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Graphene and Boron-doped Graphene by Pulsed Laser Deposition

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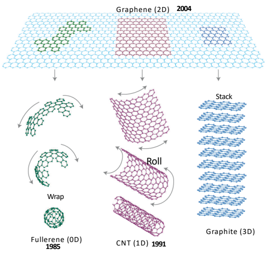
Context and Objective

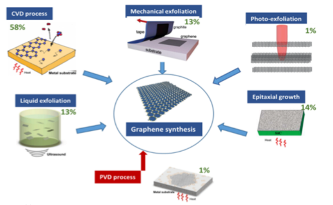
Challenge: Synthesis and nanostructure control !



- Very few study on graphene synthesis using PVD process.

PVD advantages are:

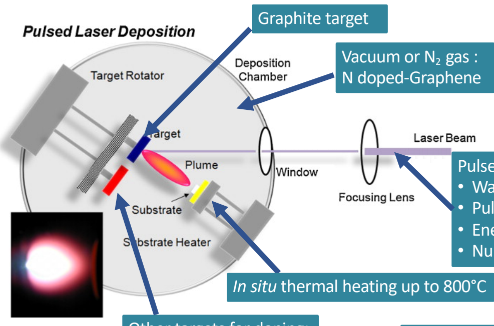
- Thickness control of carbon/metal coatings.
- Doping (B, N…) control in the carbon coating.
- Lower Temperature (vs CVD)



PLD as a PVD Versatile Process:

- Very well control of Doping (B, N…) at all concentrations, by reactive PLD or co-PLD
- Interest of thermal heating in situ during PLD

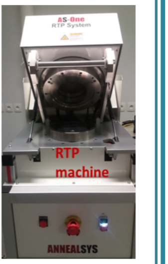
Methods and Materials



Graphite target

Vacuum or N_2 gas : N doped-Graphene

Rapid thermal process for ex-situ annealing up to 1100°C



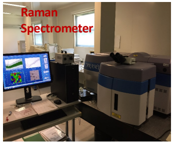
Pulsed laser:

- Wavelength
- Pulsed duration (ns or fs)
- Energy density & Power
- Number of pulses

In situ thermal heating up to 800°C

Other targets for doping: B-doped Graphene

Raman spectroscopy for rapid identification of graphene formation



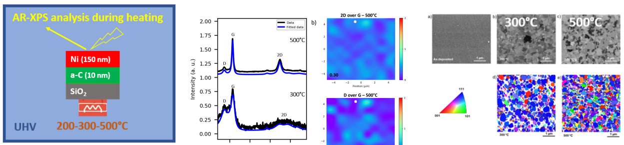
Pulsed laser deposition (PLD) system for Graphene synthesis

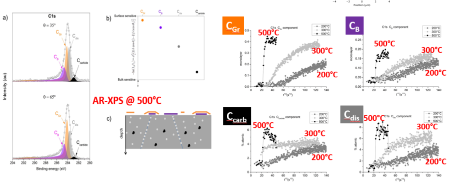
Results

Undoped Graphene (G)

- Graphene growth mechanism study
- Transfer-free graphene synthesis via PLD and RTP

Growth mechanism of Graphene from *in-situ* XPS during thermal heating

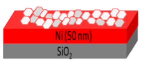




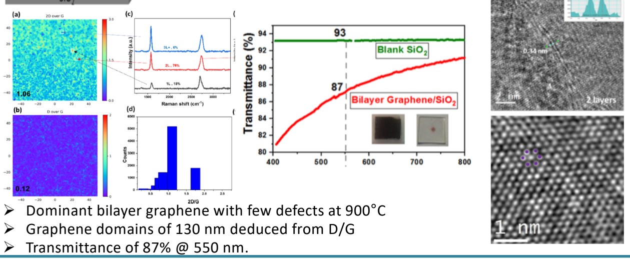
- C_{Gr} and C_B start from 200°C due to the fine Ni microstructure.
- C_{carb} up to 6% at 500°C, then decrease due NiC decomposition.
- C_{dis} up to 7 at% at 500°C

Ni catalyst evolves during annealing and influences the C diffusion kinetics and the graphene growth mechanism.

Transfer-free undoped graphene via PLD and RTP



SiO_2 / Ni (50nm) / a-C (2nm) - RTA at 900°C during 420 s - Heating Ramp: +15°C/s - Cooling Ramp: -0.5°C/s

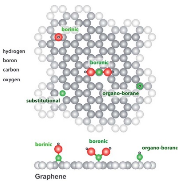


- Dominant bilayer graphene with few defects at 900°C
- Graphene domains of 130 nm deduced from D/G
- Transmittance of 87% @ 550 nm.

Boron doped Graphene (B-G)

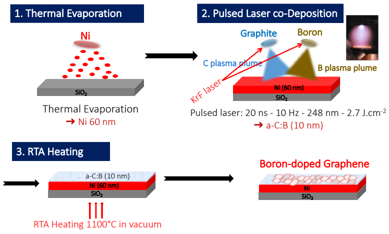
- Complementary to N-doping as a p-type doping raising hole concentration
- Versatility and simplicity of co-PLD for B incorporation control

B-G produced by PLD for the first time



DFT calculations suggest B-doping can have many advantages on N-doping:

- Easier in-plane incorporation
- Reduced lattice stress
- Preserving mechanical properties while changing thermal conductivity.

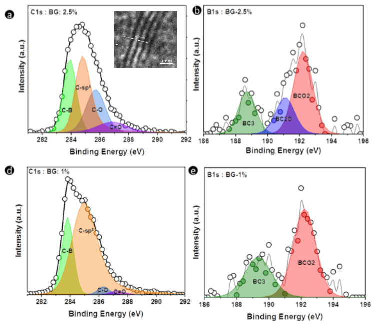


Thermal Evaporation → Ni 60 nm

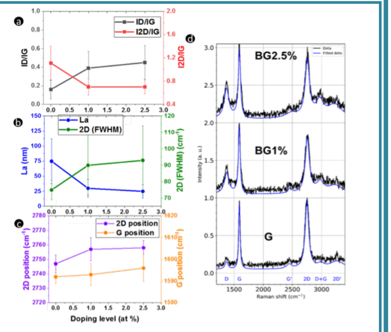
Pulsed laser: 20 ns - 10 Hz - 248 nm - 2.7 J.cm^{-2} → a-C:B (10 nm)

RTA Heating 1100°C in vacuum

Chemical characterizations: XPS - Raman

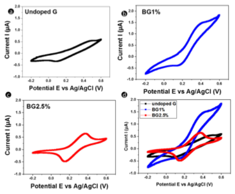


- Boron content control with systematic loss
- BC3, BC2O and BCO2 bonds confirms substitutional boron doping in the graphene structure.



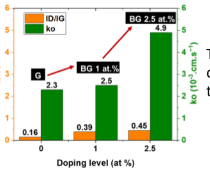
- Boron doping increases defect level and affects the graphene layer formation.
- Upshifts of G and 2D peaks with the boron doping.

Electrochemistry results



- Quasi-reversible systems
- Higher reversibility with B
- Better kinetic electronic transfer compared to the undoped G

Samples	ΔE (V)	K_0 (10^{-3} cm.s^{-1})
G	0.35	2.3
BG 1	0.17	2.5
BG 2.5	0.20	4.9



The electron transfer capability is dependent on the dopant concentration.

Conclusions and

- ✓ Easy route to produce few-layer Graphene and doped graphene with controlled dopant incorporation, by co-ablation PLD (B).
- ✓ No evidence of defect-free, single layer of graphene due to the energetic C species.
- x Optimization of the growth conditions to obtain SLG.
- x Investigations of the electronics properties of G and B-G.

Acknowledgments

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