Study of Graphene Growth Mechanism on Nickel Thin Films

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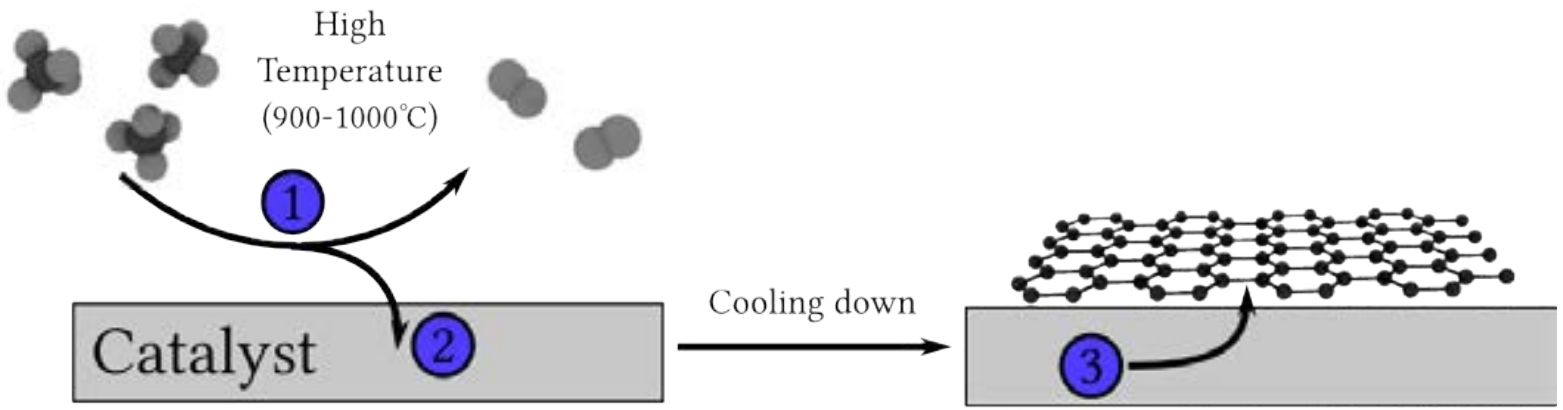
Graphita 2011 - 15/05/2011 - L'Aquila

Outline

CVD as a reliable process for graphene growth.

To date, CVD is the most advanced process for the industrial growth of graphene.
Accepted mechanism involves three steps :

1. Dissociation of the carbon precursor at high temperature on the catalyst surface
2. Carbon dissolution in the catalyst
3. Graphene precipitation at the surface of the catalyst as the sample cools down



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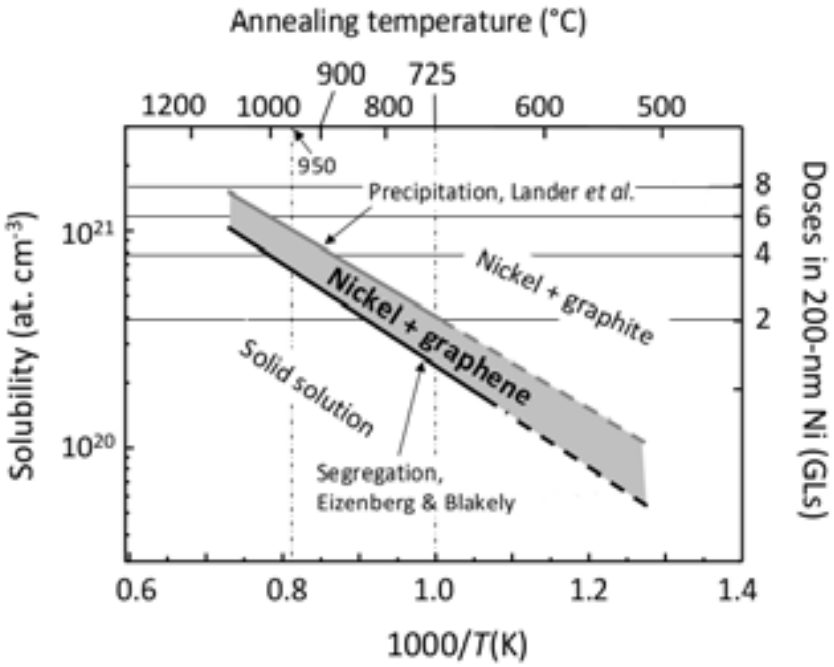
It is possible to isolate and study the last step of this mechanism using Ion Implantation (Io-I).

Carbon solubility in nickel.

In 1979, Eizenberg *et al.* analyzed nickel surfaces in-situ during thermal treatments of carbon-doped nickel samples around the precipitation temperature. They evidenced a specific 2D crystallization regime, which is a phase transition, corresponding to the formation of a single graphene layer.



Precipitation (Lander et al.):

$S_P = S_{P0}.e^{(\frac{H_P}{kT})}$, where :

$H_P = -0.421$ eV

Lander, J. J. *et al. J. App. Phys.* 23 **(1952)** 1305-1309.

Special segregation (Eizenberg et al.):

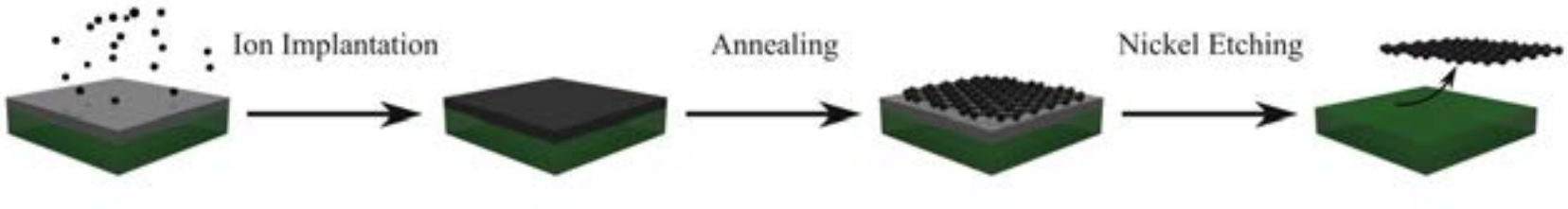
$S_S = S_{S0}.e^{(\frac{H_S}{kT})}$, where :

$H_S = -0.47$ eV

Eizenberg M. and Blakely J. M., *J. Chem. Phys.* 71 **(1979)** 3467.

Carbon ions implantation in nickel substrate.

Our experimental approach is as follow :



Baraton, L. *et al. Nanotechnology* 22 **(2011)** 085601.

Ion implantation allows to control :

- the amount of carbon dissolved in the catalyst is well controlled.
- the uniformity of the distribution of the amount of carbon in the catalyst layer allover the sample.

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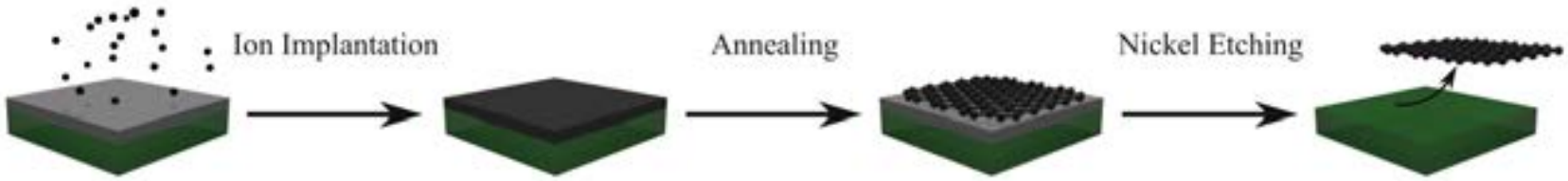

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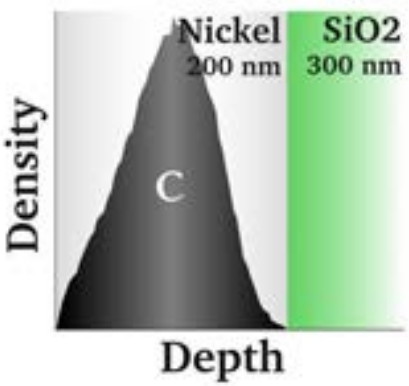
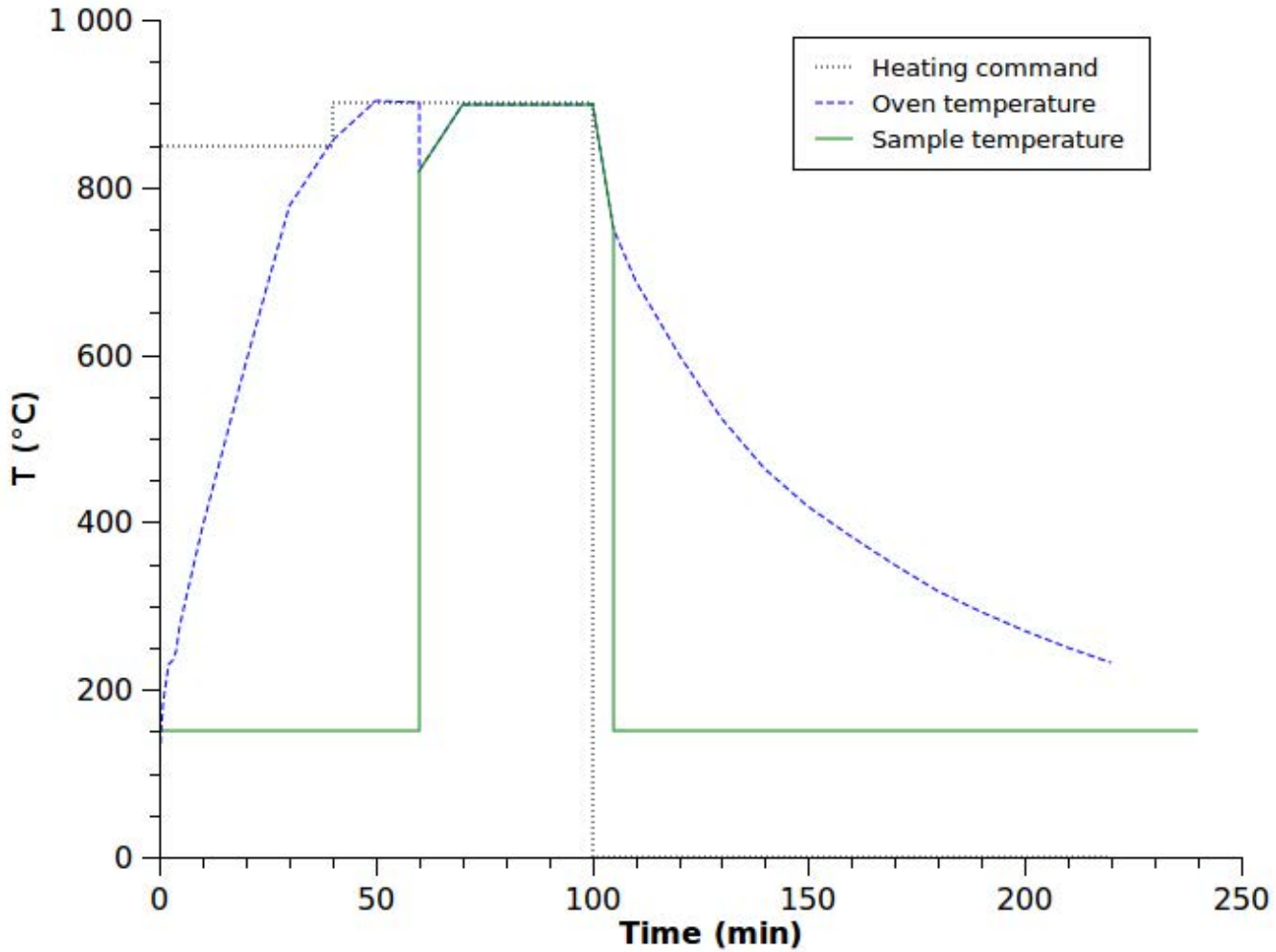


Experimental parameters :

- 200 nm Nickel thin films deposited on 300 nm thick thermal SiO_2
- 80 keV carbon ions where implated at doses of 8, 16, 24 and 32×10^{15} cm^{-2}
  Those doses correspond to 2, 4, 6 and 8 monolayers of graphene respectively.

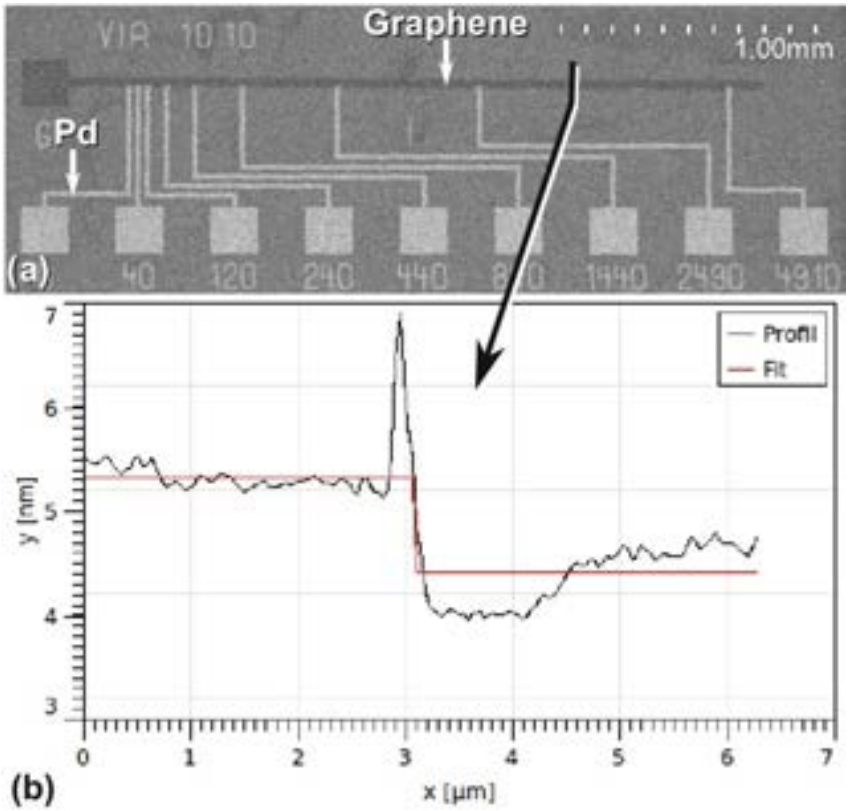
Carbon solubility in nickel and Annealing Conditions.

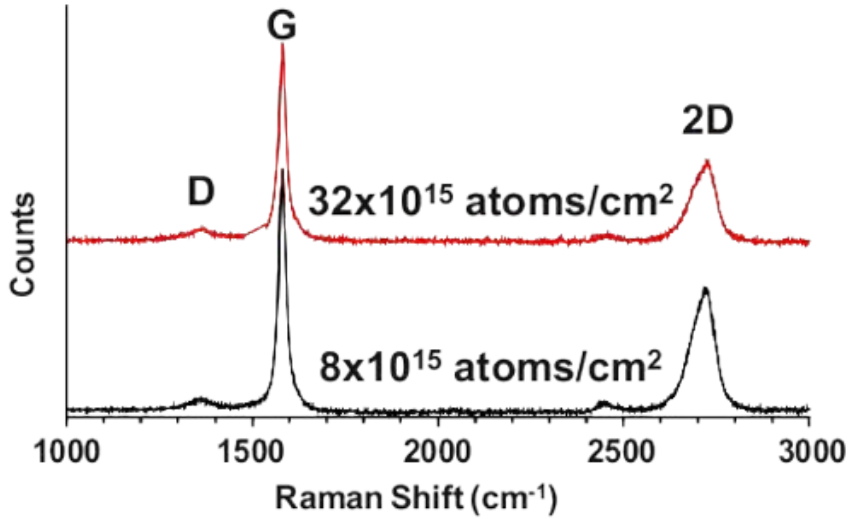
900°C for 30 minutes, cooled down to 750°C and the quenched to ∼150°C.



Characteristics of the graphene films obtained by Io-I.

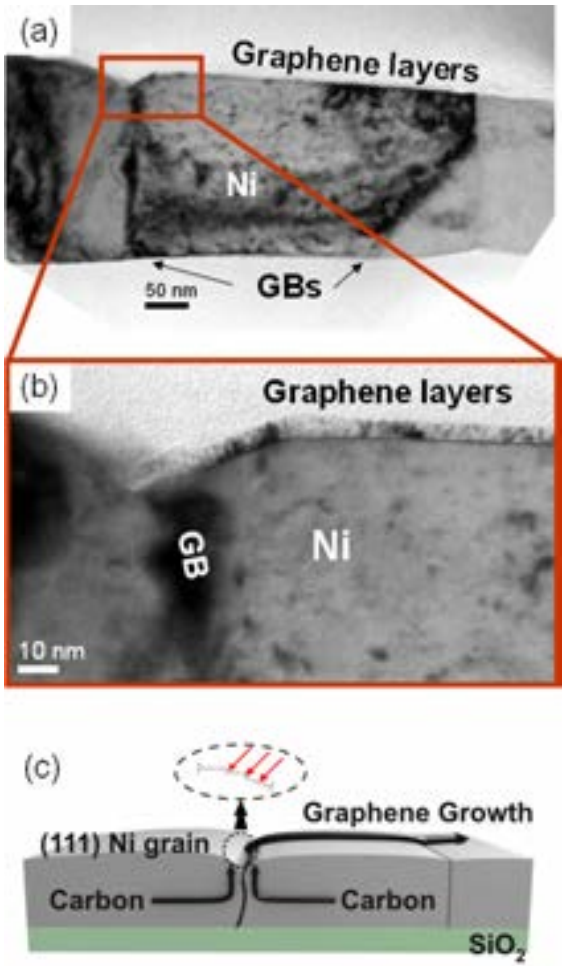
Graphene films have characterized using the classical methods :





- Initial dose shows little influence
  8 GLs : $I_G/I_{2D} = 0.88$
  2 GLs : $I_G/I_2D = 0.72$
- Transferred films are thin ($\sim$1nm).
- Sheet resistances measured using TLM-like structures are high, ranging from $100k\Omega/\square$ to $15k\Omega/\square$.

TEM observations of the Io-I Graphene films



Baraton, L. *et al. EPL submited*

Cross section the Ni layer:

- FLG film starts from the intersection with the surface of a nickel grain boundary (GB).
- the thickness of that surface graphite varies over a wide range, always in the form of large good-quality crystals with the **c** axis perpendicular to the surface.
- we find areas with few graphene layers, others with thick graphite, or with no graphene

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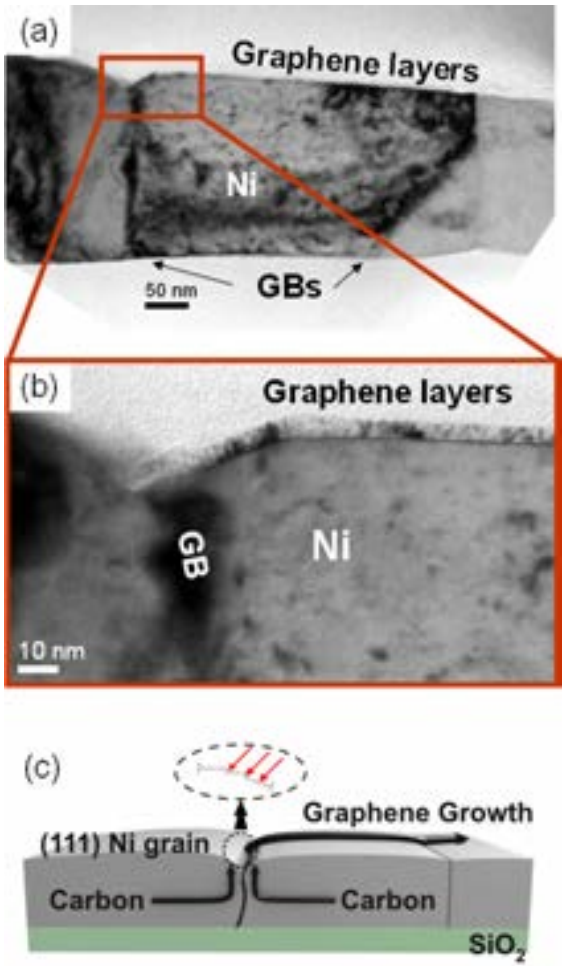

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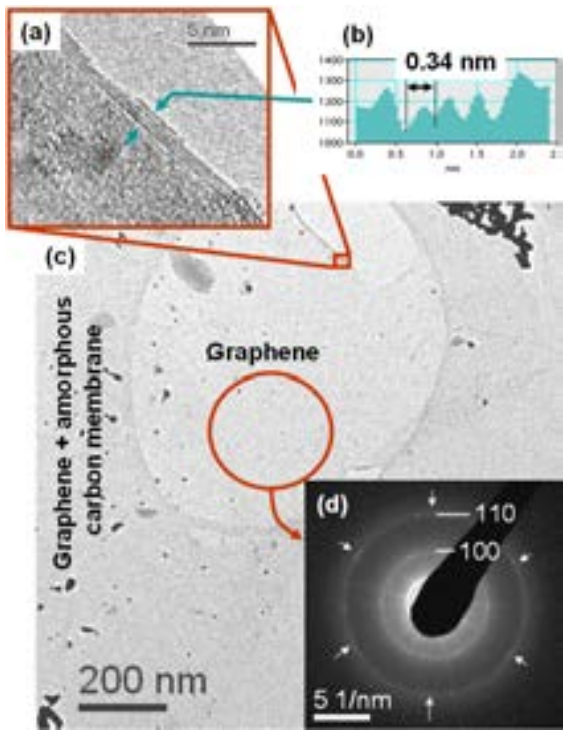
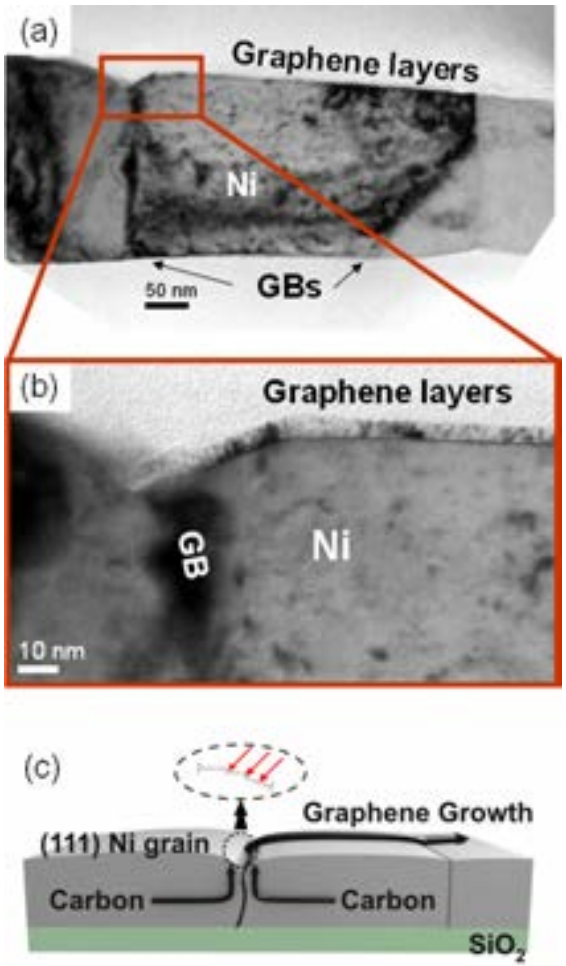


Plane view of a graphene film:

The folding of the film at its border allows one to count the number of layers (here 3 to 4 layers).

TEM observations of the Io-I Graphene films



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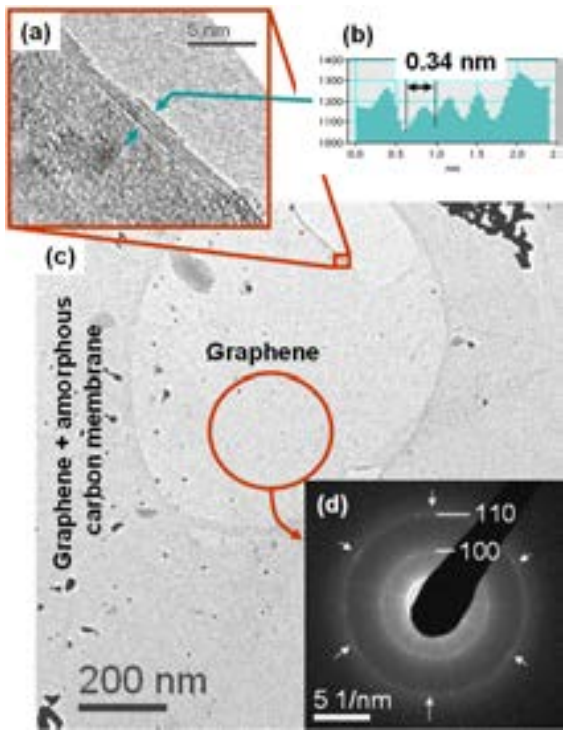

Plane view of a graphene film:

Large area EDP exhibiting 100 and 110 graphene reflections with a distribution of orientations.

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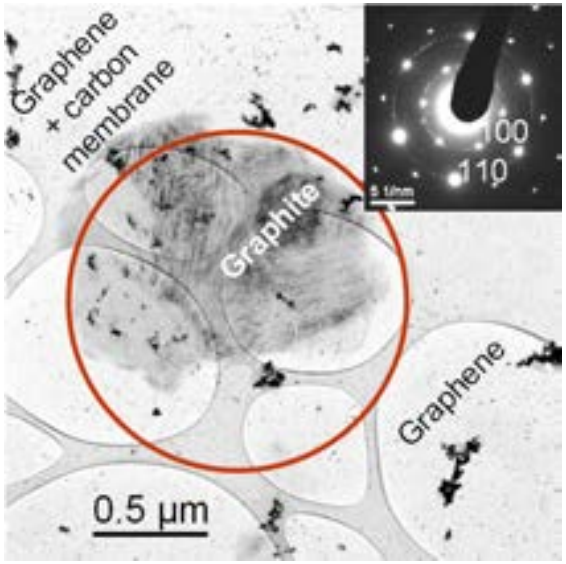


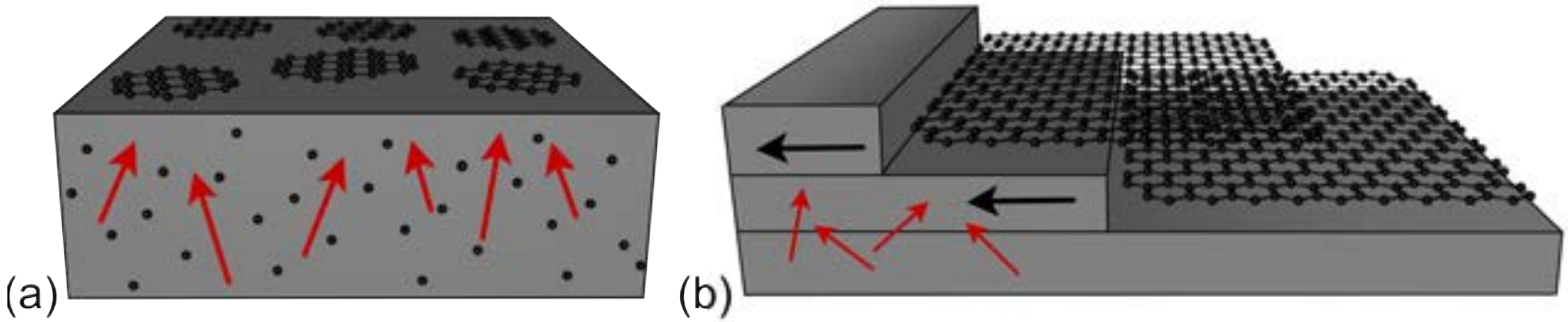
Graphene films grown by Io-I show :

- Graphite flakes and FLG : They form always at grains boundaries. The GBs act as nucleation centers.
  The local amount of carbon is largely superior of the one introduced by Io-I
  This implies a strong redistribution of the carbon density during the annealing In fact we calculated from Lander et al. work that the diffusion length of carbon in nickel at 725 °C is 1.2 μm/s

  Lander, J. J. *et al. J. App. Phys.* 23 **(1952)** 1305-1309.
- Nanocrystalline graphene : Crystal sizes ranges from 3.5 to 1.5 nm wide (from EDP rings width)
  There is no long-range order.
  Their formation of such graphene must occur at the nucleation sites on the surface due to the supersaturation as the sample cools down, as diffusion length remains significant

Two mechanisms of carbon precipitation.

In our experiments, two mechanisms compete to form either graphite or FLG and nanocrystalline graphene.
(a) local segregation at the interface
(b) long-range diffusion and precipitation at the grains boundaries.



The regime of phase transition observed by Eizenberg & Blakely is not seen because :

- doses are too high and the supersaturation favored segregation and precipitation
- precipitation occurs during quenching
- the strong redistribution of carbon in nickel implies that the local concentration is different everywhere in the sample and mostly out of the phase transition conditions.

Conclusion

We have shown that :

- ion implantation is a versatile technique to study growth mechanisms, allowing controlled and predefined amounts of carbon to be introduced inside the nickel
- during thermal annealing, a strong redistribution of carbon in nickel occurs
- at least two growth mode exist in the case of nickel
  (i) graphite and FLG precipitate at grain boundaries
  (ii) nanocrystalline graphene segregate at nucleation sites on the surface during cooling

Finally providing the right thermodynamical conditions, it is possible to envision to use ion implantation to observe the phase transition observed by Eizenberg et al. in 1979 and synthesize graphene at low-cost.

Acknowledgment

We thank Dr. G. Rizza and Dr. P.-E. Coulon, LSI, Ecole Polytechnique, France, for the use of the CM30 TEM, and Dr. G. Garry and Dr. S. Enouz-Vedrenne (Thales R&T France) for access to the Topcon 002B.

This work was supported by :

- **C'Nano IdF**, a nanoscience competence center of Paris Region, supported by **CNRS, CEA, MESR** and **Region Ile-de-France**.
- WCU program through the NRF of Korea, funded by MEST (R31-2008-000-10029-0)

Thank you for your attention.