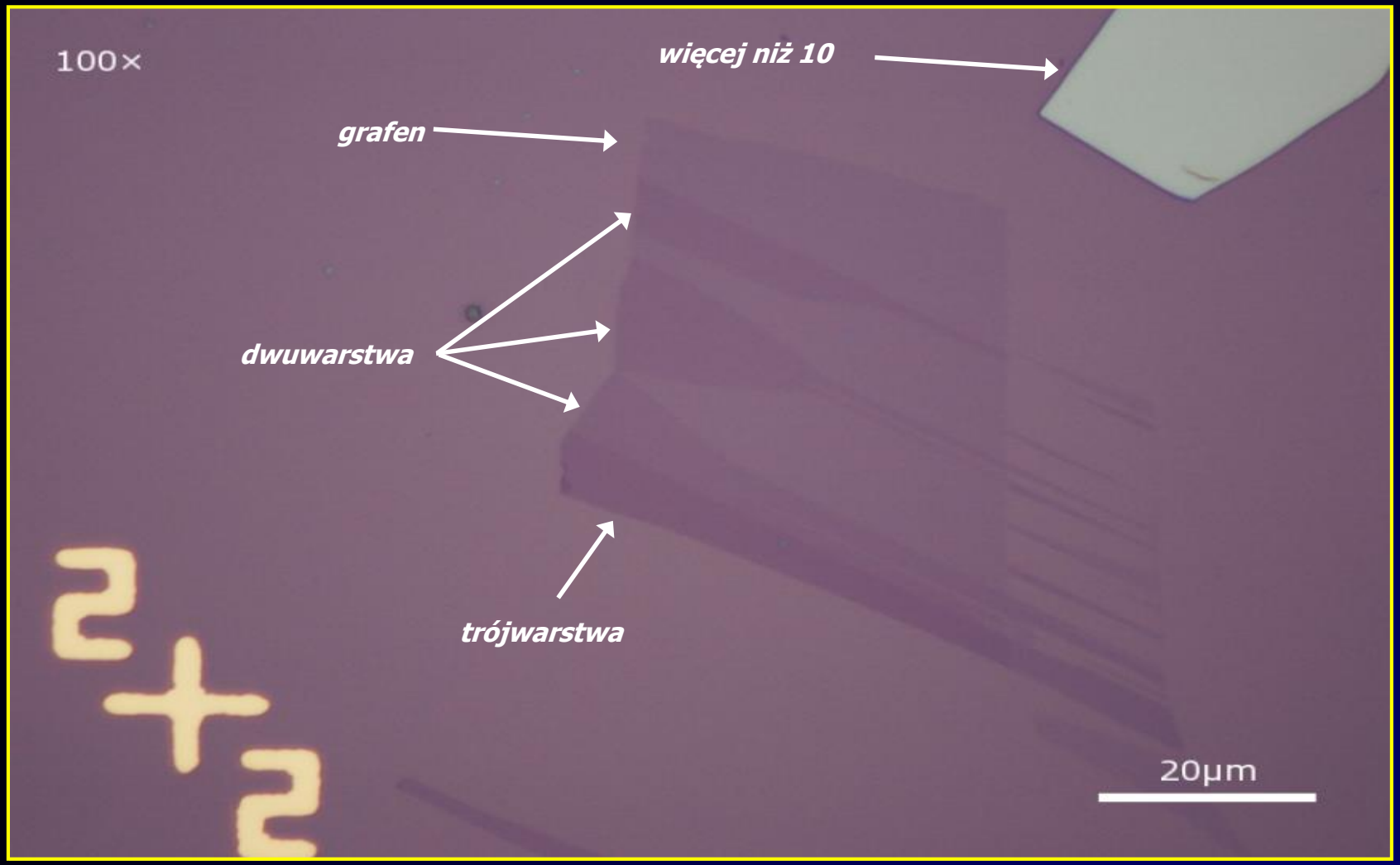
P. Blake, et al. Appl. Phys. Lett. 91, 063124 (2007).

$$C = \frac{I(n_1 = 1) - I(n_1)}{I(n_1 = 1)}$$

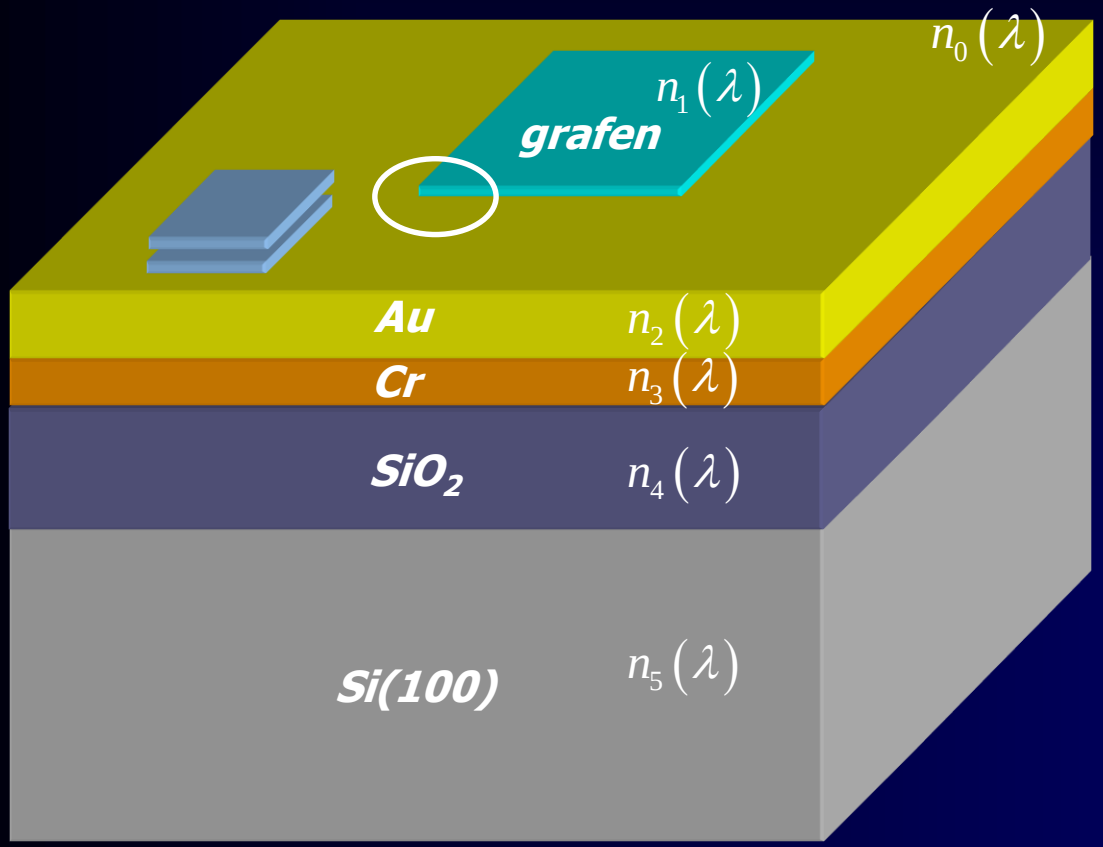


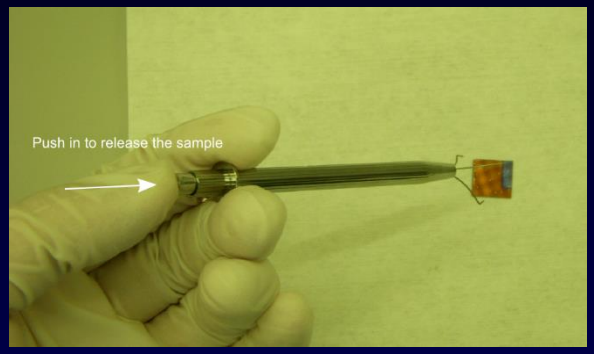
Identyfikacja optyczna grafenu na SiO_2

Identyfikacja optyczna grafenu na SiO_2



Identyfikacja optyczna grafenu na Au

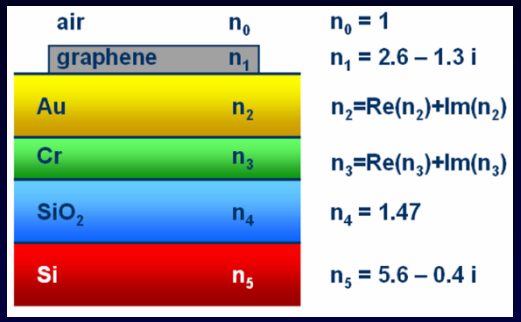


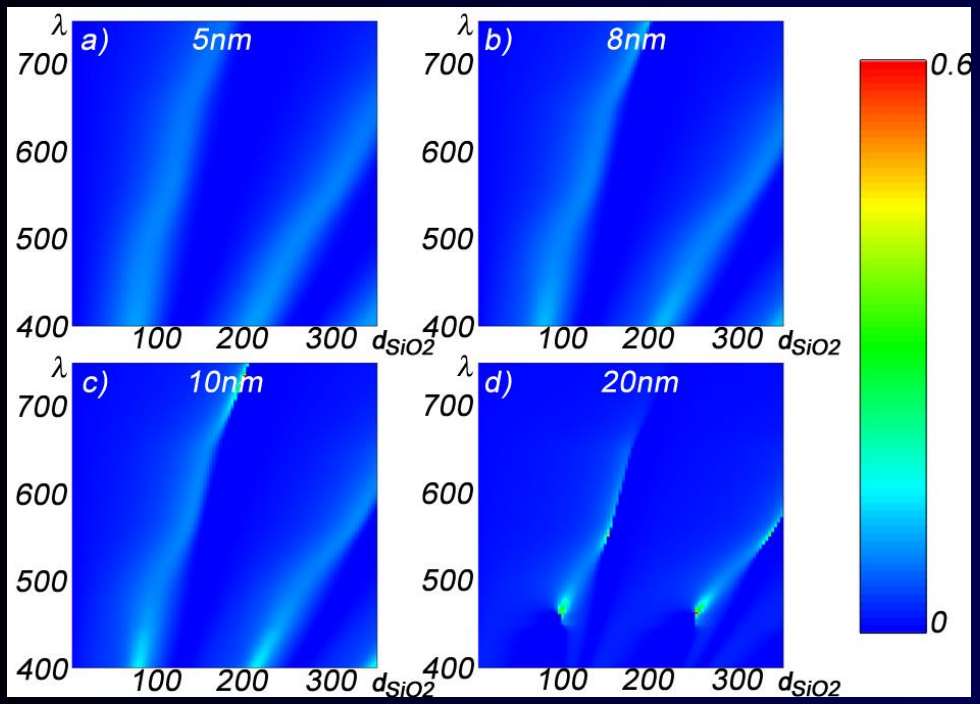


I. Wlasny, P. Dabrowski, Z. Klusek, arXiv:1102.4953v1 (2011).

Identyfikacja optyczna grafenu na Au

$$R(n_1,\lambda)=\Big|\Big(r_1+r_2e^{-i\Delta_1}+r_3e^{-i(\Delta_1+\Delta_2)}+r_4e^{-i(\Delta_1+\Delta_2+\Delta_3)}+r_1r_2r_3e^{-i\Delta_2}+r_1r_3r_4e^{-i\Delta_3}$$
$$+r_1r_2r_4e^{-i(\Delta_2+\Delta_3)}+r_2r_3r_4e^{-i(\Delta_1+\Delta_3)}\Big)\times\Big(1+r_1r_2e^{-i\Delta_1}+r_1r_3e^{-i(\Delta_1+\Delta_2)}+r_1r_4e^{-i(\Delta_1+\Delta_2+\Delta_3)}$$
$$+r_2r_3e^{-i\Delta_2}+r_3r_4e^{-i\Delta_3}+r_2r_4e^{-i(\Delta_2+\Delta_3)}+r_1r_2r_3r_4e^{-i(\Delta_1+\Delta_3)}\Big)^{-1}\Big|^2$$





$$C=\frac{I(n_1=1)-I(n_1)}{I(n_1=1)}=\frac{R(n_1=1)-R(n_1)}{R(n_1=1)}$$

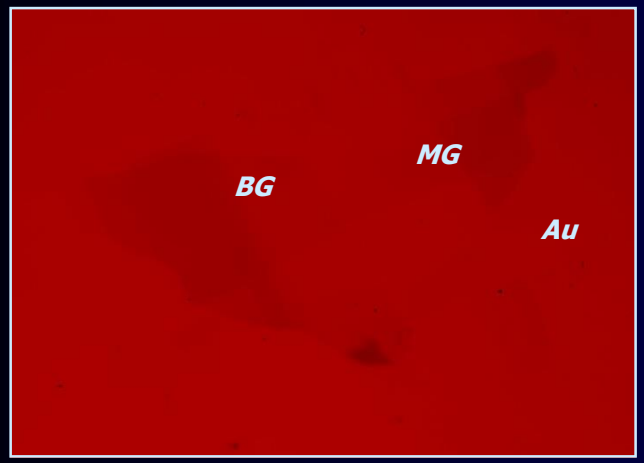
I. Wlasny, P. Dabrowski, Z. Klusek, arXiv:1102.4953v1 (2011).

UNIWERSYTET ŁÓDZKI

Identyfikacja optyczna grafenu na Au

niebieski

zielony

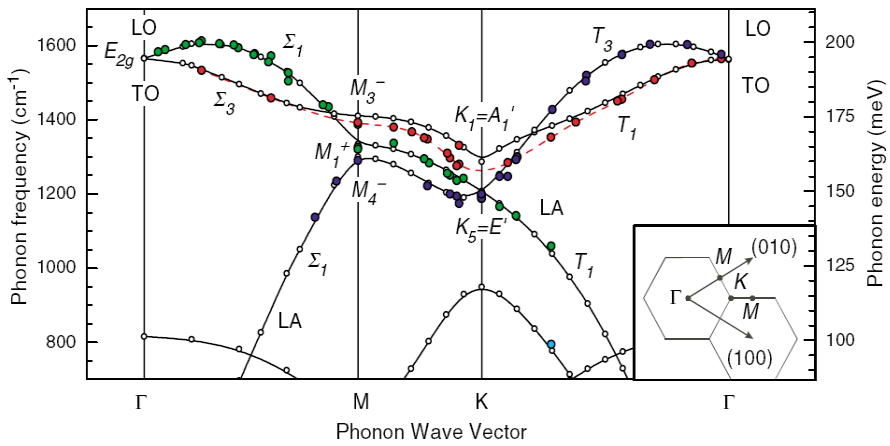


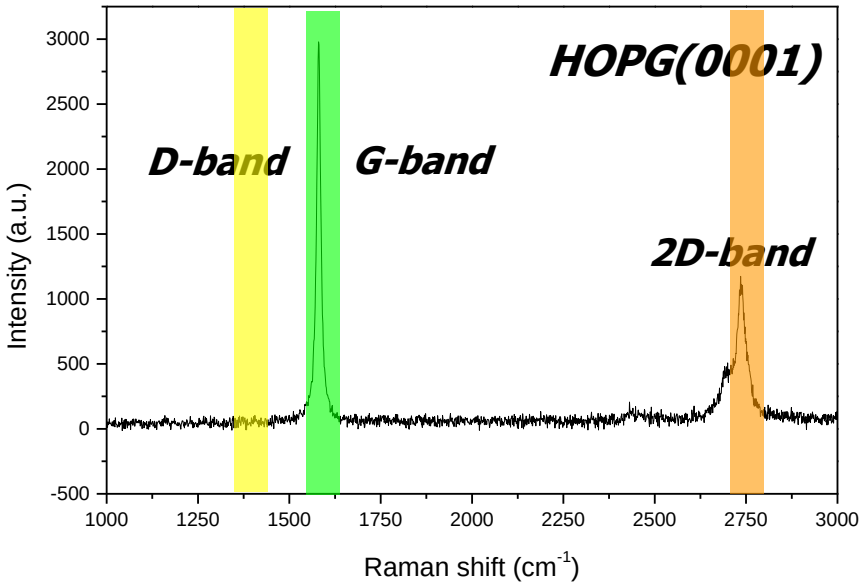
czerwony

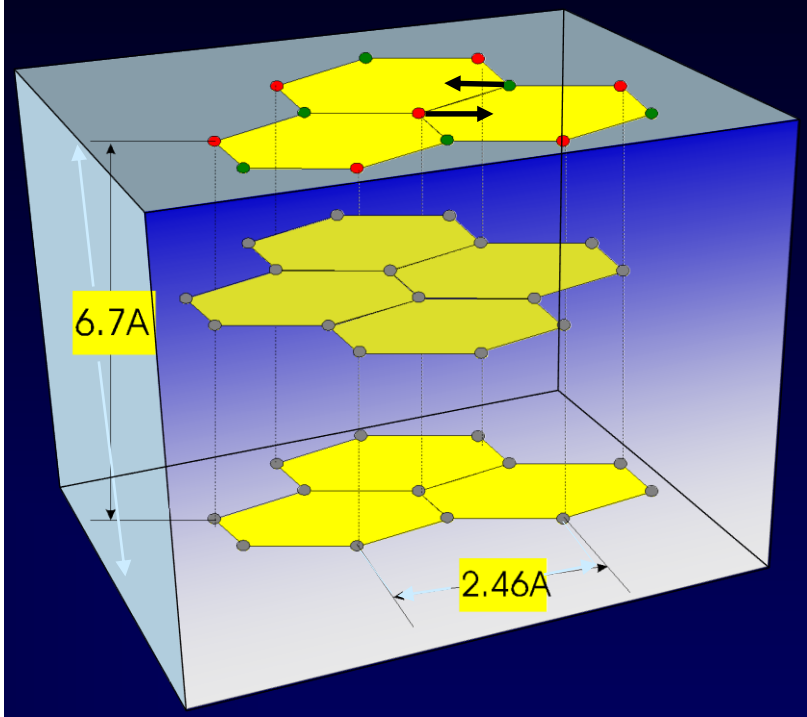
żółty

I. Wlasny, P. Dabrowski, Z. Klusek, arXiv:1102.4953v1 (2011).

Spektroskopia ramanowska grafitu







D-band : defekty (~1350 cm^{-1})
G-band : drgania w warstwie (1581.5 cm^{-1})
2D-band : od. międzywarstwowe (~2700 cm^{-1})

UNIWERSYTET ŁÓDZKI

Spektroskopia ramanowska grafenu na SiO_2

UNIVERSITY OF CAMBRIDGE — DEPARTMENT OF ENGINEERING

Teoria/Eksperyment

PRL 97, 187401 (2006) PHYSICAL REVIEW LETTERS week ending 3 NOVEMBER 2006

Raman Spectrum of Graphene and Graphene Layers

A. C. Ferrari,[1,*] J. C. Meyer,[2] V. Scardaci,[1] C. Casiraghi,[1] M. Lazzeri,[3] F. Mauri,[3] S. Piscanec,[1] D. Jiang,[4] K. S. Novoselov,[4] S. Roth,[2] and A. K. Geim[4]

[1]*Cambridge University, Engineering Department, JJ Thompson Avenue, Cambridge CB3 0FA, United Kingdom*
[2]*Max Planck Institute for Solid State Research, Stuttgart 70569, Germany*
[3]*IMPMC, Universités Paris 6 et 7, CNRS, IPGP, 140 rue de Lourmel, 75015 Paris, France*
[4]*Department of Physics and Astronomy, University of Manchester, Manchester, M13 9PL, United Kingdom*

(Received 9 June 2006; published 30 October 2006)

[1,4]), in practice, it is only possible to distinguish between one and two layers by AFM if films contain folds or wrinkles [1,4]. This poses a major limitation to the range of substrates and is a setback for the widespread utilization of this material. Here, we show that graphene's electronic structure is uniquely captured in its Raman spectrum. Raman fingerprints for single layers, bilayers, and few layers reflect changes in the electron bands and allow unambiguous, high-throughput, nondestructive identification of graphene layers, which is critically lacking in this emerging research area.

Dr Andrea C. Ferrari

Spektroskopia ramanowska grafenu na SiO_2

Powszechna procedura identyfikacji

1 - warstwa - 1 komponent
2 - warstwy - 4 komponenty
3 - warstwy - 15 komponentów ->6

Więcej niż 5 warstw

2 komponenty jak w graficie

UNIWERSYTET ŁÓDZKI

Spektroskopia ramanowska grafenu na Au

domieszkowanie

pik 2D - dodatnie przesunięcie -> typ p
pik 2D - ujemne przesunięcie -> typ n

do 10 cm^{-1}

naprężenia

Poszerzenie pików G i 2D
Przesunięcie piku 2D

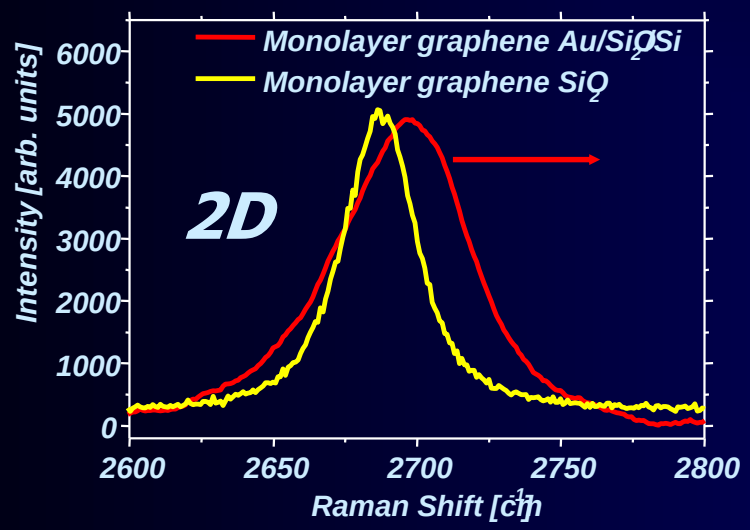
do 50 cm^{-1}

UNIWERSYTET ŁÓDZKI

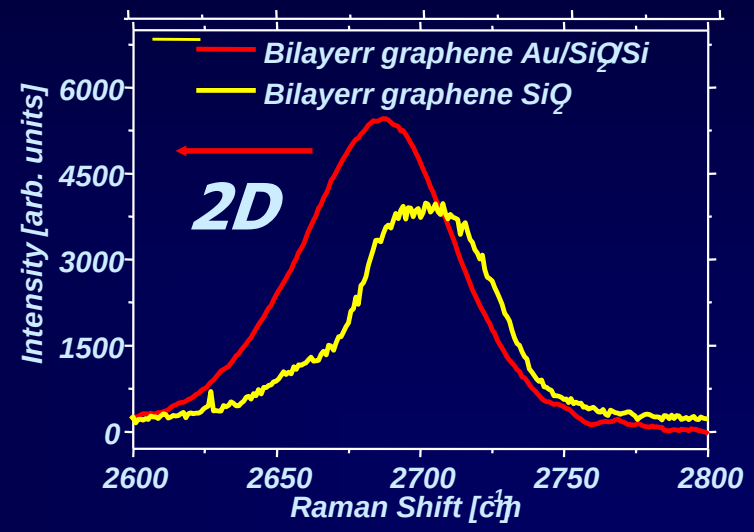
Spektroskopia ramanowska grafenu na Au

Brak teorii oddziaływania grafenu z metalami

grafen/Au/SiO_2/Si



dwuwarstwa/Au/SiO_2/Si

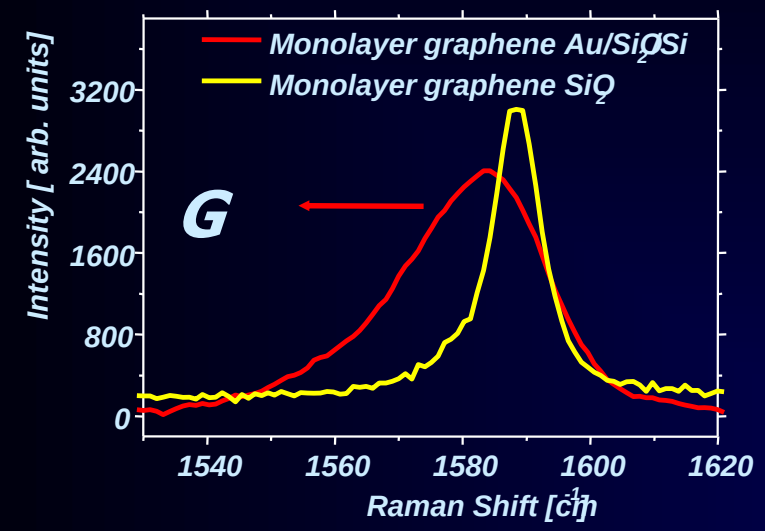


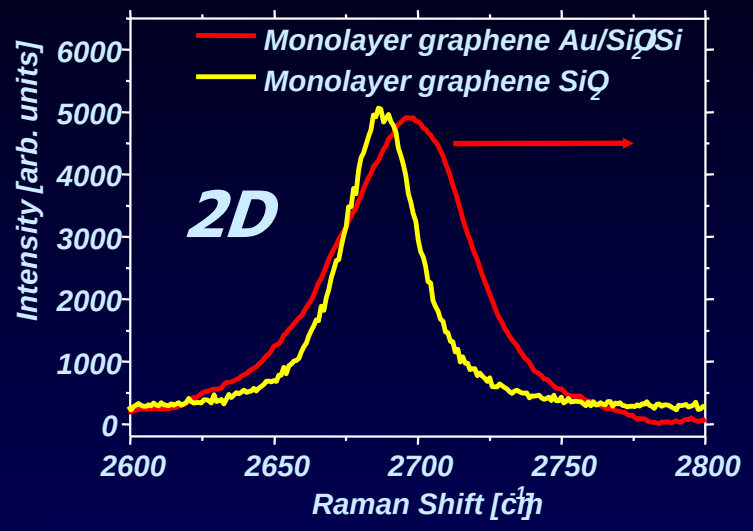
A. Sozanska, P. Dabrowski, I. Wlasny, J. Slawinska, I. Zasada, Z. Klusek
XXII International Conference on Raman Spectroscopy (ICORS 2010)
Boston, USA, August 8-13, 2010

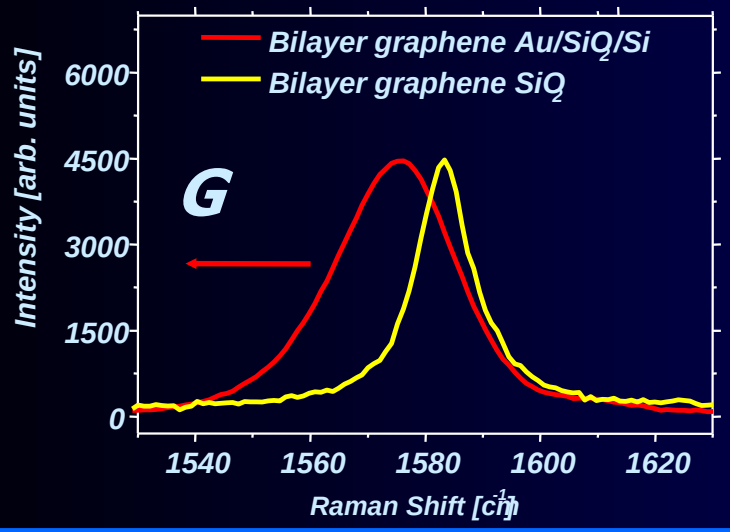
Au

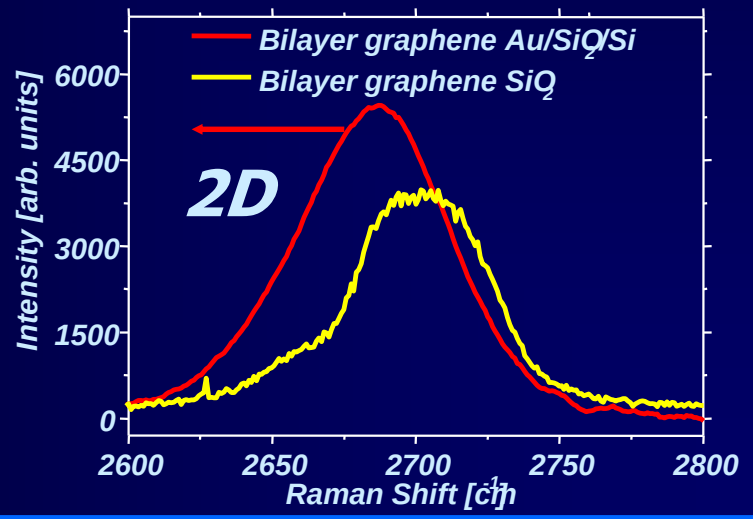
UNIWERSYTET ŁÓDZKI

Spektroskopia ramanowska grafenu na Au









Spektroskopia ramanowska grafenu na Au

$$\frac{dv_F}{v_F} = \frac{1}{q\frac{d\omega}{dq}} d\overline{\omega} = \frac{\hbar v_F}{E_L - \hbar\frac{d\overline{\omega}}{dq}} d\overline{\omega}$$

$$\frac{d\omega}{dq} = 0.08\,eVA$$
$$\hbar v_F = 6.5\,eVA$$
$$E_L = 2.41\,eV\ (514\,nm)$$
$$\hbar\frac{\omega}{2} = 2680\,cm^{-1}/2 = 1340\,cm^{-1} = 0.1663\,eV$$

$$\frac{dv_F}{v_F} = \frac{36.21\,d\overline{\omega}}{eV}$$

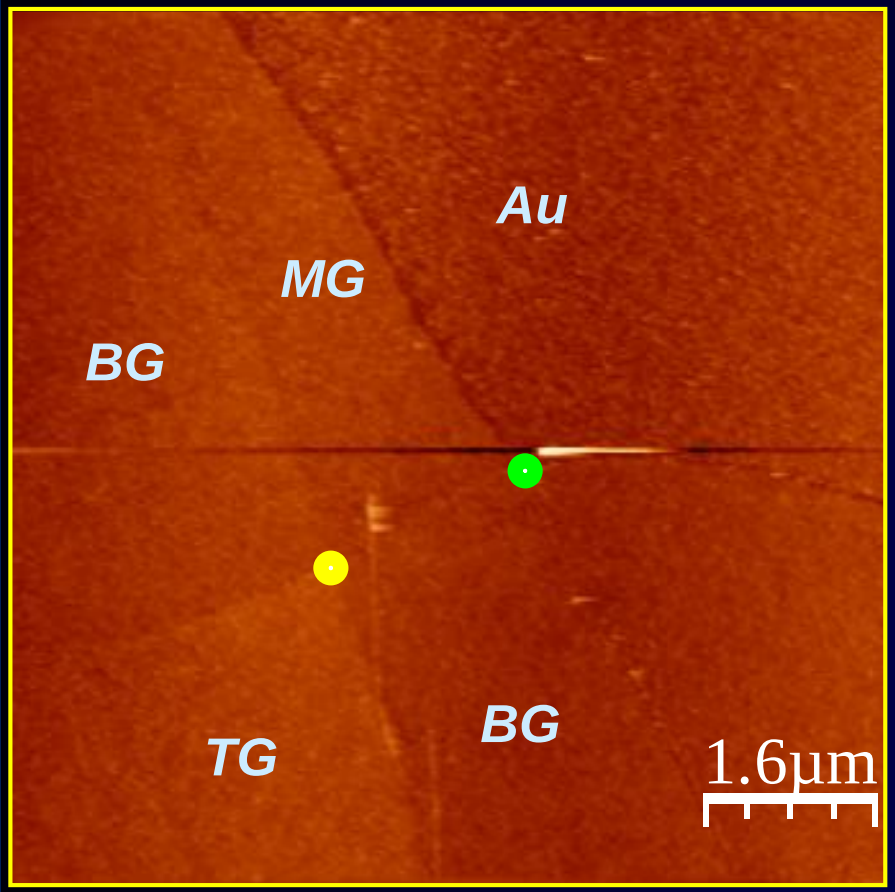
2D $d\overline{\omega} = 17\,cm^{-1} \longrightarrow$ **7.6 %**

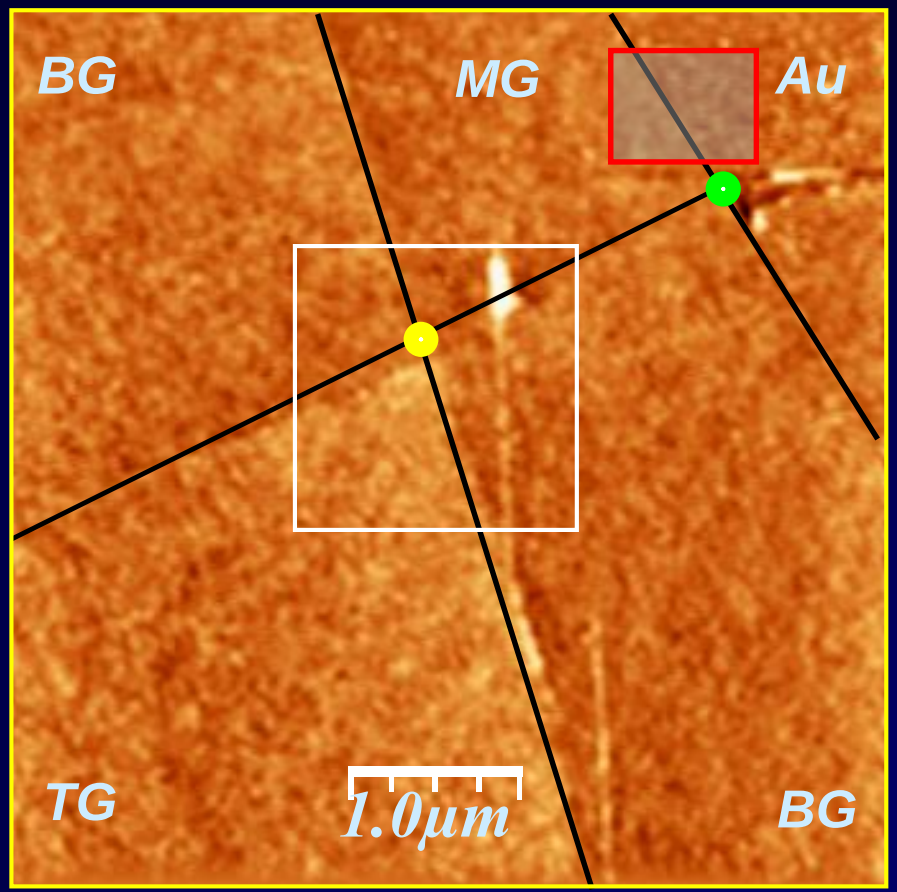
UNIWERSYTET ŁÓDZKI

Badania STM/STS grafenu na Au

Istotą badanej próbki jest to, że warstwy o różnej grubości badane są jednocześnie

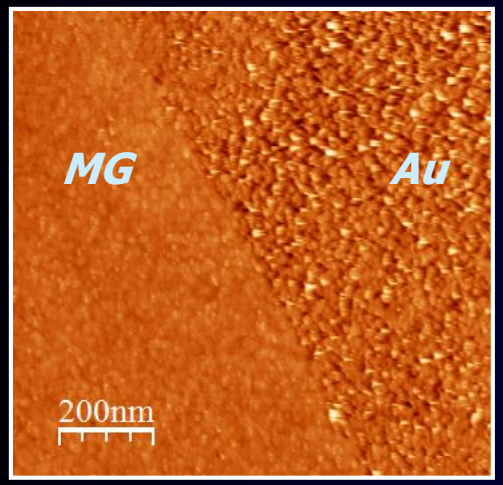
W dużej skali rozdzielczość pomiędzy Au, MG, BG, TG jest bardzo słaba

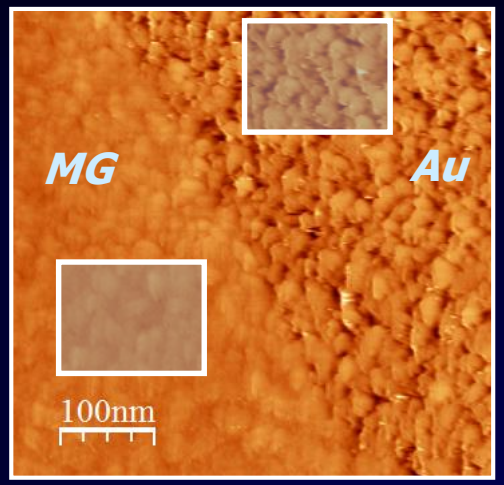


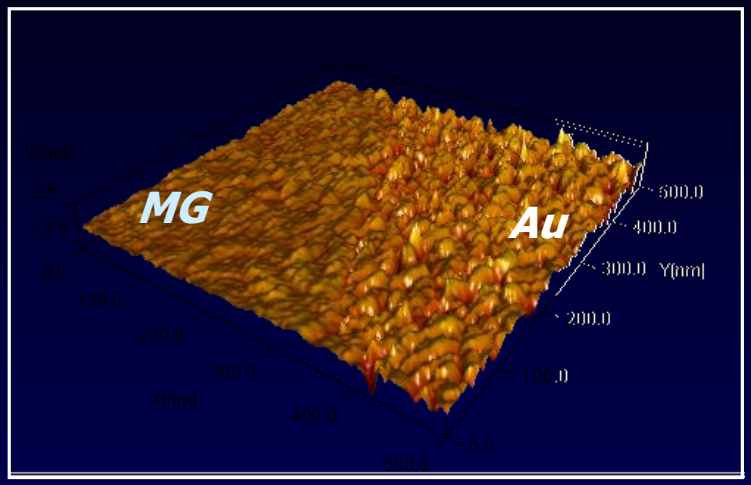


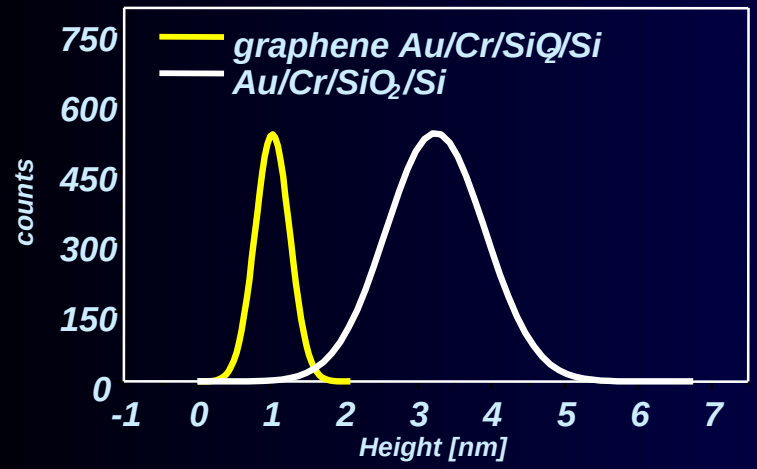
UNIWERSYTET ŁÓDZKI

Badania STM/STS grafenu na Au





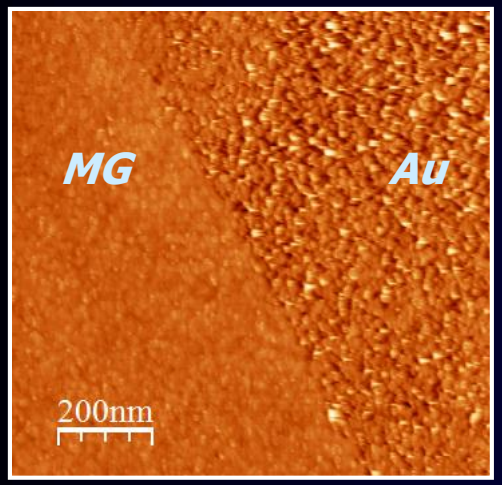


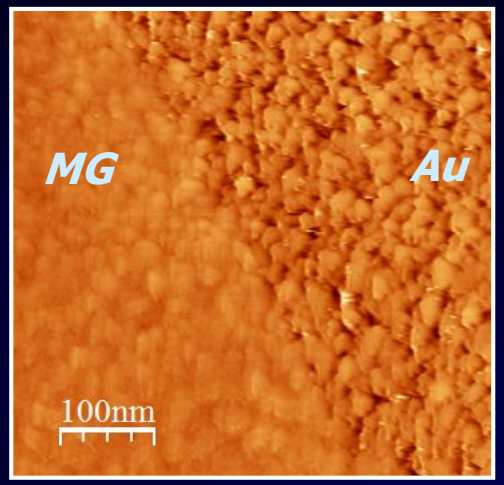


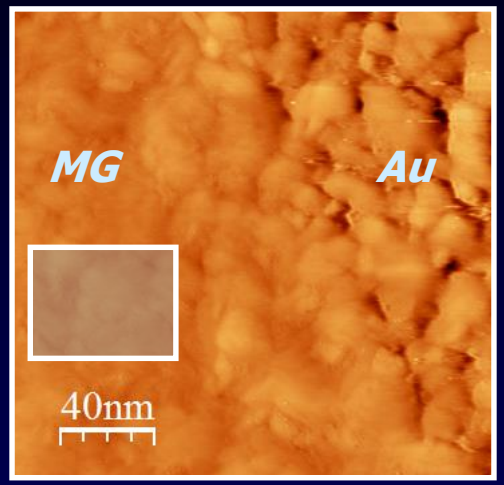
Rozkład wysokości podłoża $Au/Cr/SiO_2/Si$ i $MG/ Au/Cr/SiO_2/Si$

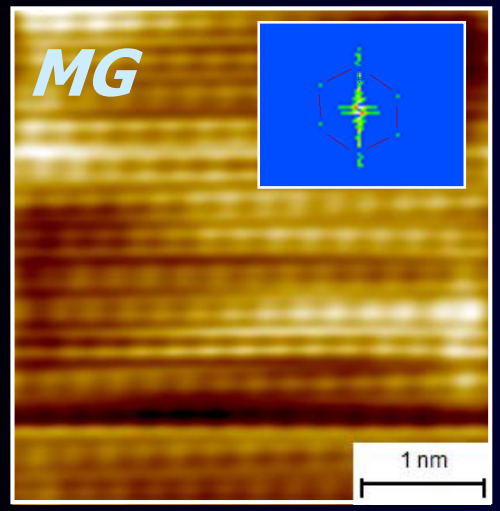
UNIWERSYTET ŁÓDZKI

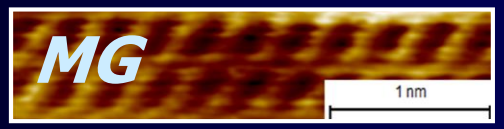
Badania STM/STS grafenu na Au









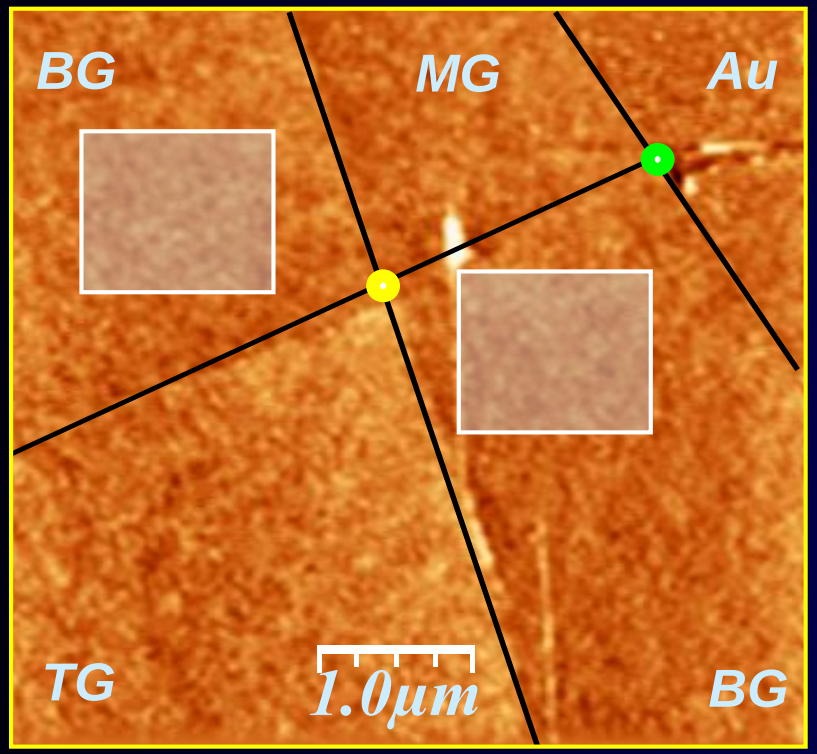


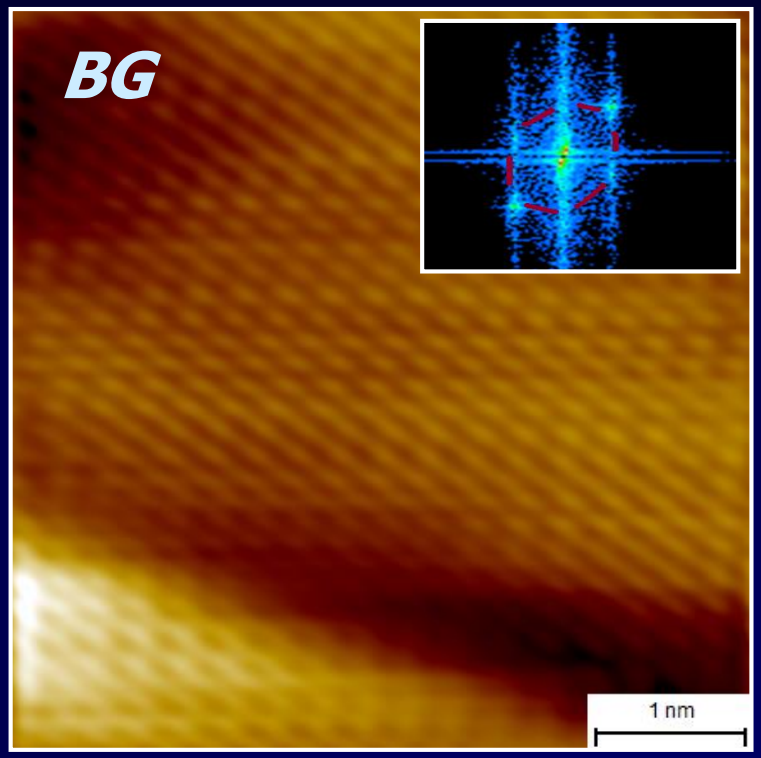
Atomowa zdolność rozdzielcza

Obserwowano strukturę trójkątną i sześciokątną. Struktura typowa dla grafitu była obserwowana częściej.

Badania STM/STS grafenu na Au

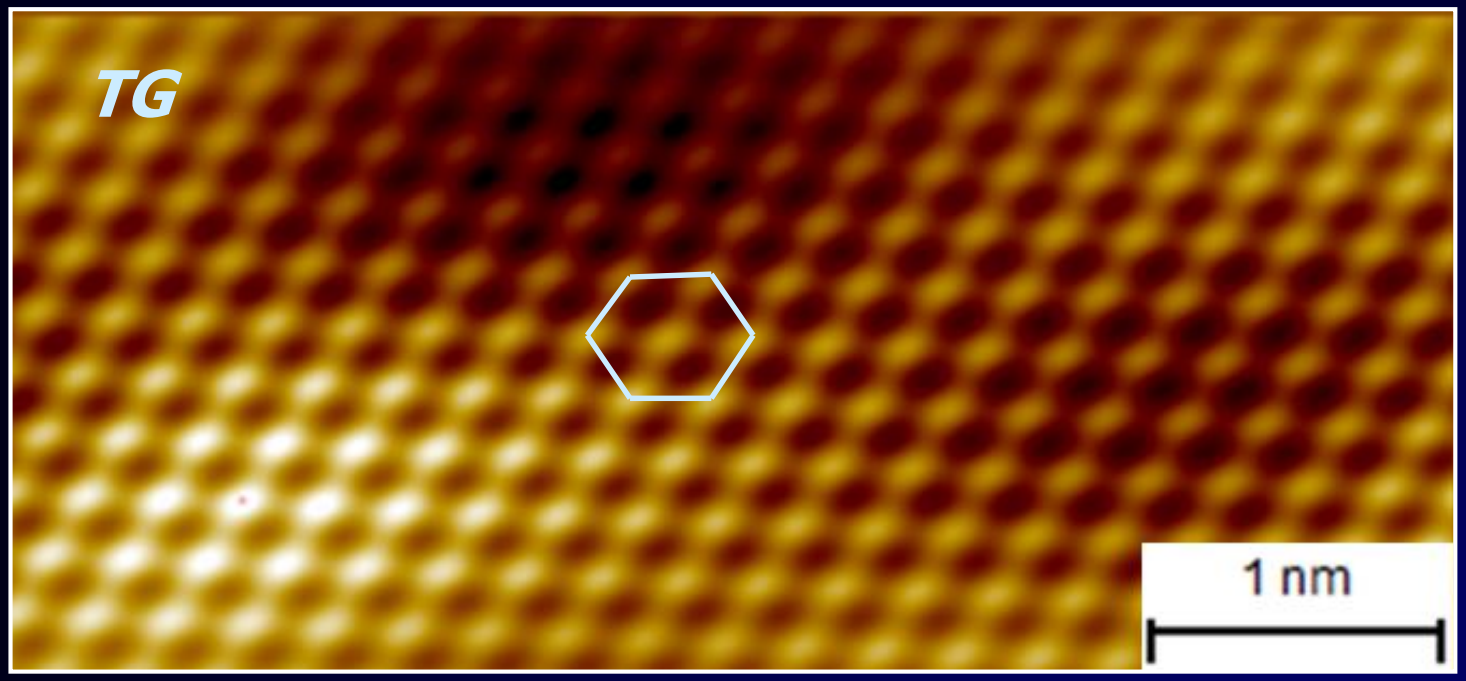
Rozdzielczość atomowa





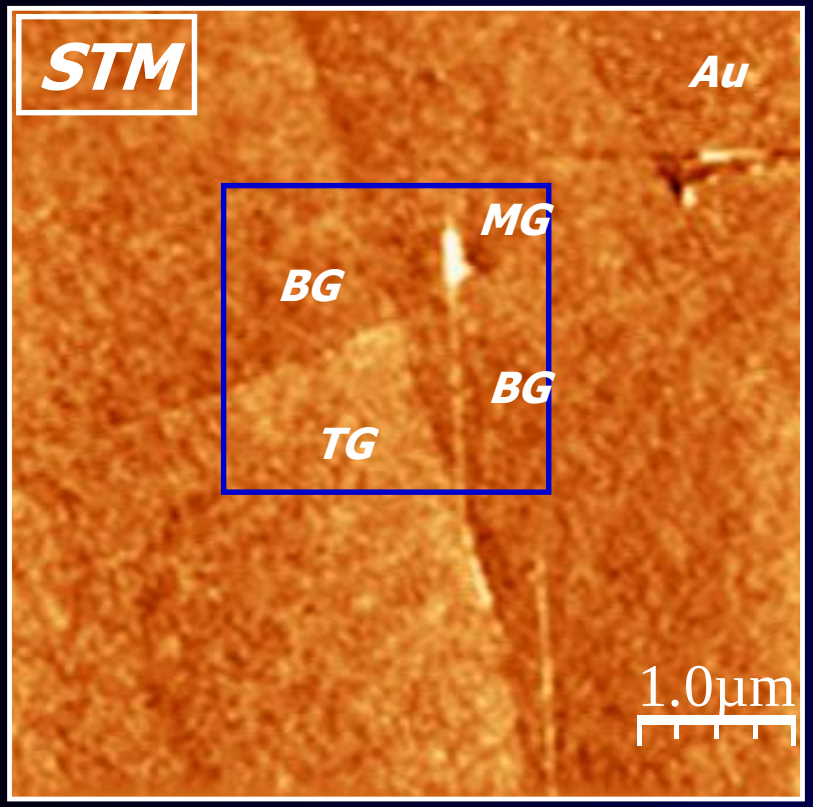
Badania STM/STS grafenu na Au

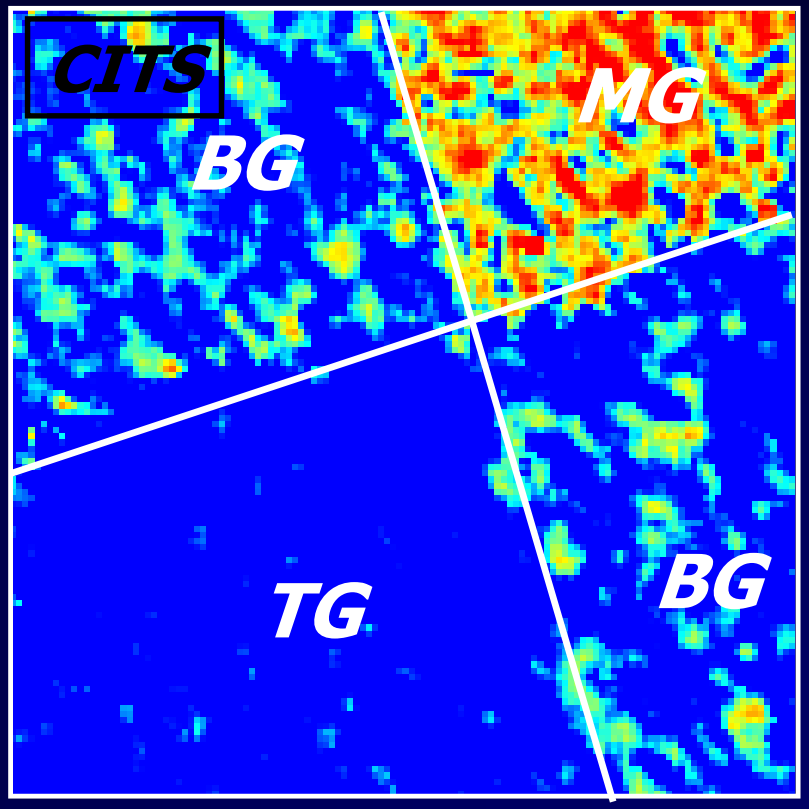
Rozdzielczość atomowa



Oddziaływanie grafen/Au - LDOS

Mapy elektronowej funkcji gęstości stanów



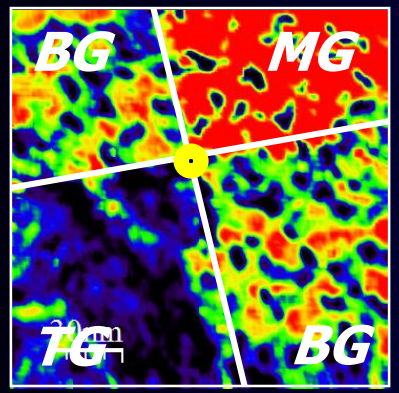


LDOS(x,y, E_F+0.010 eV)

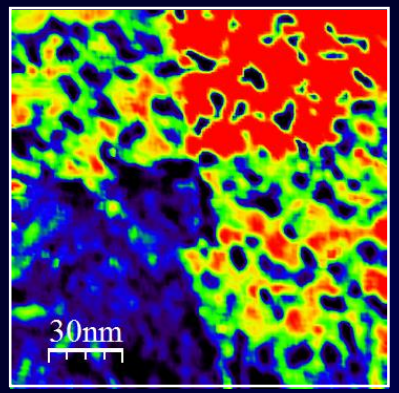
UNIWERSYTET ŁÓDZKI

Oddziaływanie grafen/Au - LDOS

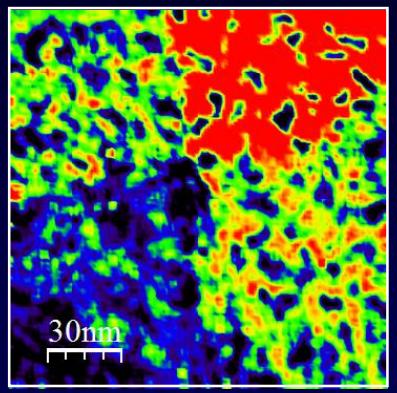
Mapy elektronowej funkcji gęstości stanów (CITS)



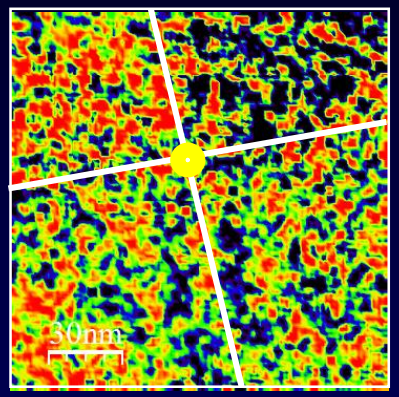
E_F+0,03 eV



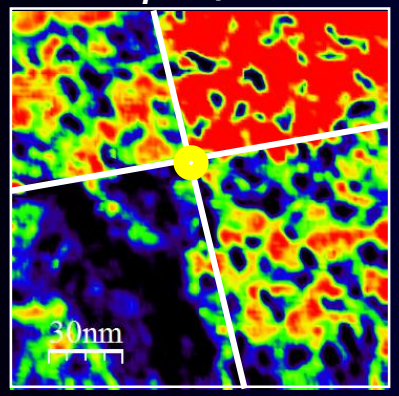
E_F+0,07 eV



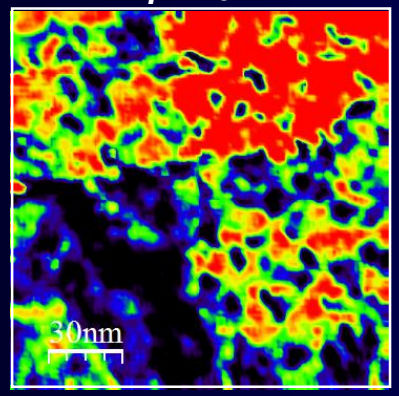
E_F+0,2 eV



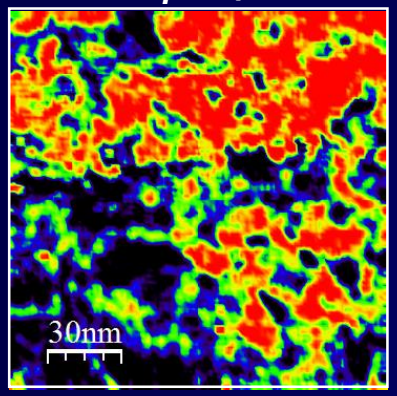
E_F+0,6 eV



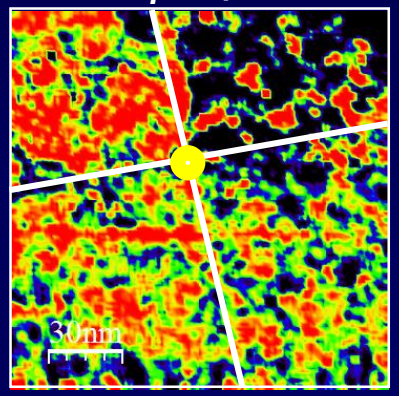
E_F-0,03 eV



E_F-0,07 eV



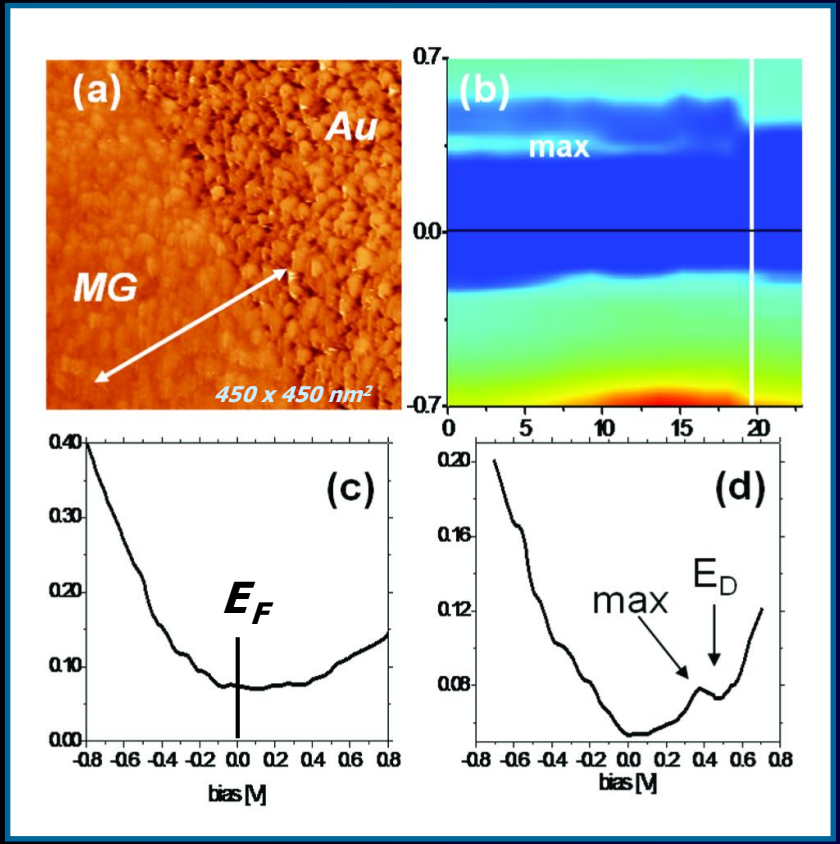
E_F-0,2 eV

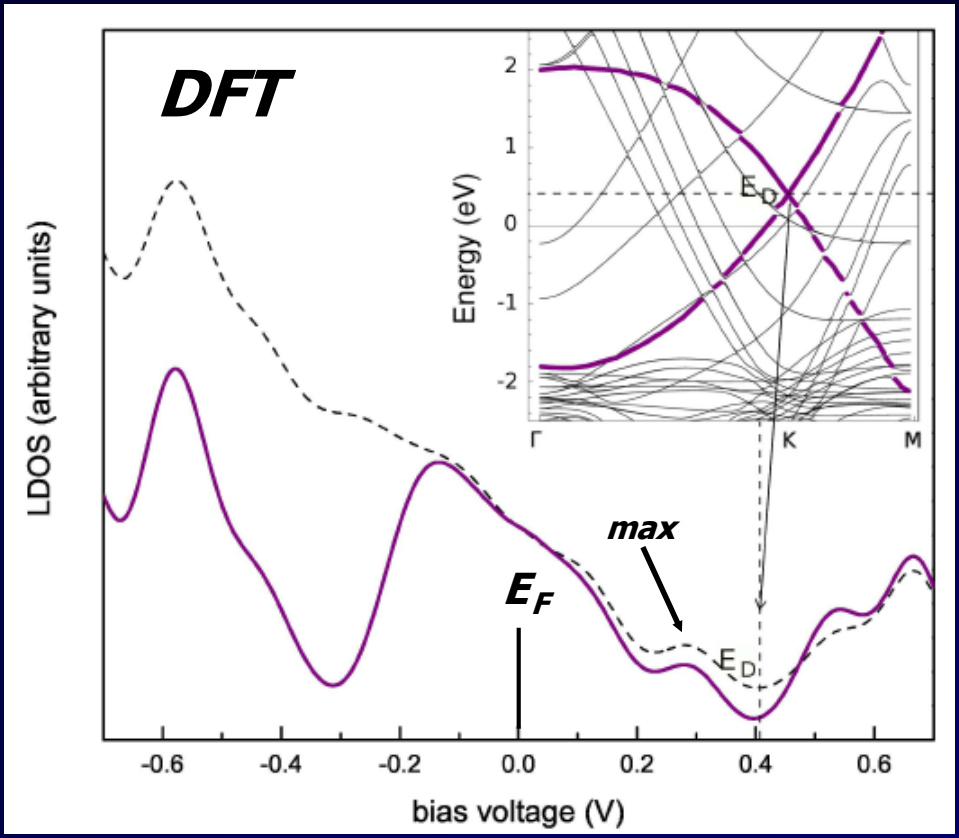


E_F-0,6 eV

Oddziaływanie grafen/Au - LDOS

$$\frac{dI}{dV} = \rho_s(r,eV)\rho_t(r,0)T(eV,eV,z) + \int \rho_s(r,E)\rho_t(r,E-eV)\frac{dT(E,eV,z)}{dV}dE$$

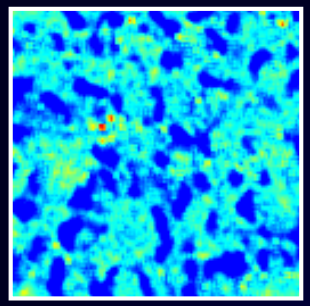




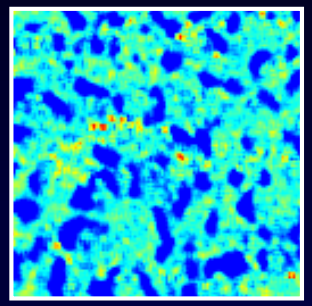
UNIWERSYTET ŁÓDZKI

Badania STS grafenu na Au

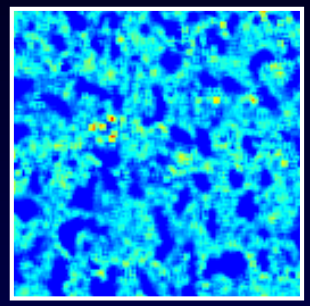
MG



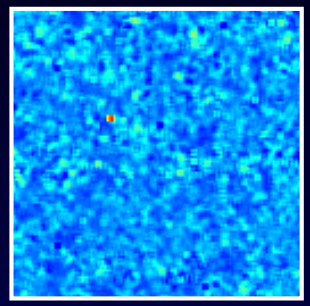
E_F+ 0.01 eV



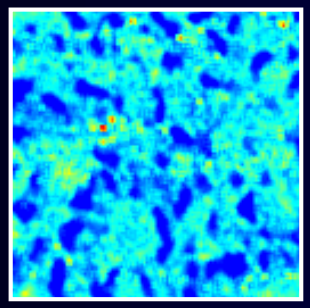
E_F+ 0.08 eV



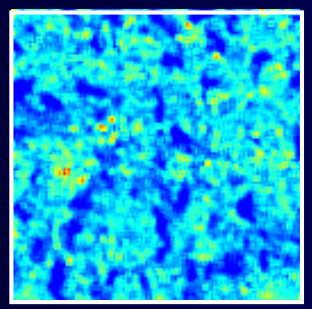
E_F+ 0.15 eV



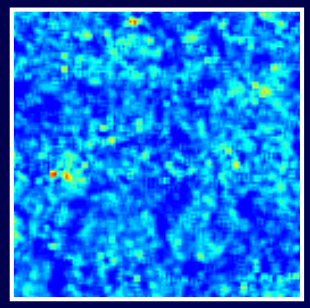
E_F+ 0.27 eV



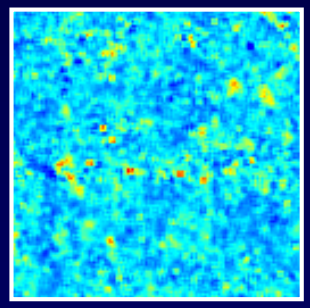
E_F- 0.01 eV



E_F- 0.08 eV



E_F- 0.15 eV

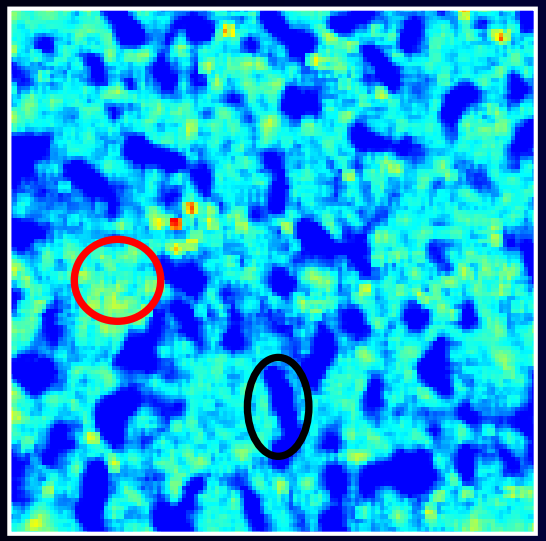


E_F- 0.27 eV

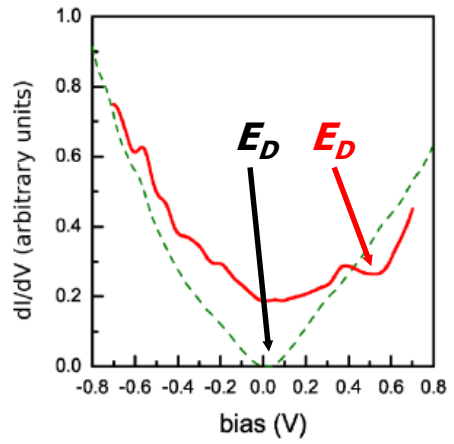
LDOS (E, x, y) na MG/Au - obszar 100 nm x 100 nm

Badania STS grafenu na Au

$$\frac{dI}{dV} = \rho_s(r,eV)\rho_t(r,0)T(eV,eV,z) + \int \rho_s(r,E)\rho_t(r,E-eV)\frac{dT(E,eV,z)}{dV}dE$$



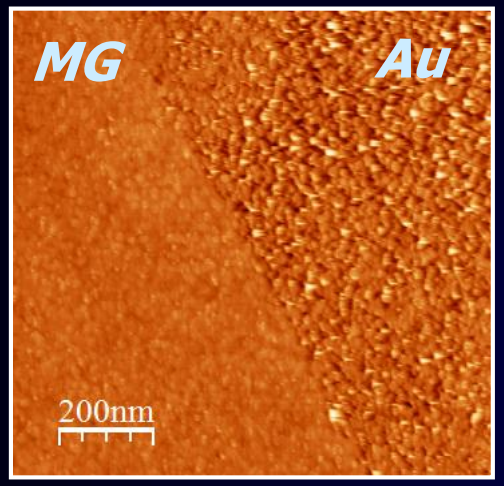
LDOS (E, x, y) na MG/Au - obszar 100 nm x 100 nm

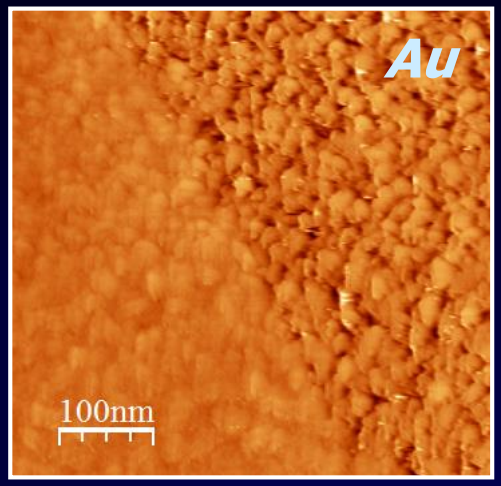


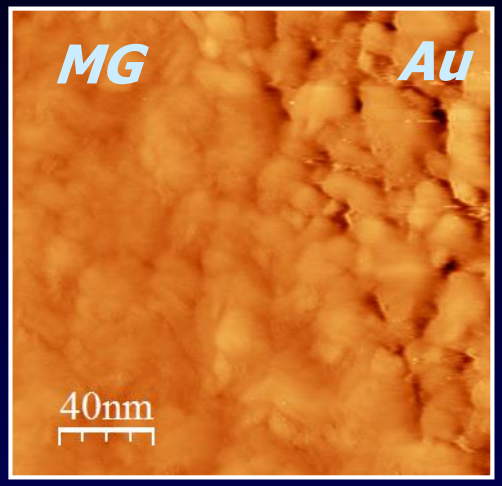
Na ciemnoniebieskim zachowanie typowe dla MG/Au(111)

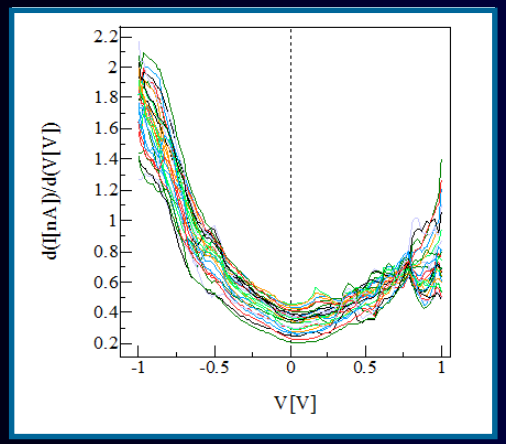
J. Slawinska, I. Wlasy, P. Dabrowski, Z. Klusek, I. Zasada
Phys. Rev. B 85 (2012)

Badania STS grafenu na Au

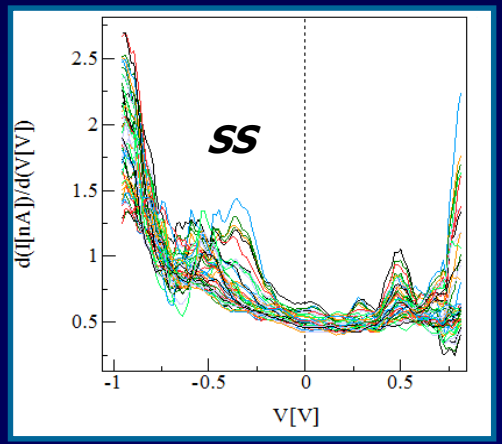






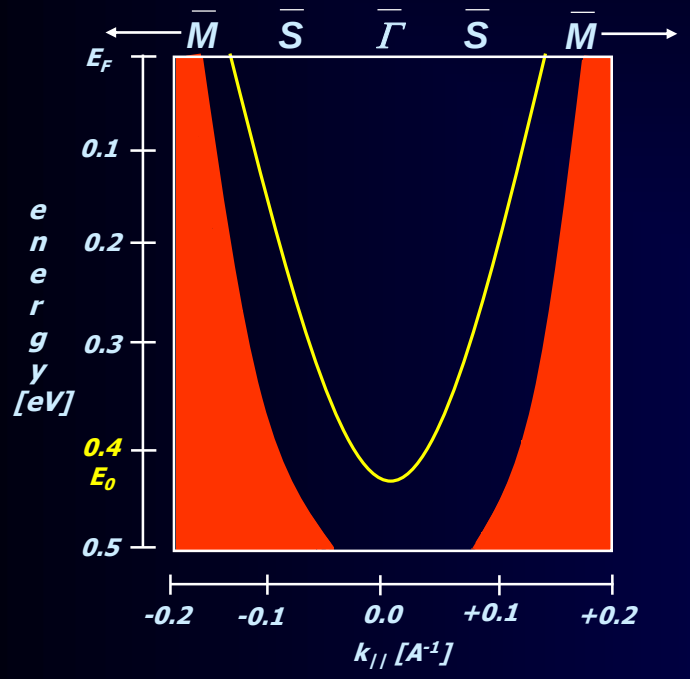


Na Au obserwowaliśmy dwa zachowania



Badania STM/STS Au

Au(111)



$$E(k) = E_F - E_0 + \frac{\hbar^2 k^2}{2m^*}$$

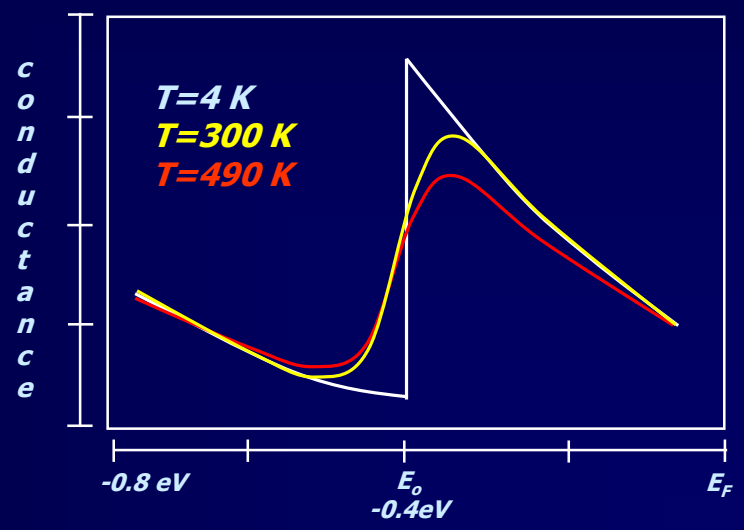
Stan powierzchniowy Schockleya

L.C. Davis, M.P. Everson, R.C. Jaklevic, W. Shen, Phys. Rev. B 43 (1991) 3821.

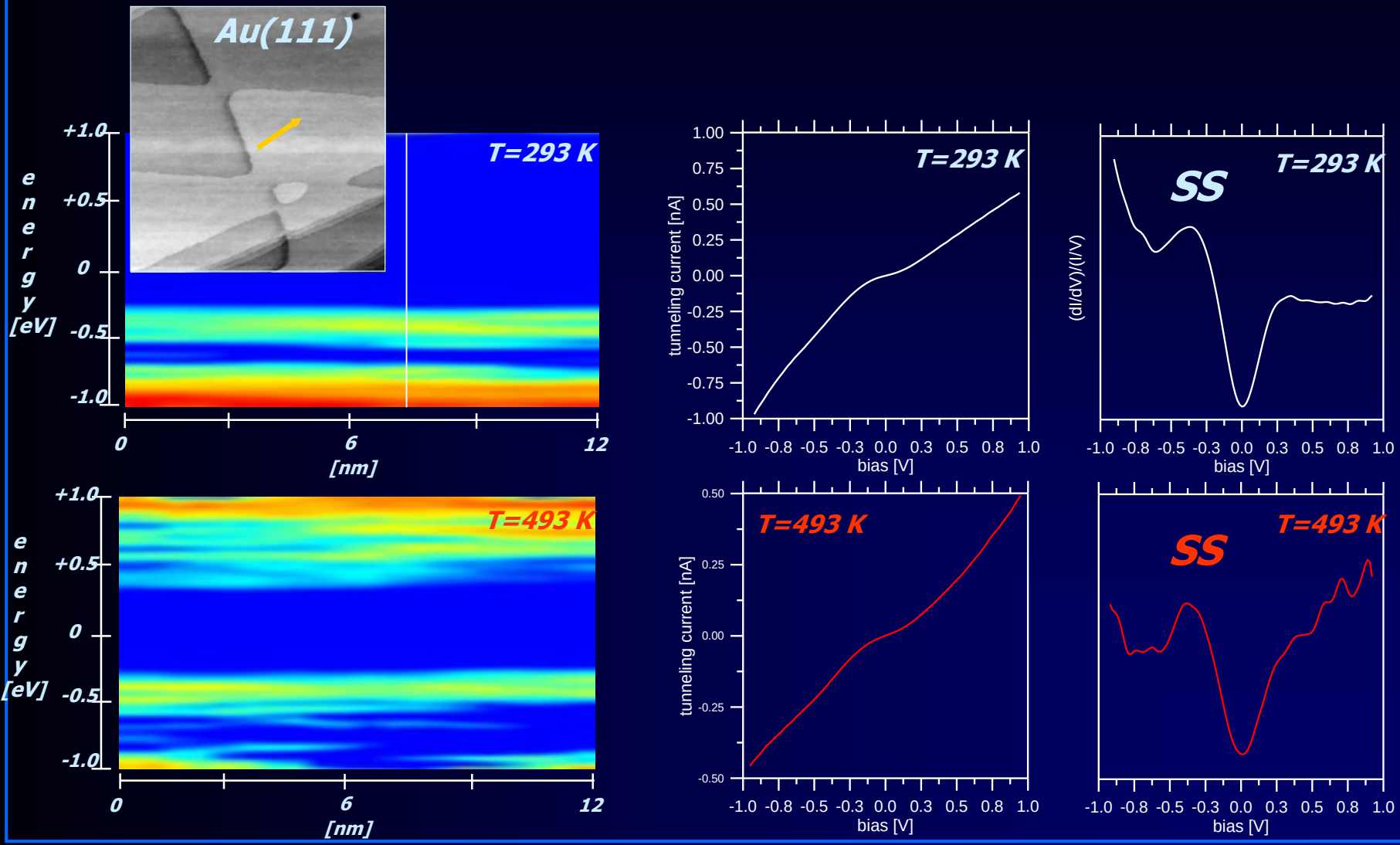
$$I = G_0 \exp\left(V/V_0\right) \times \int_0^\infty dE \exp\left((E_0 - E)/E_1\right)$$
$$\times \left[f\left(E_F - E_0 + E\right) - f\left(E_F - E_0 + E + eV\right) \right]$$

$$V_0 = \frac{2\left(\hbar^2 \Phi / 2m\right)^{1/2}}{ed}$$

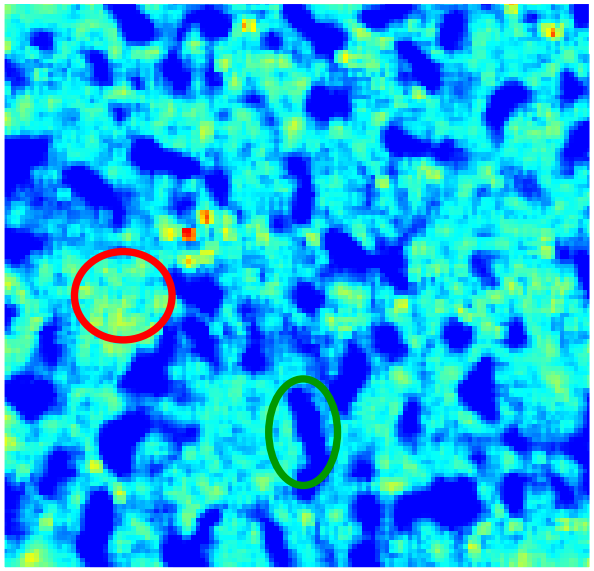
$$E_1 = E_a / \left[(1 + d(1 - m/m^*)/a \right]$$

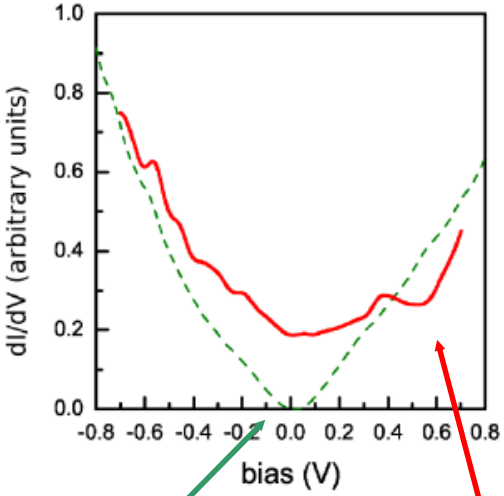


Badania STM/STS Au



Badania STS grafenu na Au





LDOS (E, x, y) na MG/Au - obszar 100 nm x 100 nm

Au(111)

poli

UNIWERSYTET ŁÓDZKI

Przewodnictwo złącza grafen-metal

nature nanotechnology
ARTICLES
PUBLISHED ONLINE: 6 FEBRUARY 2011 | DOI: 10.1038/NNANO.2011.6

The origins and limits of metal-graphene junction resistance

Fengnian Xia*†, Vasili Perebeinos†, Yu-ming Lin, Yanqing Wu and Phaedon Avouris*

$$G = \frac{1}{R_C} = \frac{4e^2}{h} TM$$

$$\frac{1}{R_C} = \frac{4e^2}{h} \int_{-E_0}^{E_0} dE_1 Voigt\left(E_1 - \Delta E_{FM}, t_1, \eta\right)$$

$$\int_{-\infty}^{\infty} dE_2 G\left(E_2 - \Delta E_{FG}, t_2\right) \frac{1}{W} \sum_{n=0}^{\min\{M_1, M_2\}} T\left(k_y = \frac{n\pi}{W}, E_1 E_2\right)$$

$$Voigt\left(E_1 - \Delta E_{FM}, t_1, \eta\right)$$

Konwolucja funkcji Gaussa o szerokości t_1 i funkcji Lorentza o szerokości η i energii odcięcia E_0.

$$G(x, t_2) = \frac{1}{t_2\sqrt{\pi}} \exp\left(-x^2 / t_2^2\right)$$

$$t_2 = \hbar v_F \sqrt{2\pi n_0}$$

$$M_{1,2} = W \frac{|E_{1,2}|}{\pi \hbar v_F}$$

$$T = \frac{T_K T_{GM}}{1 - (1 - T_K)(1 - T_{GM})}$$

UNIWERSYTET ŁÓDZKI

Przewodnictwo złącza grafen-metal

Teoria
DFT

ΔE_{FM}
????

eksperyment
STS
ARPES

$$\frac{1}{R_C} = \frac{4e^2}{h} \int_{-E_0}^{E_0} dE_1 Voigt\left(E_1 - \Delta E_{FM}, t_1, \eta\right)$$

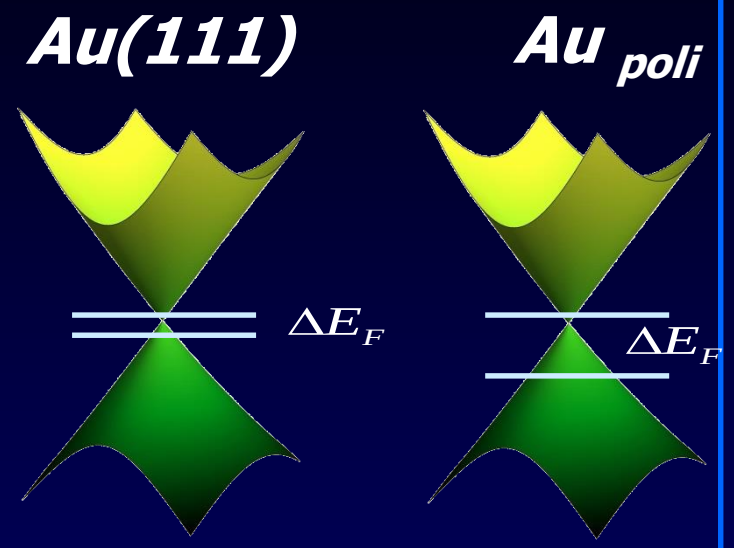
$$\int_{-\infty}^{\infty} dE_2 G\left(E_2 - \Delta E_{FG}, t_2\right) \frac{1}{W} \sum_{n=0}^{\min\{M_1, M_2\}} T\left(k_y = \frac{n\pi}{W}, E_1, E_2\right)$$

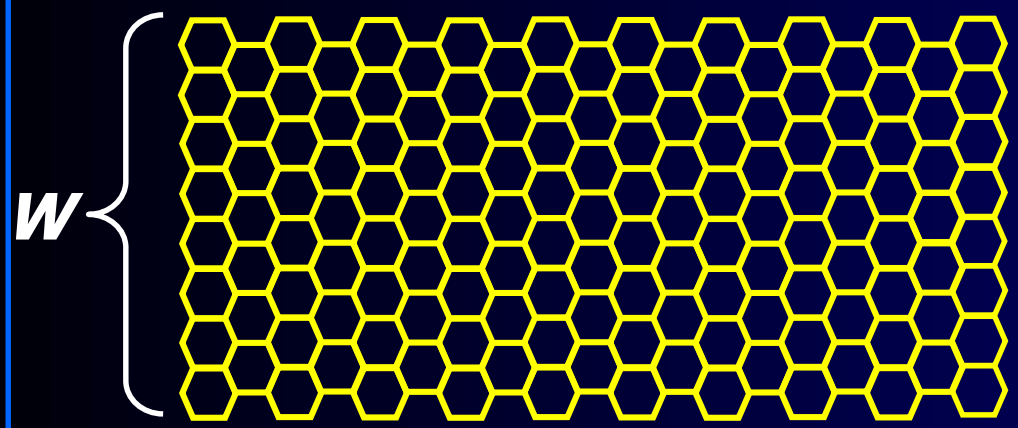
Oddziaływanie grafen/Au - LDOS

Formuła Landauera

$$G = \frac{4e^2}{h} TM$$

M – liczba modów przewodnictwa w grafenie
T – współczynnik transmisji nośników





$$M = \frac{\Delta E_F}{\pi \hbar v_F} W$$

Au poli wstrzykuje więcej nośników

Podsumowanie

FACULTY OF PHYSICS AND APPLIED INFORMATICS
University of Lodz

GRAPH MET-IN

Własności elektronowe grafenu zmieniają się na skutek oddziaływania z podłożem

Niezaburzony grafen nie istnieje

Struktura elektronowa grafenu może być zmieniona na skutek zewnętrznego domieszkowania