CONGRESSO NAZIONALE

SOCIETA' ITALIANA DI FISICA

Graphene and Transition metal dichalcogenides from stuctural properties to doping

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UNIVERSITÀ DEGLI STUDI DI PALERMO

Outline

INTRODUCTION

EXPERIMENTAL DETAILS

RESULTS & DISCUSSION

CONCLUSIONS

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Introduction

Birthdate 2004

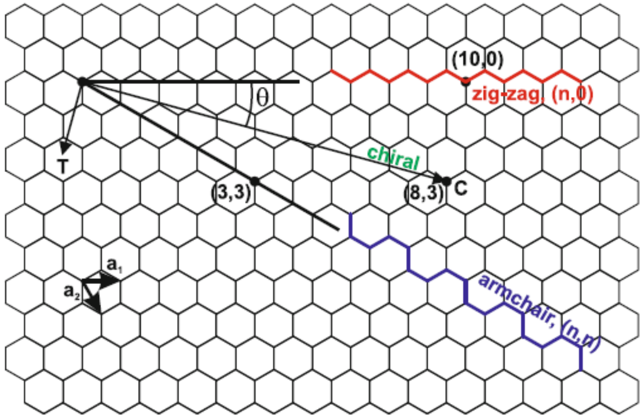

Fig. 17.1. Schematic atomic arrangement in graphene; the C–C bond length is $d_{C-C} = 0.142$ nm. Several vectors for making carbon nanotubes (cf. Sect. 17.2) are shown

GRAPHENE: MATERIALS IN THE FLATLAND

Nobel Lecture, December 8, 2010

by

KONSTANTIN S. NOVOSELOV

School of Physics and Astronomy, The University of Manchester, Oxford Road, Manchester M13 9PL, UK.

The major draw to people in the field, though, is graphene's unique properties, each of which seems to be superior to its rivals. This material is the first 2D atomic crystal ever known to us [3]; the thinnest object ever obtained; the world's strongest material [12]; its charge carriers are massless Dirac fermions [7, 13–14]; it is extremely electrically [15] and thermally [16] conductive; very elastic; and impermeable to any molecules [17] – the list goes on. Even a simple inventory of graphene's superlative qualities would require several pages, and new entries are being added on a monthly basis.

Introduction

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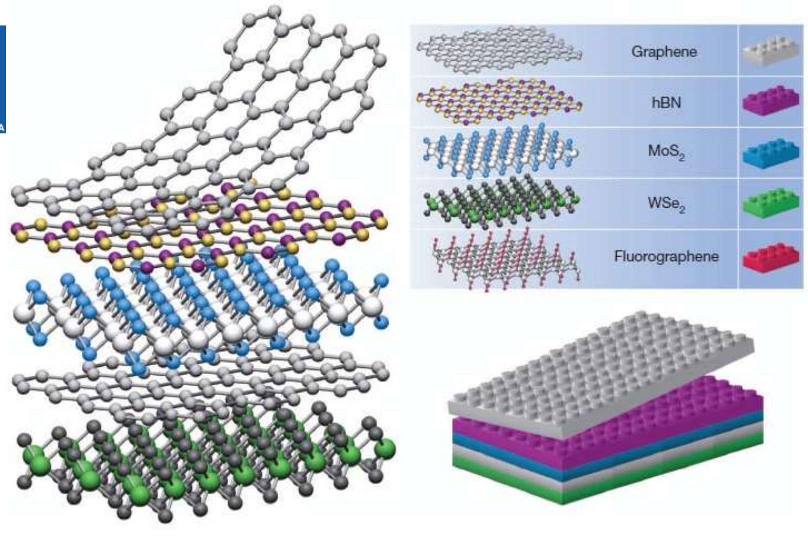


Van der Waals heterostructures

A. K. Geim[1,2] & I. V. Grigorieva[1]

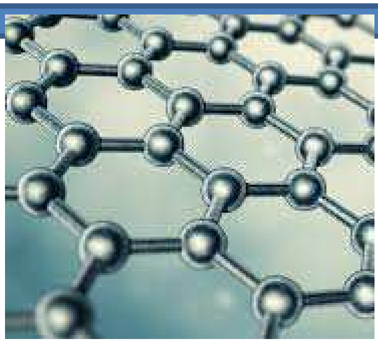
Research on graphene and other two-dimensional atomic crystals is intense and is likely to remain one of the leading topics in condensed matter physics and materials science for many years. Looking beyond this field, isolated atomic planes can also be reassembled into designer heterostructures made layer by layer in a precisely chosen sequence. The first, already remarkably complex, such heterostructures (often referred to as 'van der Waals') have recently been fabricated and investigated, revealing unusual properties and new phenomena. Here we review this emerging research area and identify possible future directions. With steady improvement in fabrication techniques and using graphene's springboard, van der Waals heterostructures should develop into a large field of their own.

[1]School of Physics and Astronomy, University of Manchester, Manchester M13 9PL, UK. [2]Centre for Mesoscience and Nanotechnology, University of Manchester, Manchester M13 9PL, UK.

25 JULY 2013 | VOL 499 | NATURE | 419

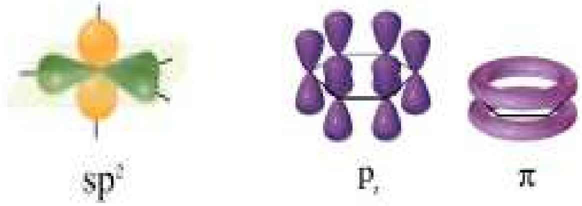
Graphene family	Graphene	hBN 'white graphene'	BCN	Fluorographene	Graphene oxide
2D chalcogenides	MoS_2, WS_2, $MoSe_2$, WSe_2	Semiconducting dichalcogenides: $MoTe_2$, WTe_2, ZrS_2, $ZrSe_2$ and so on	Metallic dichalcogenides: $NbSe_2$, NbS_2, TaS_2, TiS_2, $NiSe_2$ and so on	Layered semiconductors: GaSe, GaTe, InSe, Bi_2Se_3 and so on	
2D oxides	Micas, BSCCO	MoO_3, WO_3	Perovskite-type: $LaNb_2O_7$, $(Ca,Sr)_2Nb_3O_{10}$, $Bi_4Ti_3O_{12}$, $Ca_2Ta_2TiO_{10}$ and so on	Hydroxides: $Ni(OH)_2$, $Eu(OH)_2$ and so on	
	Layered Cu oxides	TiO_2, MnO_2, V_2O_5, TaO_3, RuO_2 and so on		Others	

Introduction



Graphene: 2D layer of sp^2 hybridized carbon atoms arranged in an hexagonal lattice

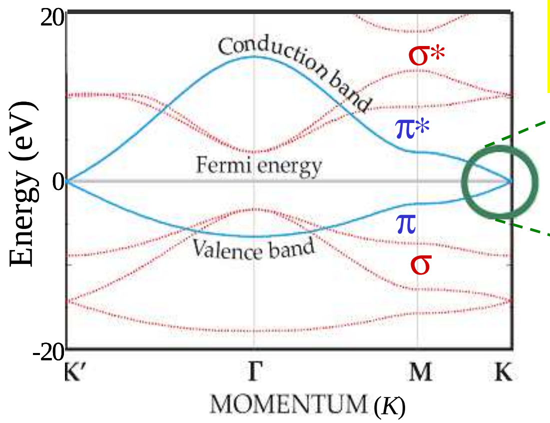
$Z = 6$ $\qquad 1s_2 2s_2 2p_2$



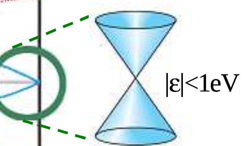
Electronic band structure

Graphene	Semiconductor (Si)

A. H. Castro Neto et al. Rev. Mod. Phys., 2009, 81, 109



zero band gap

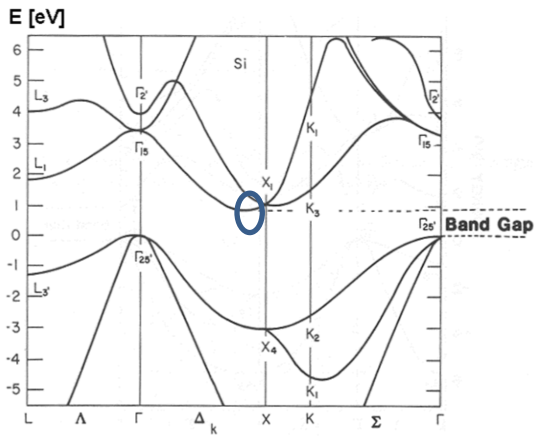


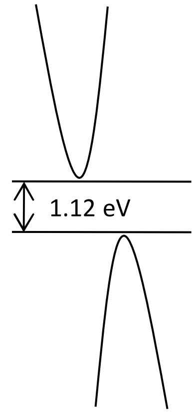
$$E^{\pm} \approx \pm \hbar v_F k$$

Band gap = 0 eV

m*=0

$$v_F \approx \frac{c}{300} \approx 10^6 \frac{m}{s}$$





Band gap ≠ 0

m* ≠ 0

$$E = \frac{\hbar^2 k^2}{2m}$$

Introduction

OXYGEN molecular doping

Molecular doping is strategically used to induce gap opening and shift of the Fermi level for electronic devices application

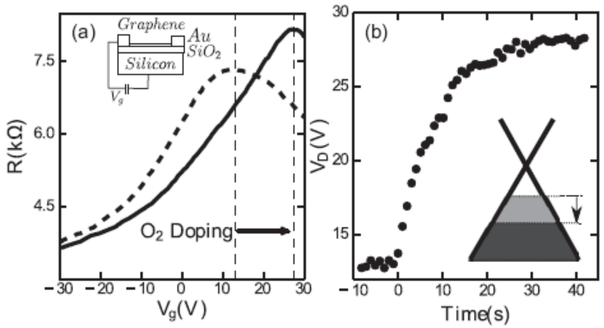


FIG. 1. (a) Resistance versus gate voltage before and after oxygen exposure (dashed and solid lines, respectively). The positions of the Dirac points are indicated by the dotted lines. The inset shows the sample layout. (b) The Dirac point position as a function of time after oxygen exposure. The oxygen was admitted to the chamber at $t = 0$ s. The inset shows the band structure of graphene with the corresponding change in the Fermi level.

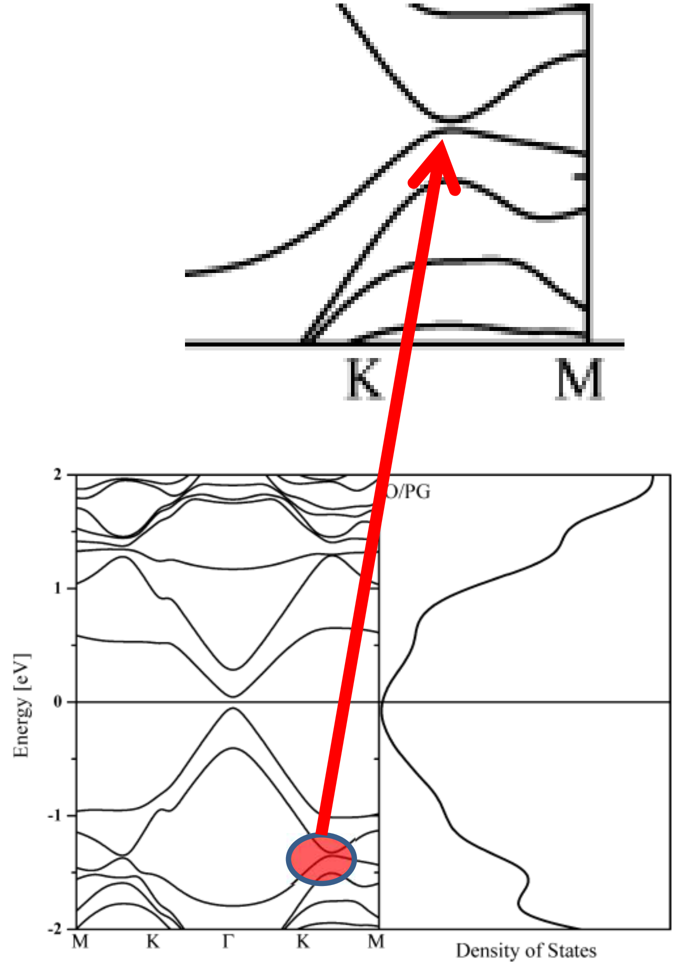
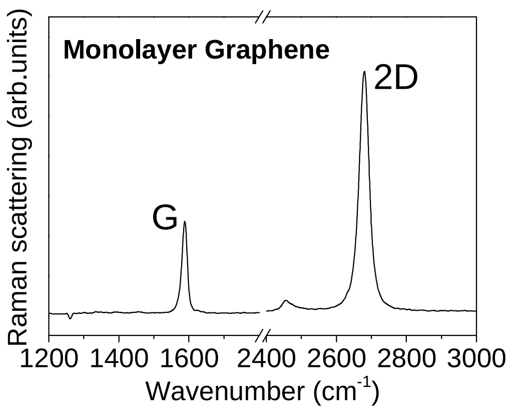
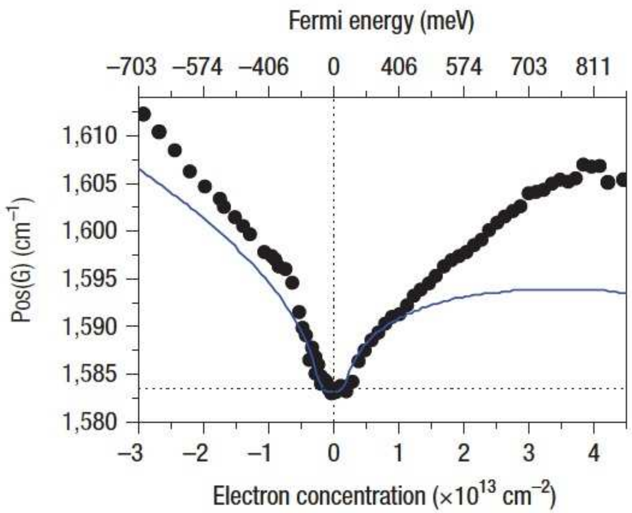


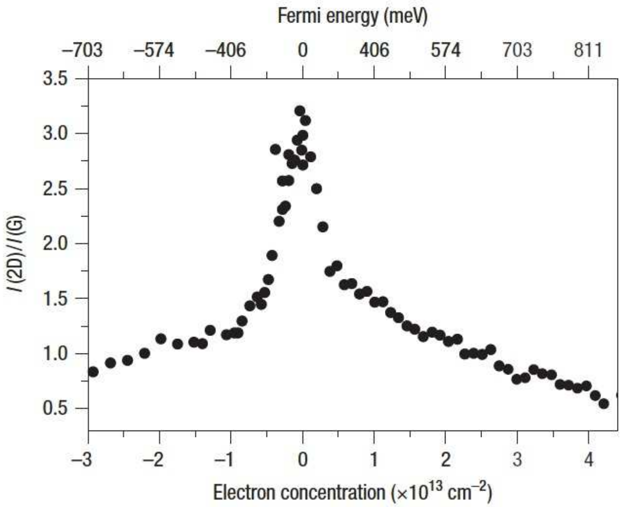
Figure 3. Band structure and total density of states of O-doped graphene.

S.M. Hornett et al.; Phys. Rev. B 2014, 90, 081401(R)   F. Mehmood et al.; J. Phys. Chem. C 2013, 117, 10366

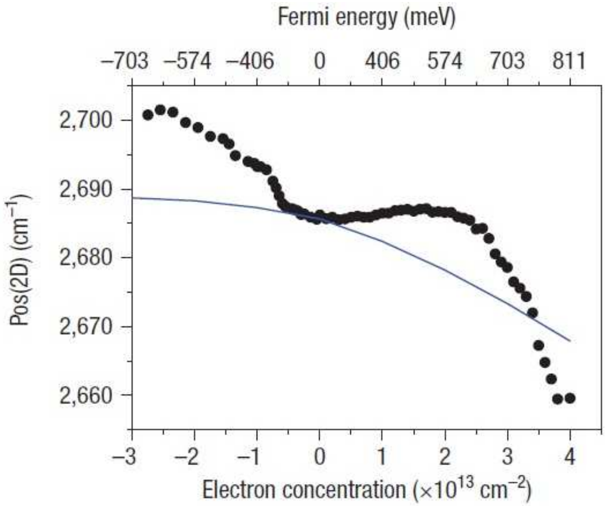
Doping vs Raman spectra







Same effects for p-type or n-type doping



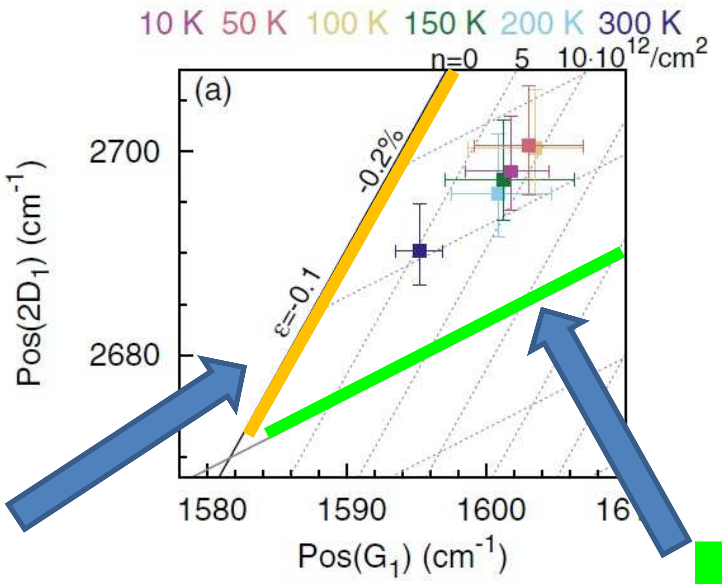
Different effects for p-type — **Blue shift**

or n-type doping — **Red shift**

A. Das et al; Nature Nanot. 2008, 3, 210

Modifications vs Raman spectra

Strain and doping in monolayer graphene



Strain line

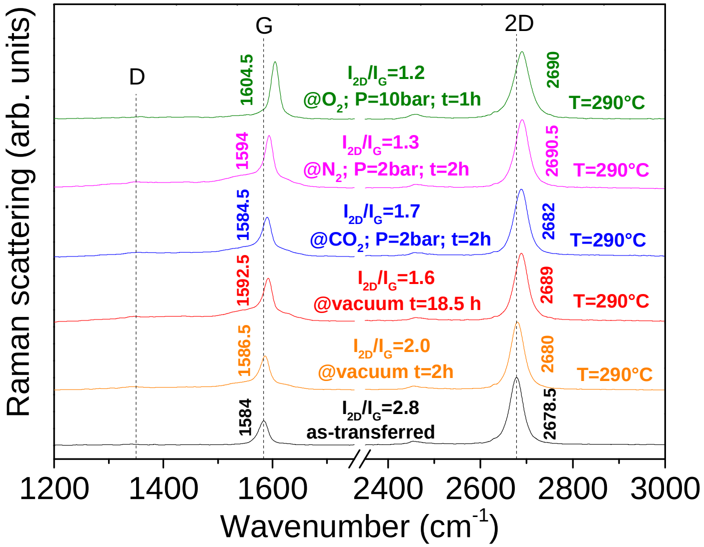
Doping line

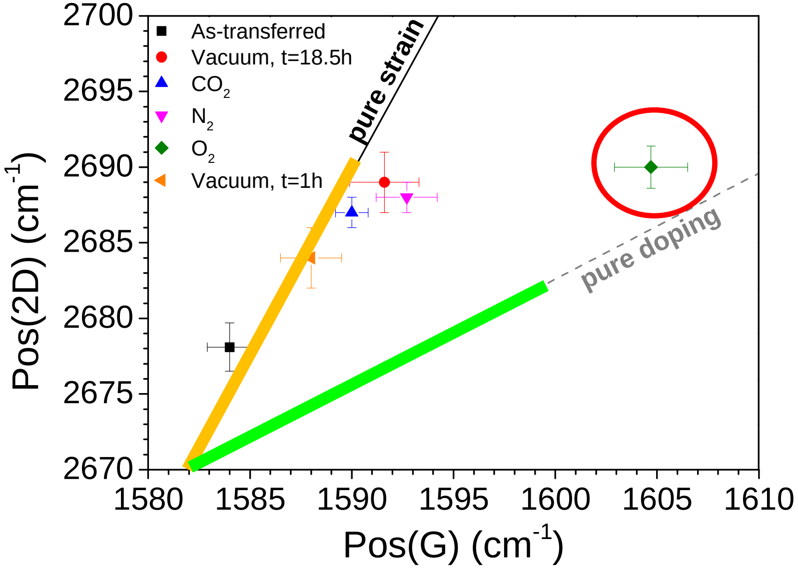
2D vs G
RAMAN MAP

T.G.A. Verhagen et al.; Phys. Rev. B 2015, 92, 125437

Thermal treatments

Gr/SiO_2/Si





- STRESS IS INDUCED BY NOT OXYGEN ATMOSPHERE

- OXYGEN INDUCES DOPING

A. Piazza et al **J.Phys.Chem.C 119 (2015) 22718**
A. Piazza et al **Carbon 107 (2016) 696**
A. Armano et al **Carbon 127 (2018) 270**

AIMS

> EVALUATE THE SUBSTRATE EFFECT

> DETERMINE MICROSCOPIC FEATURES

> CONSIDER THERMAL EFFECTS ON OTHER 2D MATERIALS: MoS_2

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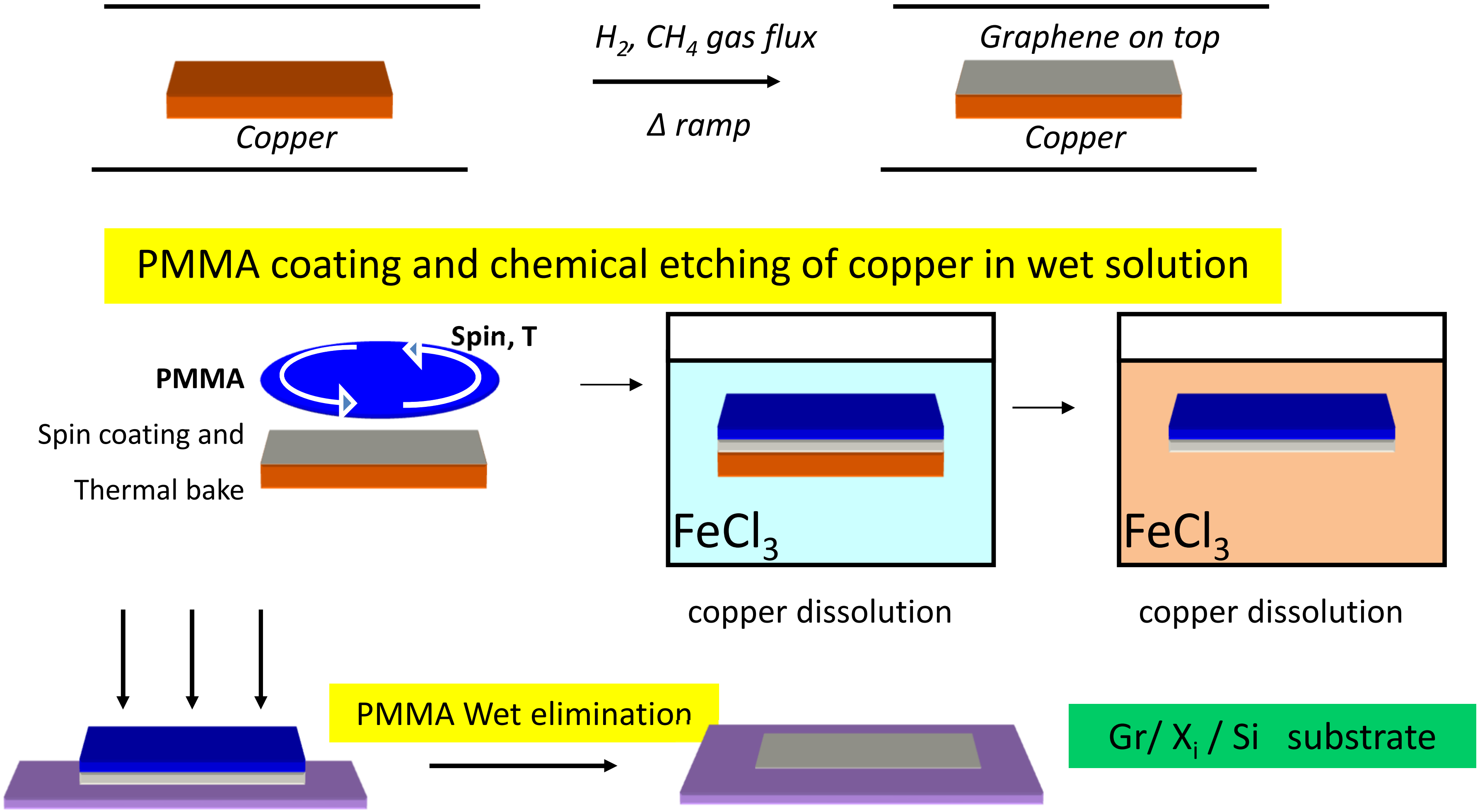


H_2, CH_4 gas flux
Δ ramp
Copper
Graphene on top
Copper
PMMA coating and chemical etching of copper in wet solution
PMMA
Spin, T
Spin coating and
Thermal bake
$FeCl_3$
copper dissolution
$FeCl_3$
copper dissolution
PMMA Wet elimination
Gr/ X_i / Si substrate

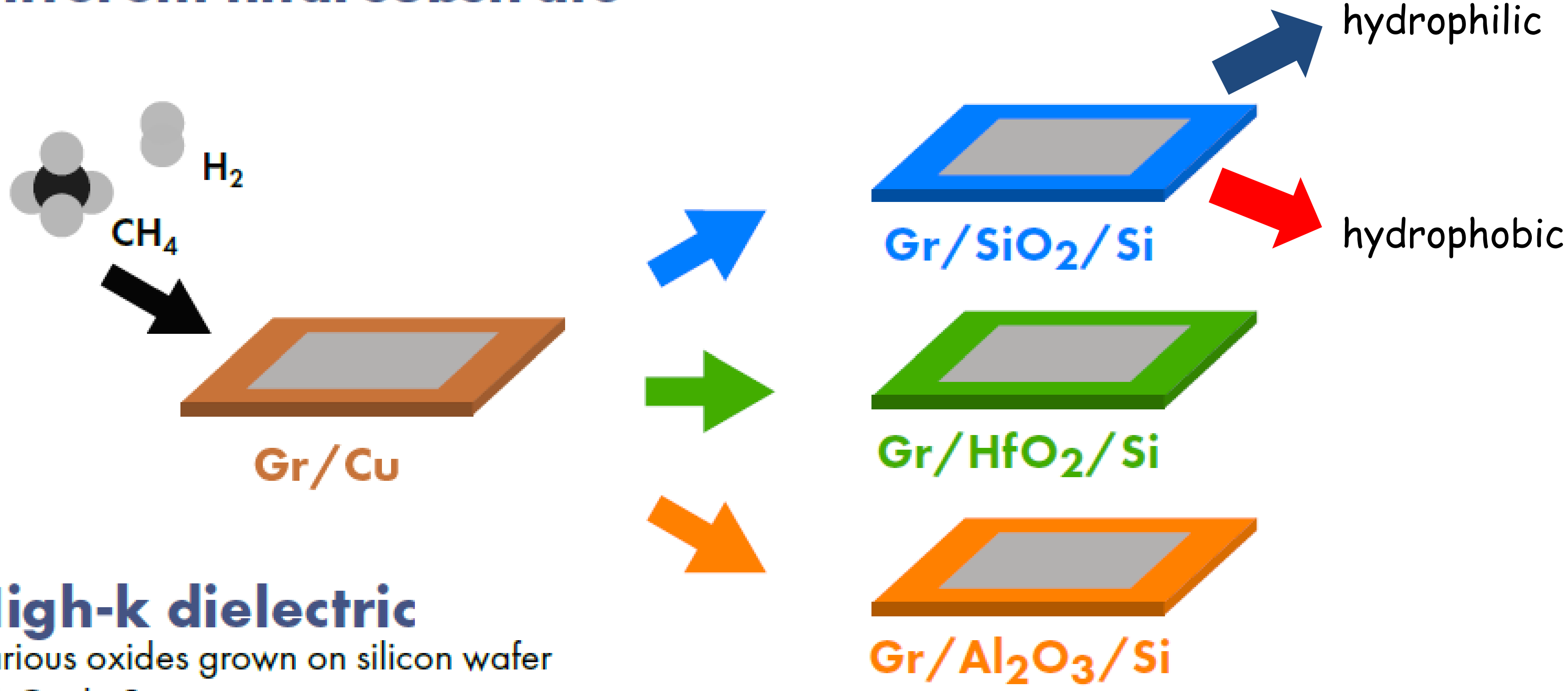
Gr/ X_i / Si substrate

X_1 = 300 nm SiO_2 (therm.)

X_2 = 50 nm Hf_2O (ALD)

X_3 = 40 nm Al_2O_3 (ALD)

Different final substrate

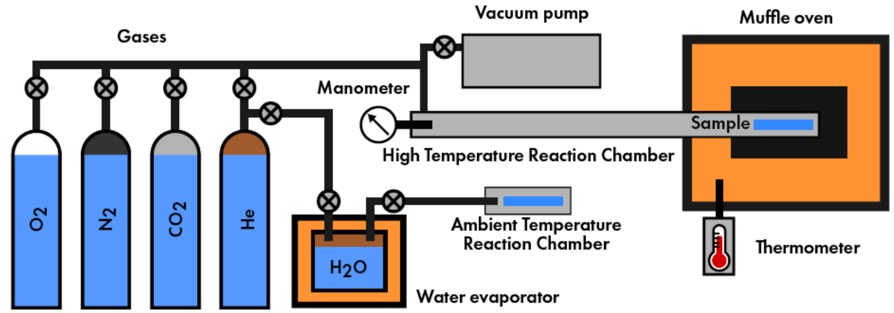


High-k dielectric

Various oxides grown on silicon wafer

Al_2O_3 k=9 > **SiO_2** k=3.9

HfO_2 k=25



Thermal processing in controlled atmosphere

5 x10^{-8} bar< Vacuum < 7 x10^{-4} bar

T_{amb}

Static pressure

Dry gas 2 bar

$[H_2O]$ < 3 ppm

T_{amb}

CONTROLLED ATMOSPHERE

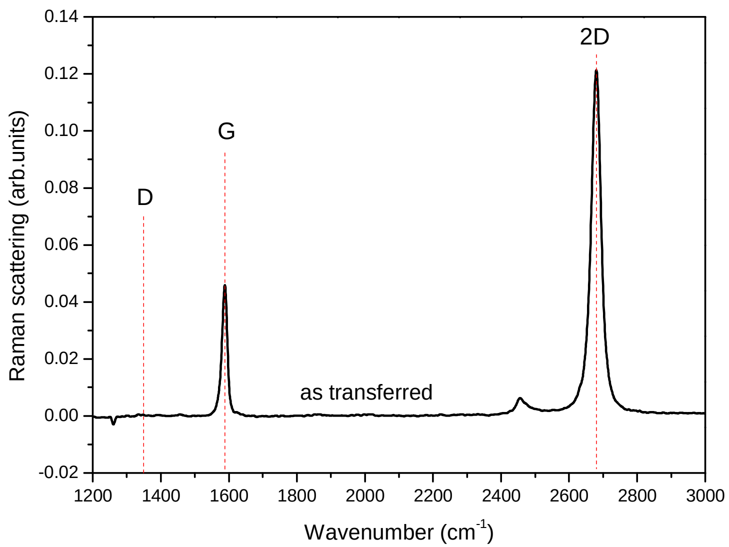
Dry gas

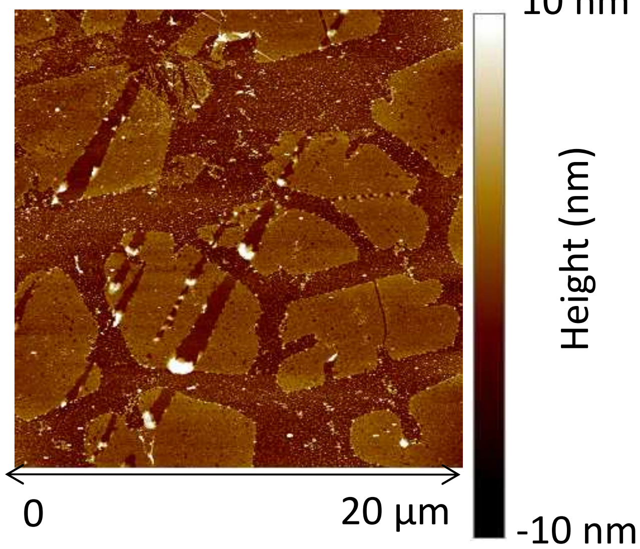
40°C <T< 400°C

~0.1 h <time< 20 h

AFM / Raman characterization

μ-Raman @ 532 nm





- No evident presence of D-Band
- Ratio $I_{2D}/I_G > 2.5$ → Monolayer Gr

AFM: μm extended flakes

<3 nm height

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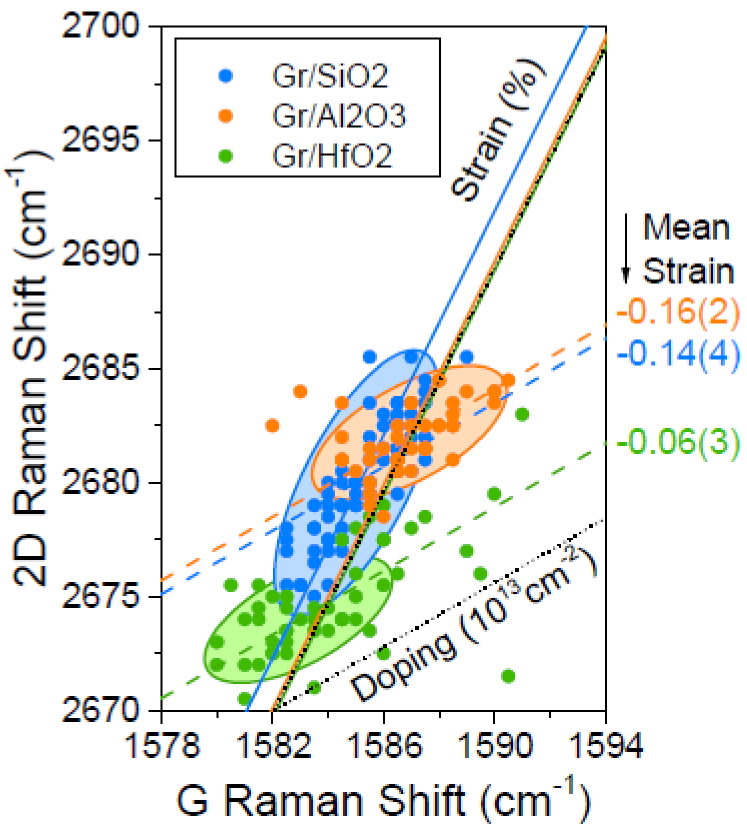
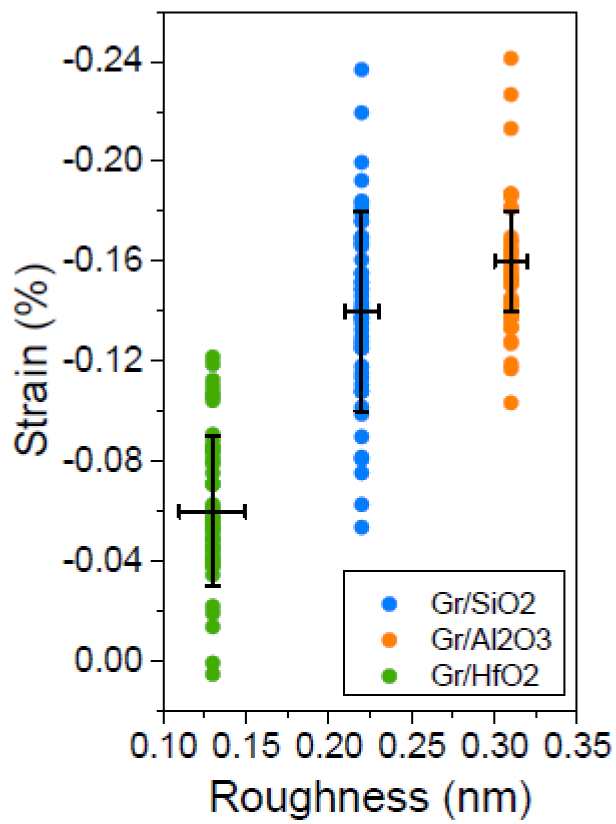
G2D correlation

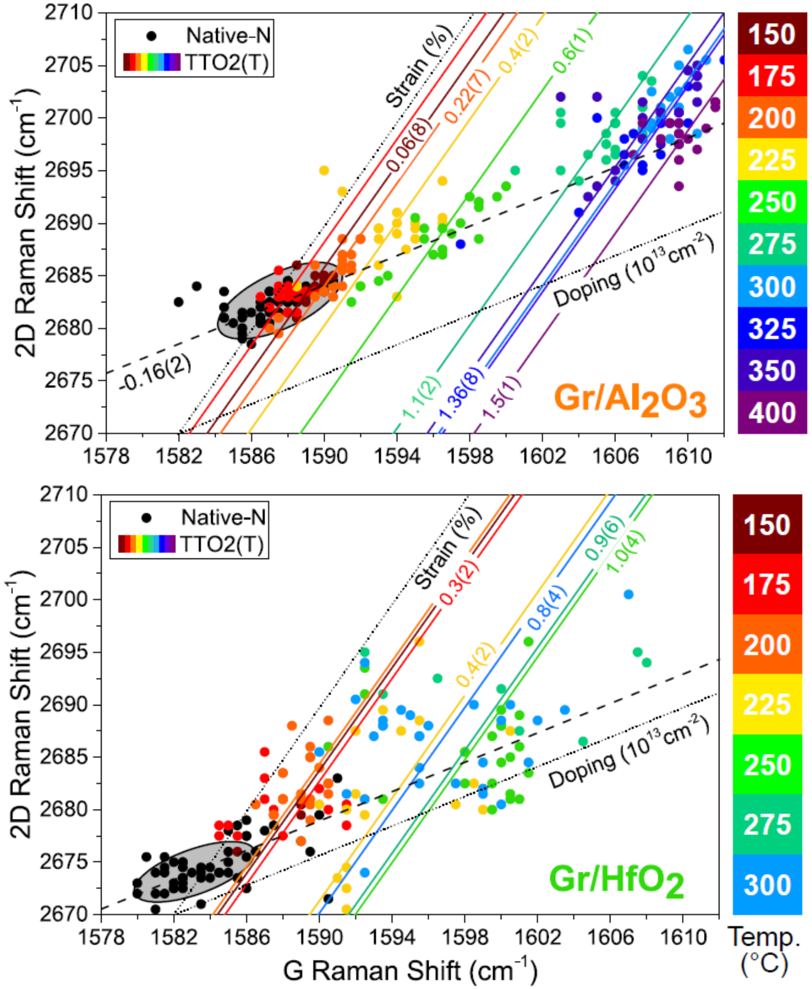
Substrate dependent strain





A. Armano et al **Carbon 149 (2019) 546**

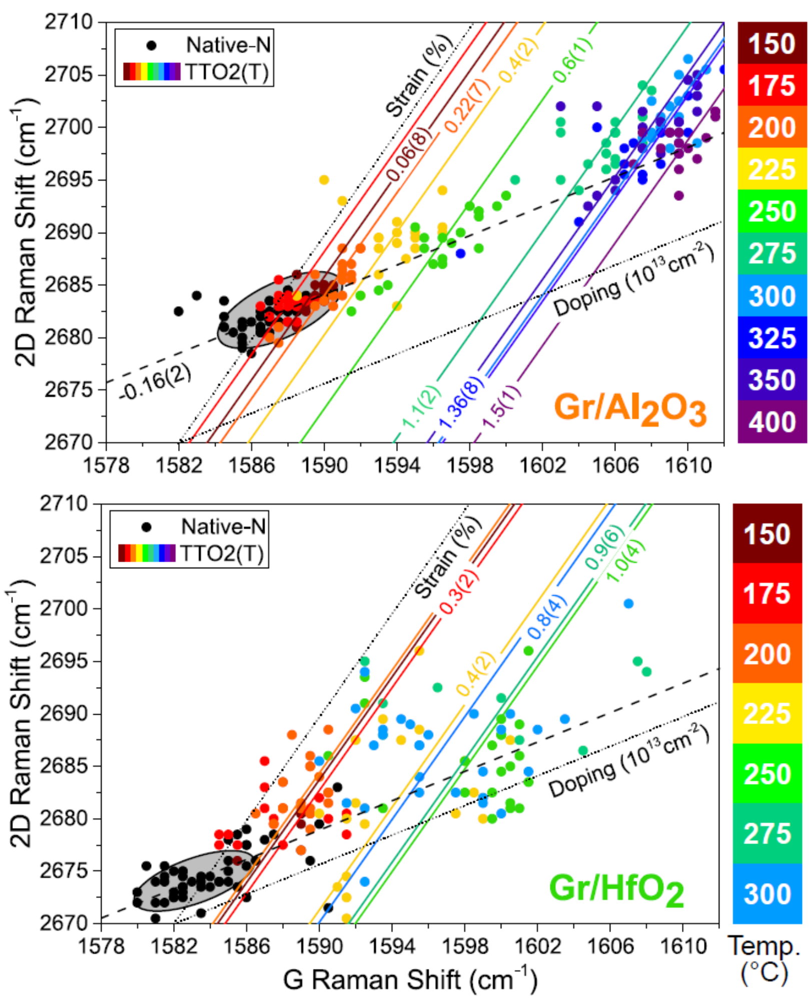
Thermal treatments: O_2 , time 2h

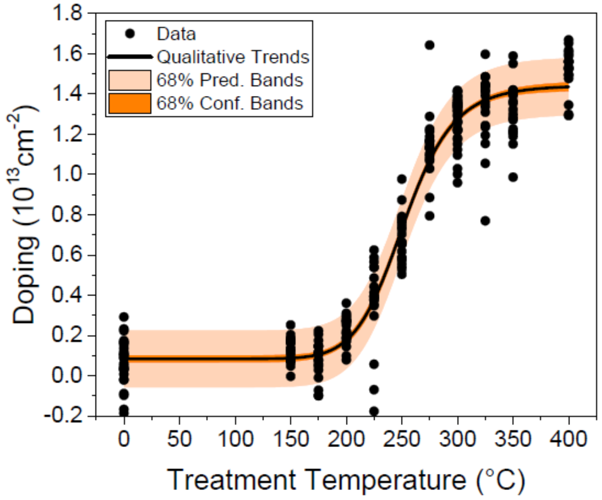


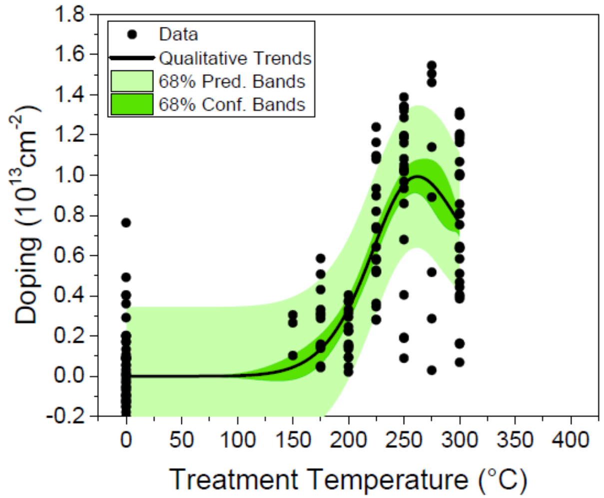
Effectiveness of doping

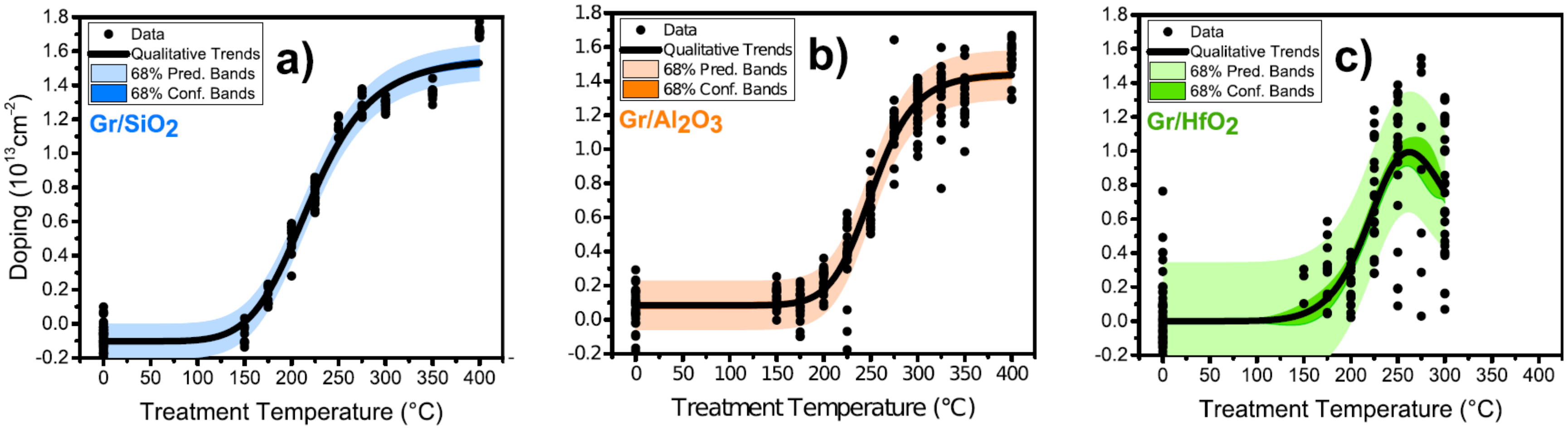
A. Armano et al **Carbon 149 (2019) 546**

Thermal treatments: O_2 , time 2h



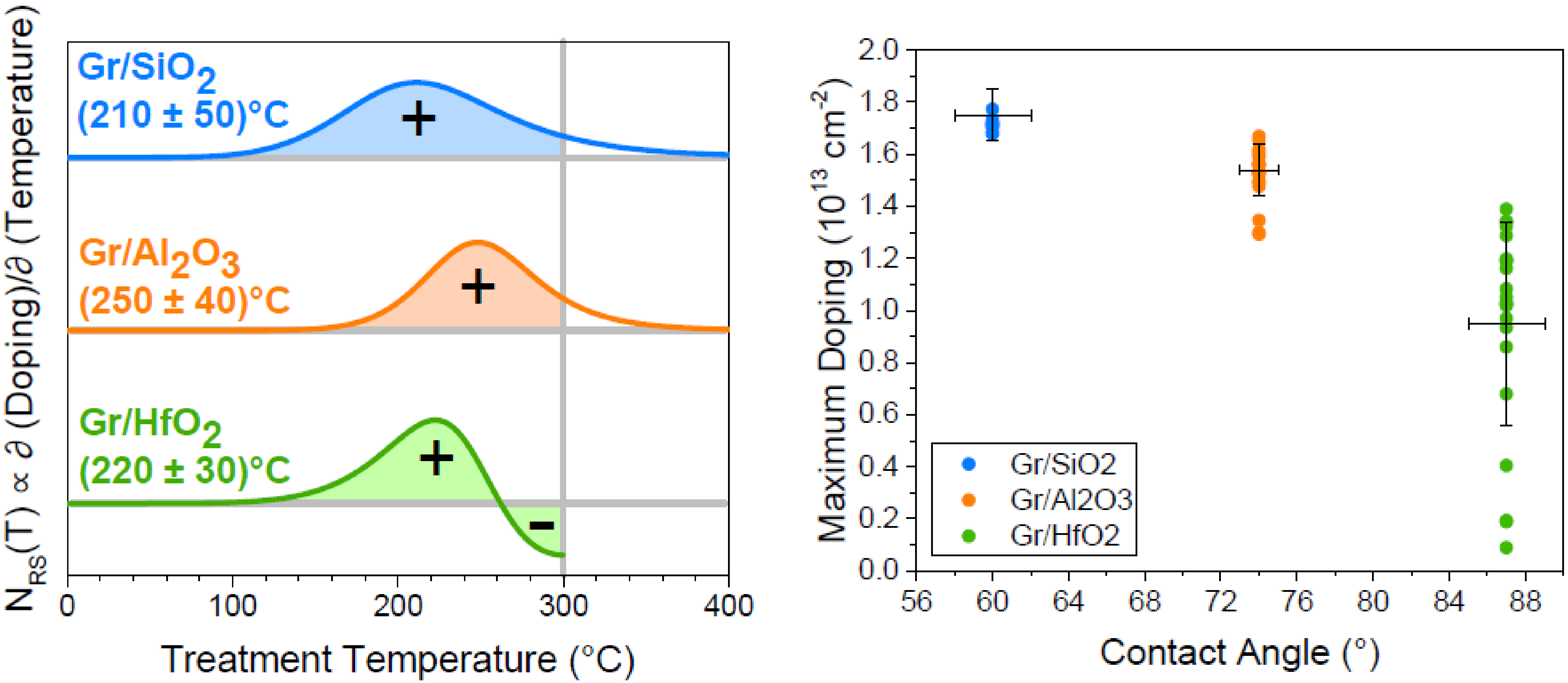




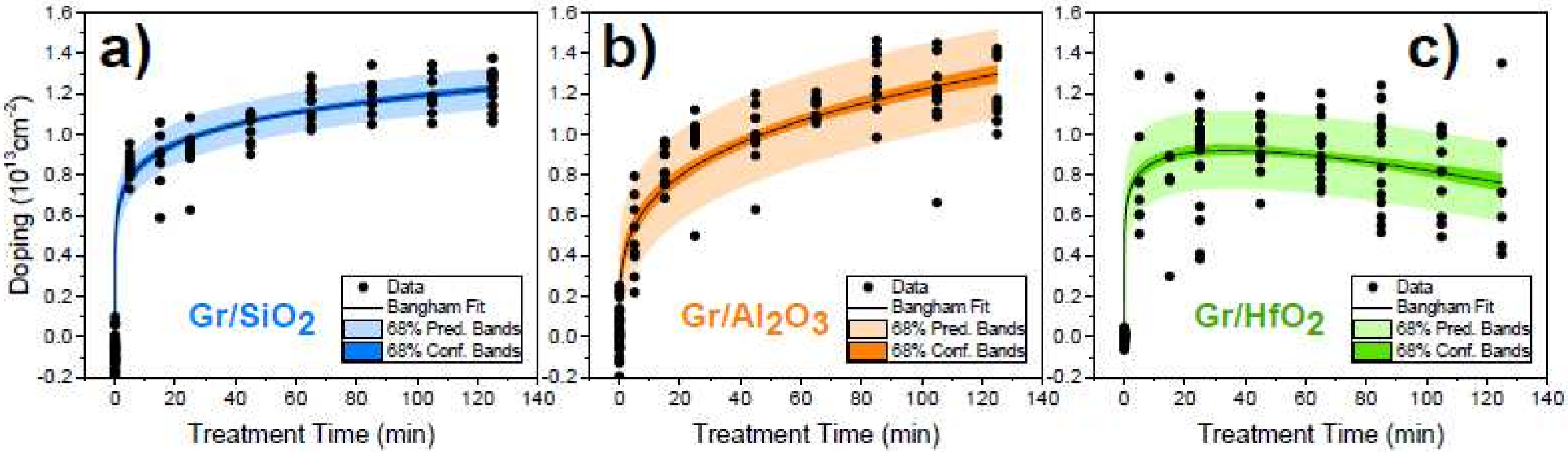


Substrate affects the threshold temperature

A. Armano et al **Carbon 149 (2019) 546**



Doping level and stability depend on substrate features

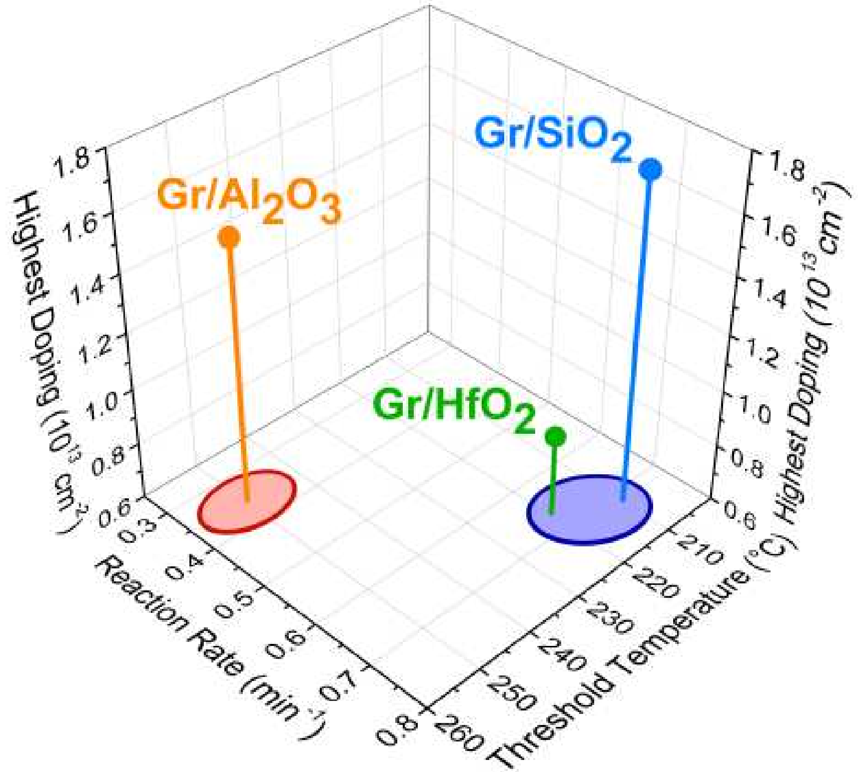


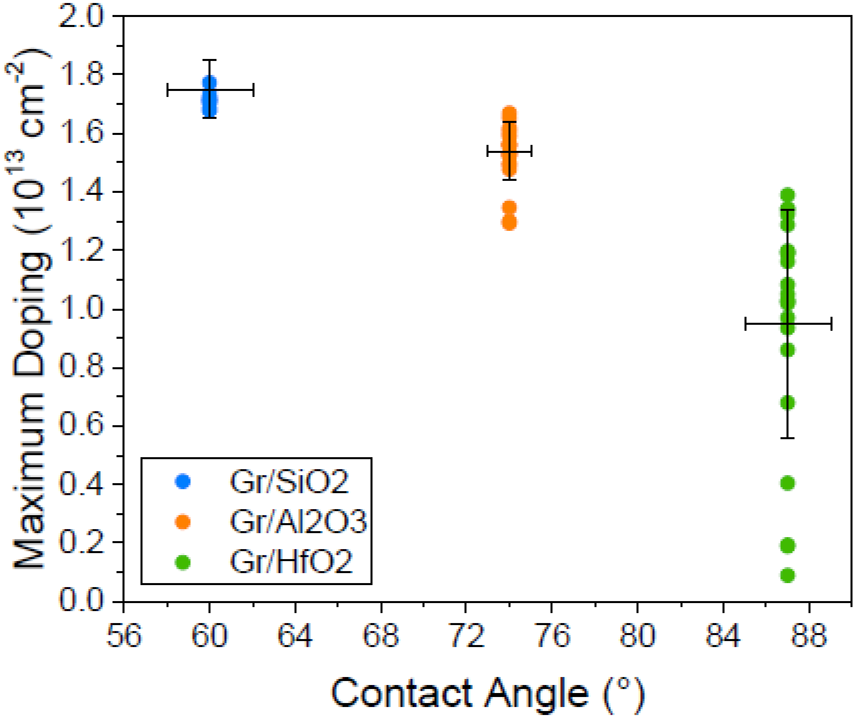
$$D(t) = c \cdot (\underbrace{kt^{\vartheta}}_{\text{Bangham model}} + \overbrace{st}^{\text{Loss term}}), \qquad c = 10^{13}\text{cm}^{-2}$$

Sample	k (min^{-1})	ϑ	s (min^{-1})
Gr/SiO_2	0.72(3)	0.13(1)	–
Gr/Al_2O_3	0.36(5)	0.27(3)	–
Gr/HfO_2	0.67(3)	0.13(1)	-0.004(6)

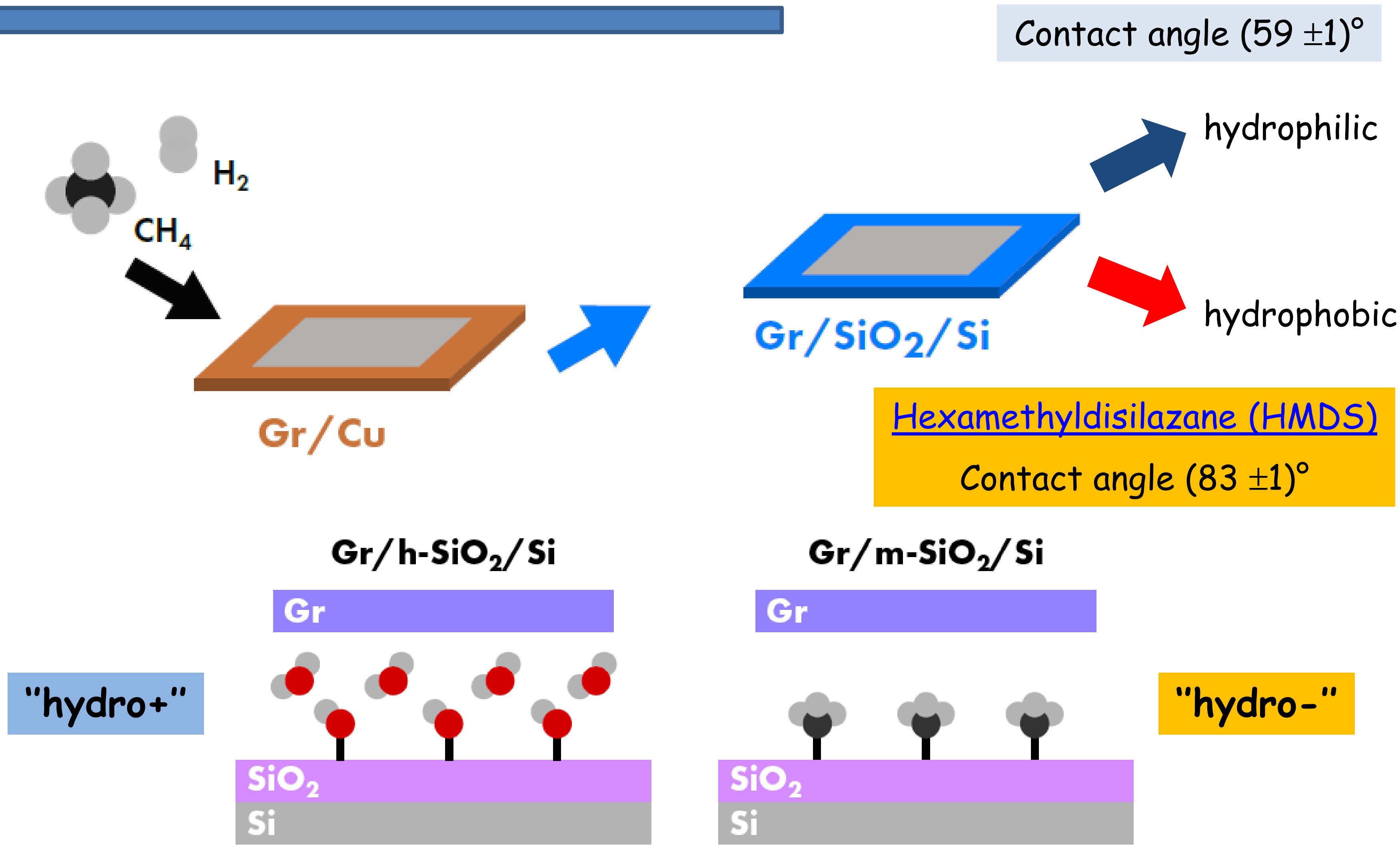
Diffusion limited process

A. Armano et al **Carbon 149 (2019) 546**



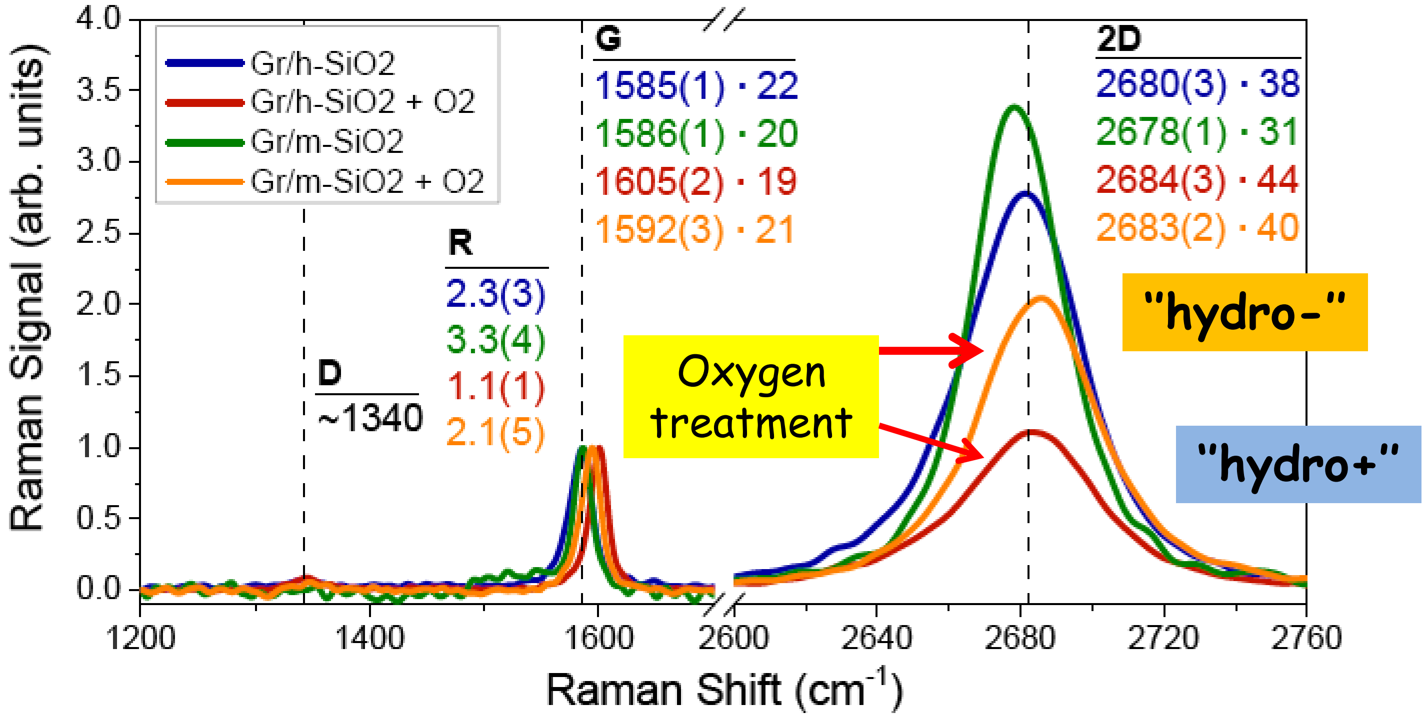


Doping effectiveness depends on substrate wettability

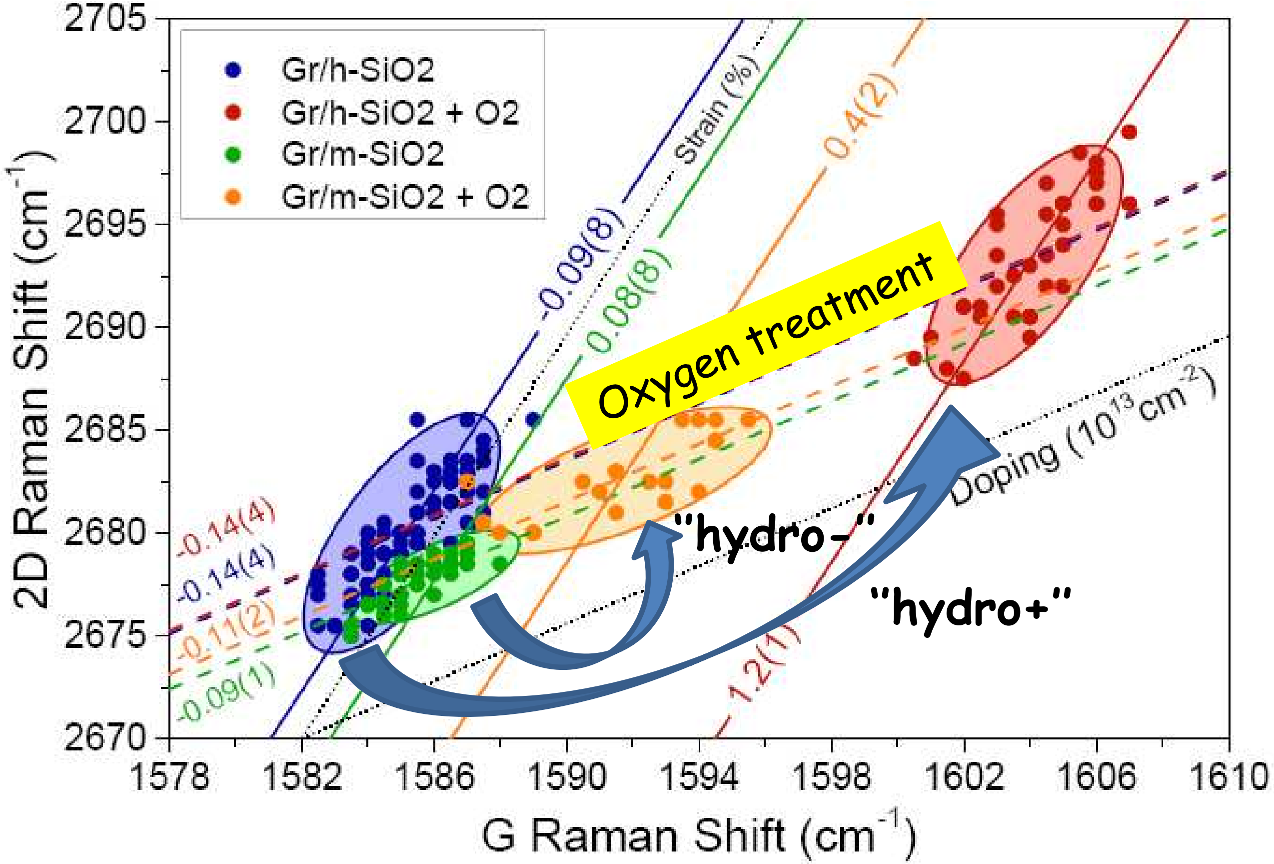


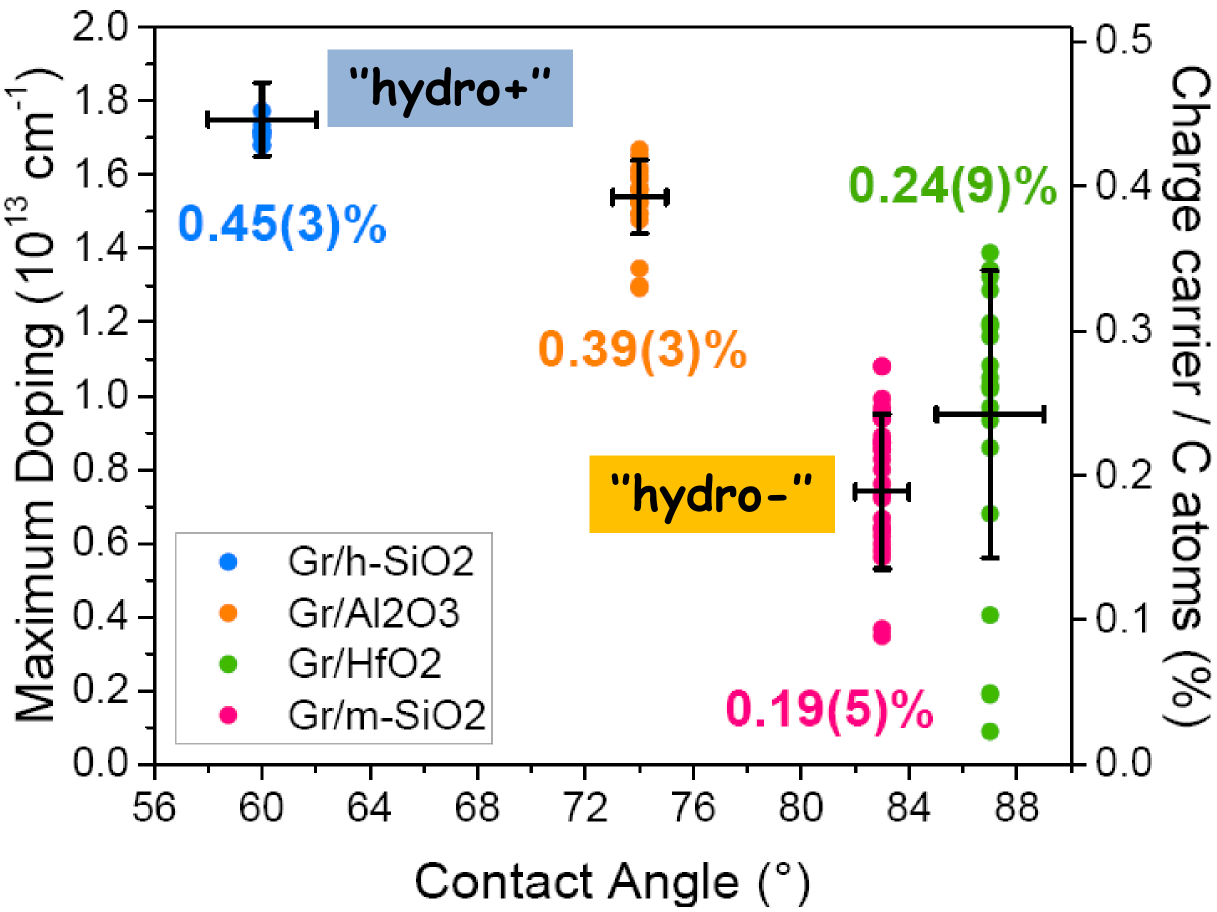
Contact angle (59 ±1)°
hydrophilic
hydrophobic
H2
CH4
Gr/Cu
Gr/SiO2/Si
Hexamethyldisilazane (HMDS)
Contact angle (83 ±1)°
Gr/h-SiO2/Si
Gr/m-SiO2/Si
Gr
Gr
"hydro+"
"hydro-"
SiO2
Si
SiO2
Si

TT O_2 @ 300°C



Hydrophilic character --> Higher doping

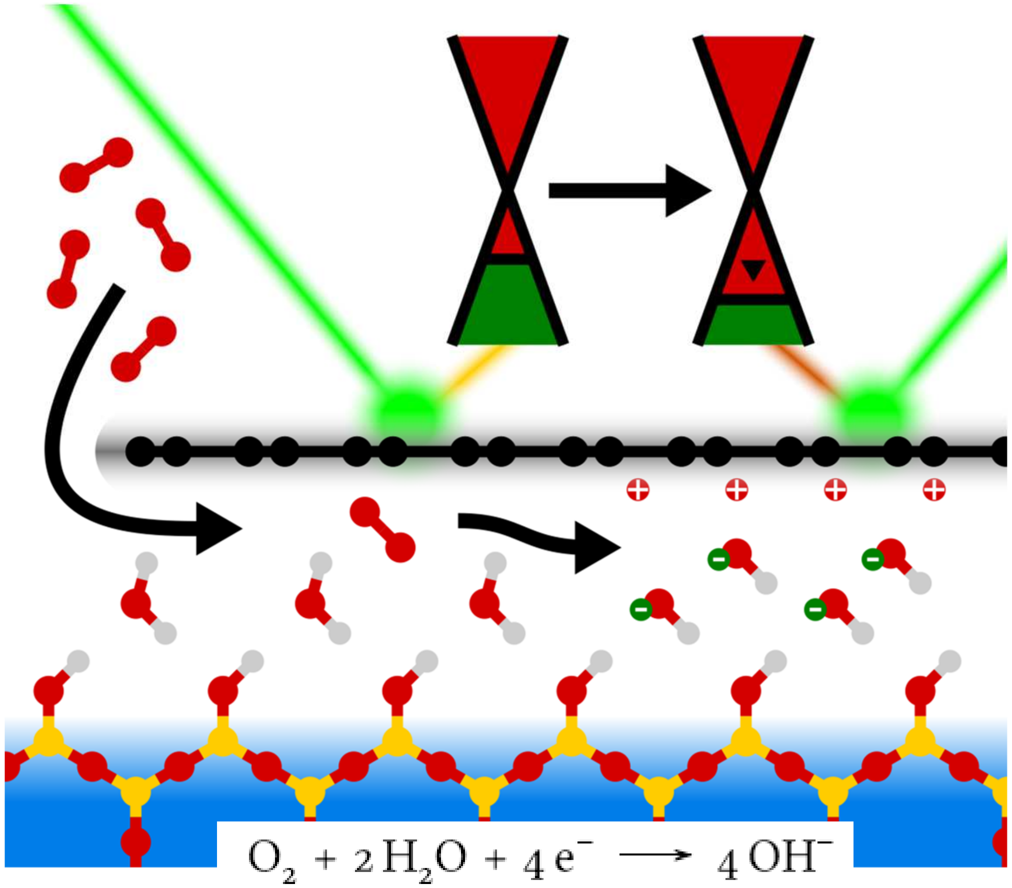

2705
2700
2695
2690
2685
2680
2675
2670
1578
1582
1586
1590
1594
1598
1602
1606
1610
2D Raman Shift (cm-1)
G Raman Shift (cm-1)
Gr/h-SiO2
Gr/h-SiO2 + O2
Gr/m-SiO2
Gr/m-SiO2 + O2
Strain (%)
-0.09(8)
0.08(8)
0.4(2)
1.2(1)
-0.14(4)
-0.14(4)
-0.11(2)
-0.09(1)
Doping (10^13 cm^-2)
Oxygen treatment
"hydro-"
"hydro+"



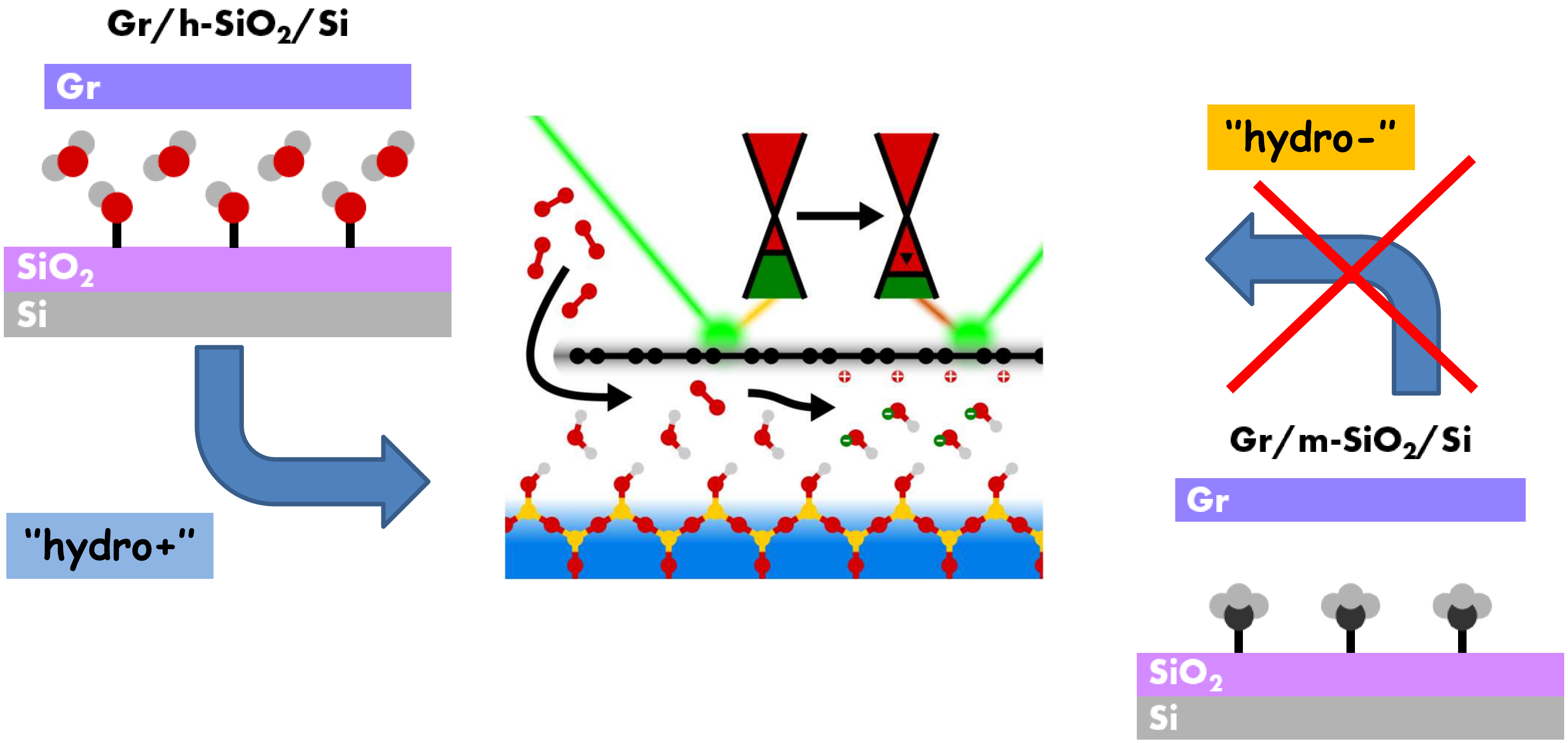
"hydro+"
"hydro-"
0.45(3)%
0.39(3)%
0.24(9)%
0.19(5)%
Gr/h-SiO2
Gr/Al2O3
Gr/HfO2
Gr/m-SiO2
Maximum Doping (10^13 cm^-1)
Charge carrier / C atoms (%)
Contact Angle (°)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
1.6
1.8
2.0
0.1
0.3
0.5
56
60
64
68
72
76
80
84
88

MODEL: reduction process

Doping process



Doping process "sensitive" to substrate --> interlayer region

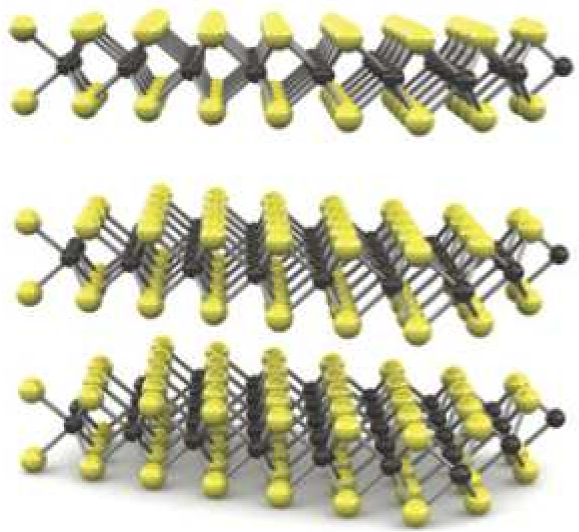


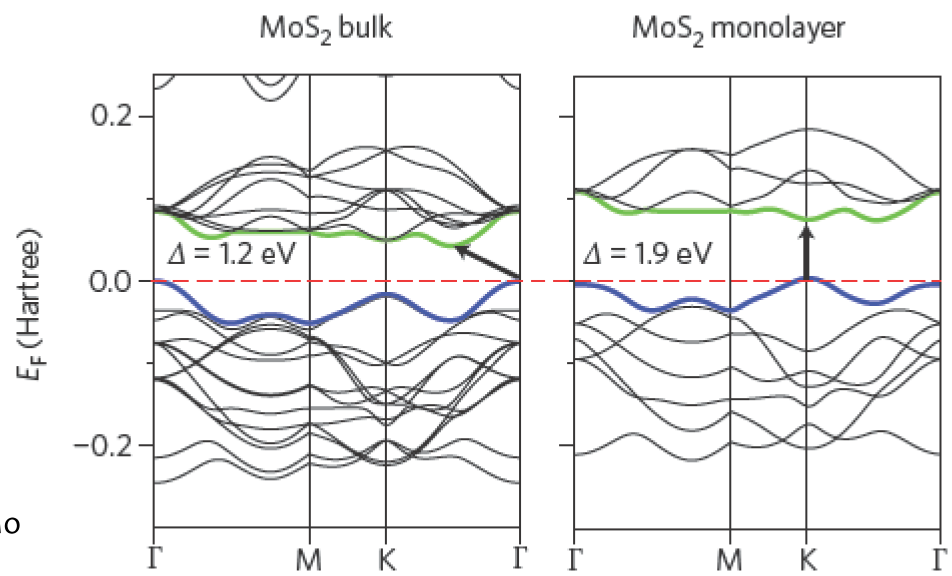
SUMMARY

- Exposure to O_2 at opportune T induces p-doping of graphene transferred on dielectric substrates
- The substrate affects both doping level and diffusion dynamics
- The doping process can be tuned by modifying the surface features of the substrate

Introduction

2D MoS_2 shows specific electronic features



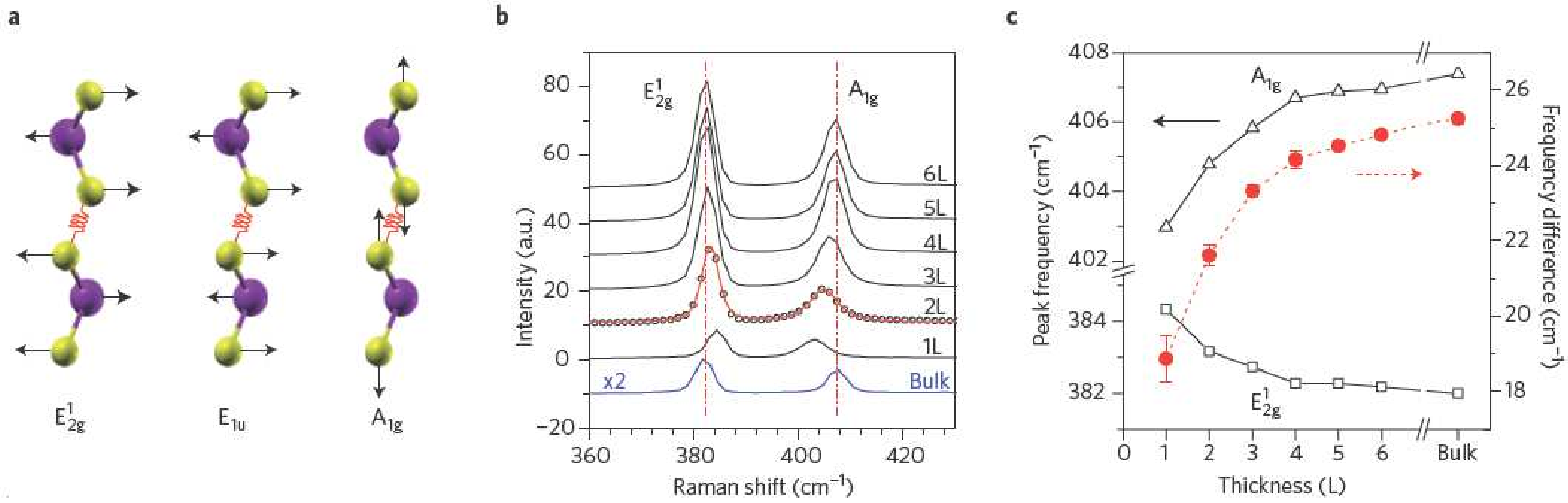


Indirect band gap

direct band gap

Q. H. Wang et al.; Nat. Nanotech. 2012, 7, 699

Raman spectra identifies number of layers



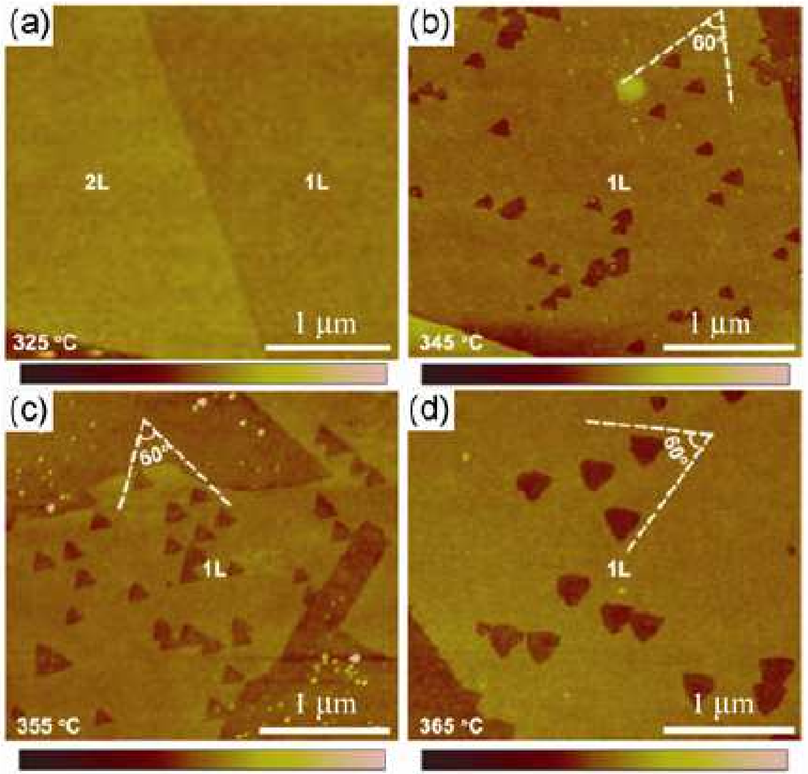
Q. H. Wang et al.; Nat. Nanotech. 2012, 7, 699

Introduction

Triangular pitchs formed by thermal treatments (2h) in air

325°C

345°C



355°C

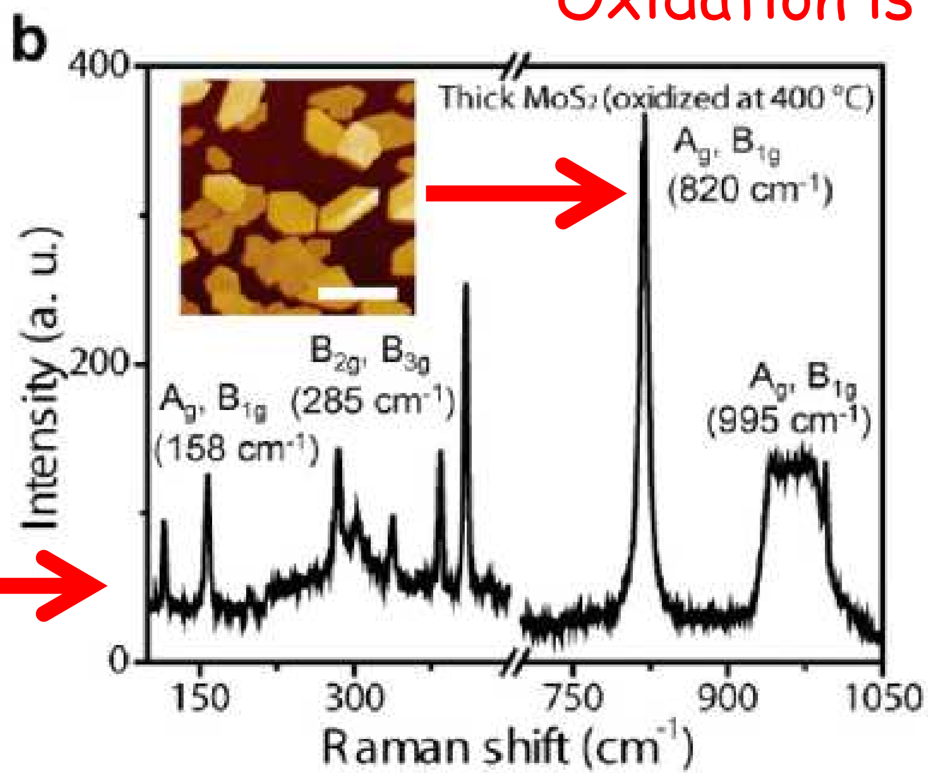
365°C

H. Zhou et al.; Nano Research 2013, 6, 703

Introduction

Oxidation is thermally induced

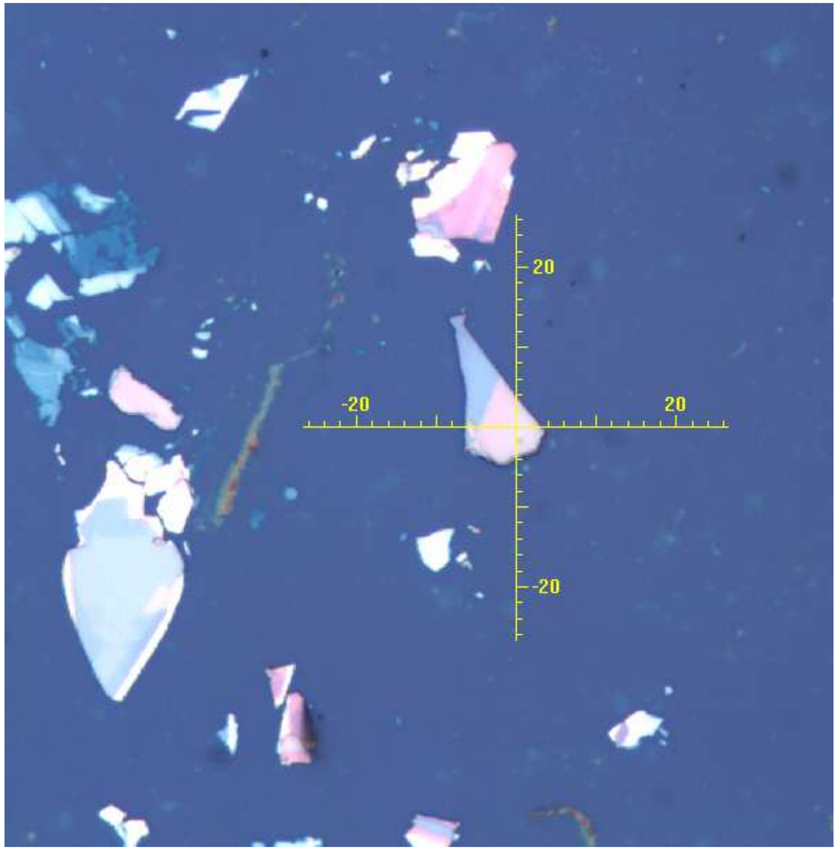
MoO$_3$ bands

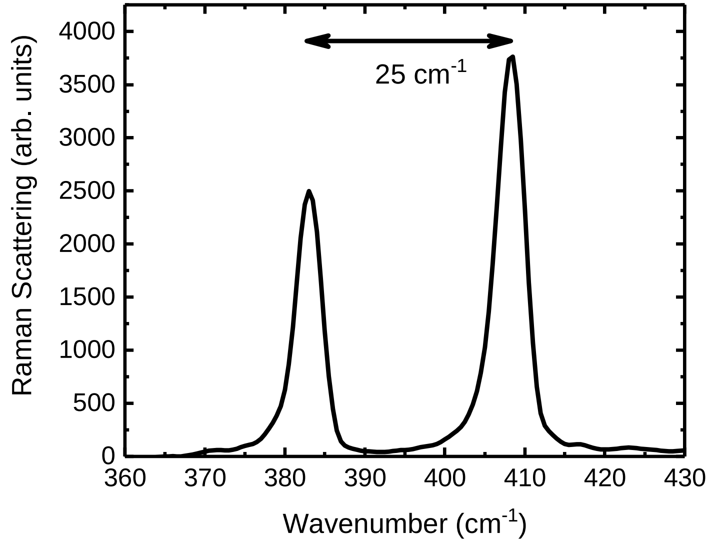


M. Yamamoto et al.; J. Phys. Chem. C 2013, 117, 25643

Material

MoS_2





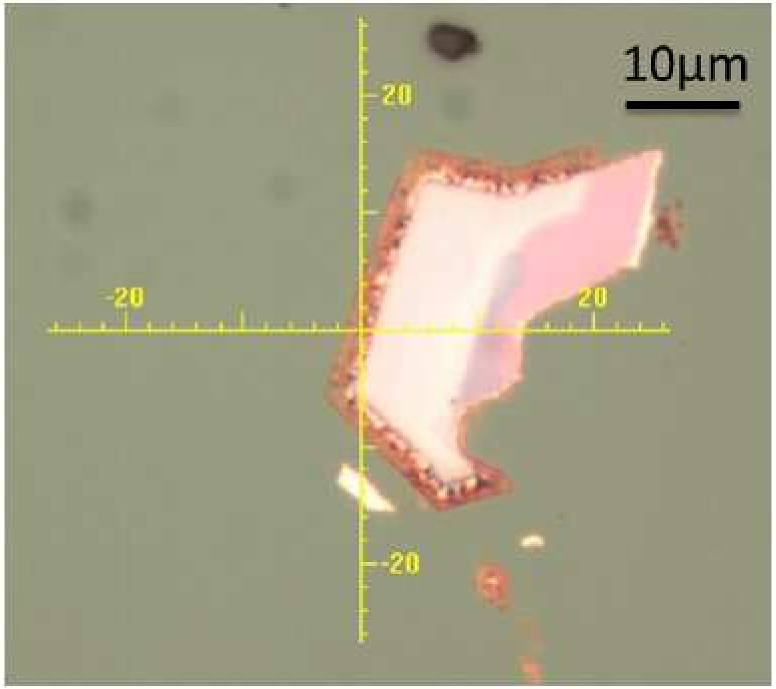
Mechanical exfoliation of Molybdenite crystal

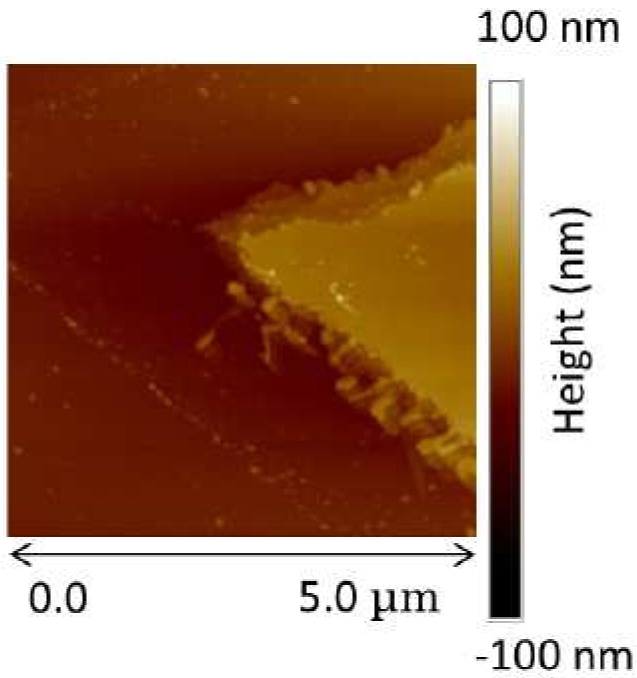
Thermal release tape and thermocompression on

SiO_2/Si

>10μm lateral size flakes

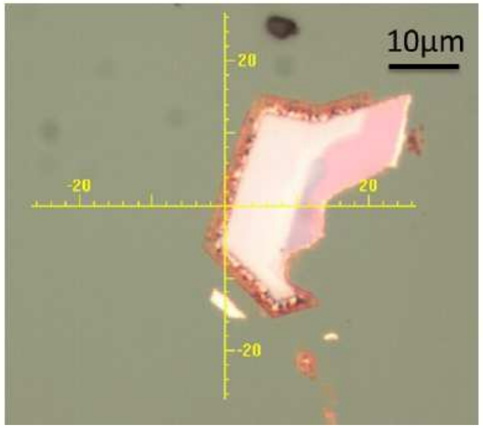
TT O_2 up to 430°C



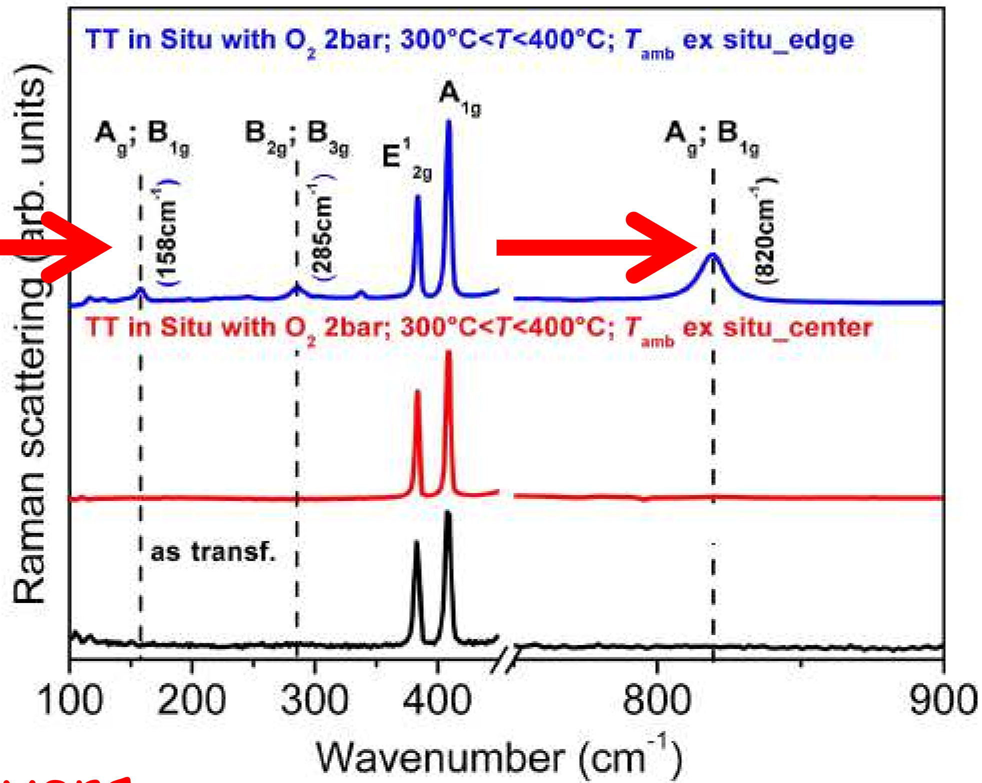


Flakes erosion edge size thinning

A. Piazza et al **Bel.Jour. Nano 8 (2017) 418**



MoO_3 bands



Oxidative effect of edge layers

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CONCLUSIONS

- Exposure to O_2 at opportune T induces oxidation and structural changes of 2D MoS_2
- The thermal treatments in controlled atmosphere are useful to modify physical properties of 2D materials
- Interaction with the substrate has to be deepened

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Thank you all for your kind attention