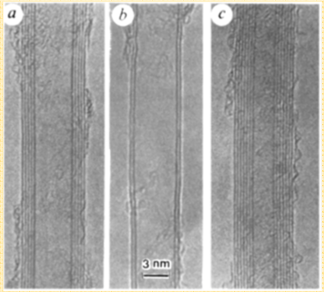


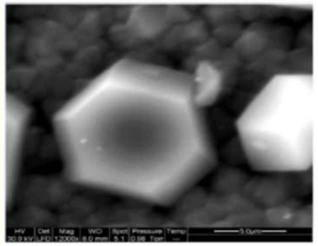
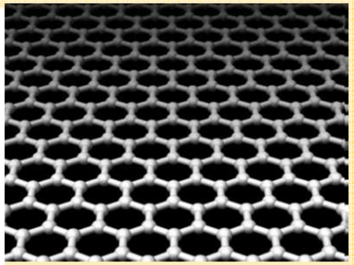


FIG. 2. SEM image of the diamond coating on GaN layer. A diamond crystal (size 5–6 μm) displays a hexagonal morphology.



Transitions de phase dans la croissance de matériaux carbonés

F. Le Normand

ICube-MAPECV, CNRS/Université de Strasbourg,
STRASBOURG, FRANCE

Colloque GDR Remisol, Strasbourg, 10/2015

Plan

- Diagramme de phase du carbone

- Spectroscopies d’électrons (XPS, AES) appliquées au carbone

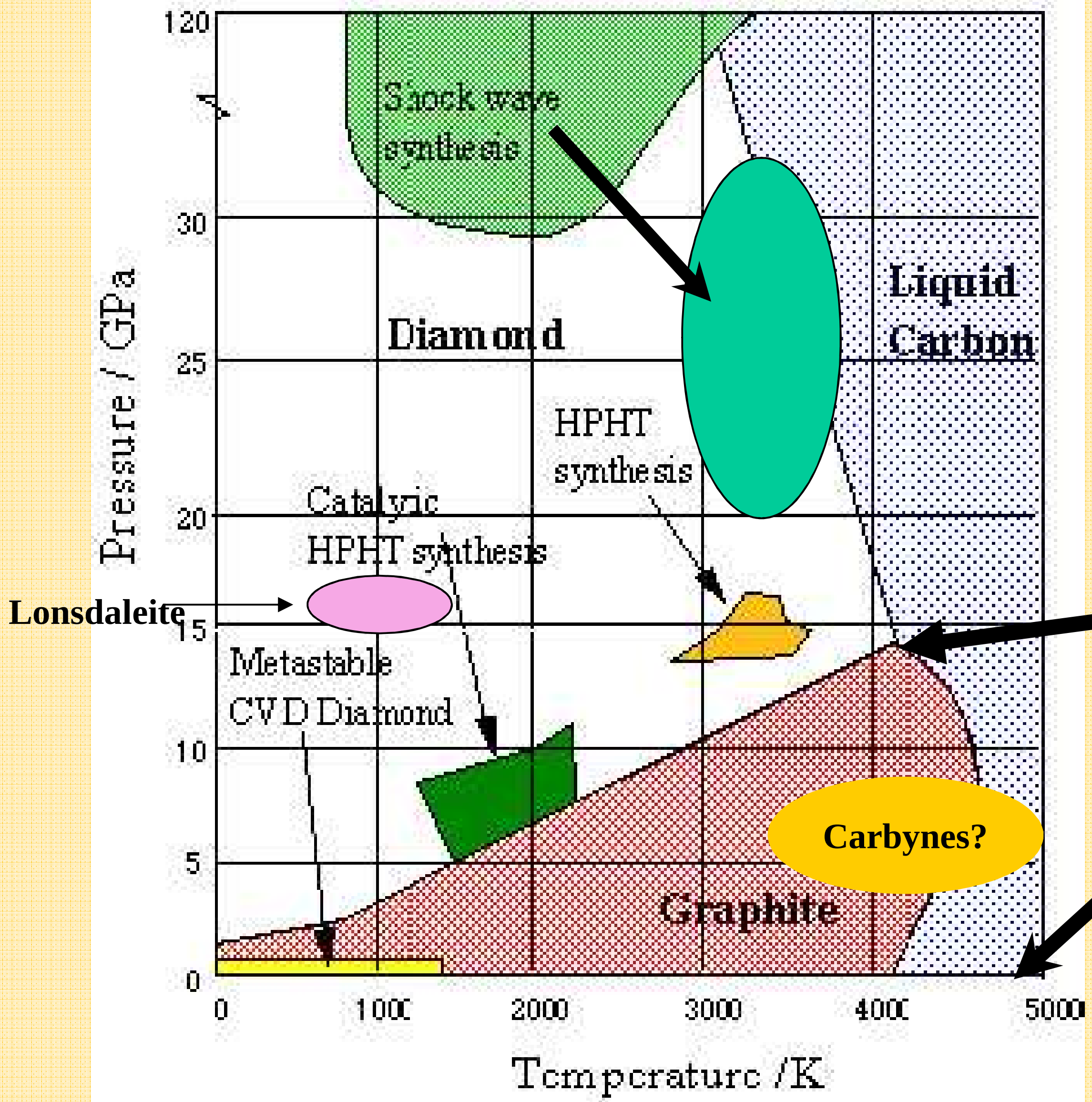
- Exemples de transition de phase du carbone

  **** La nucléation hétérogène du diamant métastable***

  **** Le graphène sur diamant***

Diagramme de phase du carbone

(diagramme de Bundy)



Pour obtenir la transition du graphite au diamant

Très fortes pressions
Hautes températures

Point triple

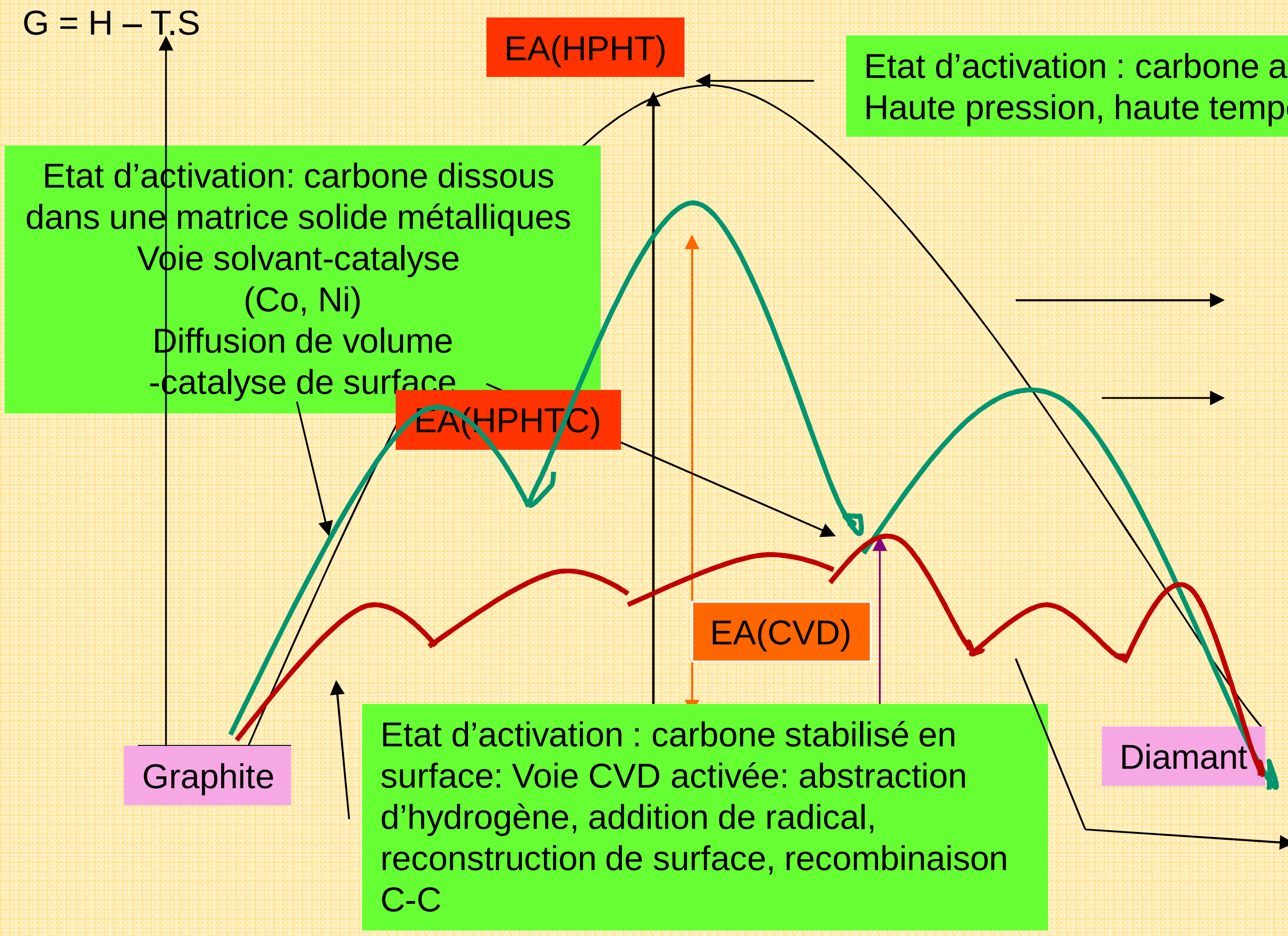
Vaporisation du carbone
4800K; 0.1 GPa

Transition Graphite-Diamant

$$p_{eq}/\text{atm} = 7000 + 27T \text{ (for } T>1200 \text{ K)}$$

Bundy's equation

La différence des énergies libres entre diamant et graphite est faible, mais l'énergie d'activation est énorme car il faut rompre toutes les liaisons dans une transformation en phase solide



$G = H – T.S$

EA(HPHT)

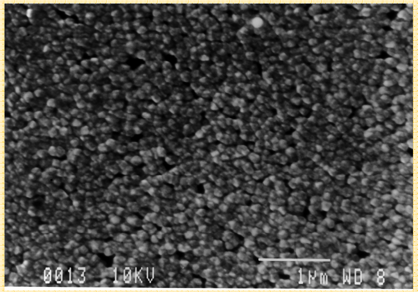
Etat d'activation : carbone atomique
Haute pression, haute temperature HPHT

Etat d'activation: carbone dissous dans une matrice solide métalliques
Voie solvant-catalyse
(Co, Ni)
Diffusion de volume
-catalyse de surface

EA(HPHTC)

EA(CVD)

Etat d'activation : carbone stabilisé en surface: Voie CVD activée: abstraction d'hydrogène, addition de radical, reconstruction de surface, recombinaison C-C



C1s XPS du carbone

*From Egelhoff Jr, Surface Science Report **6**, (1986) 264*

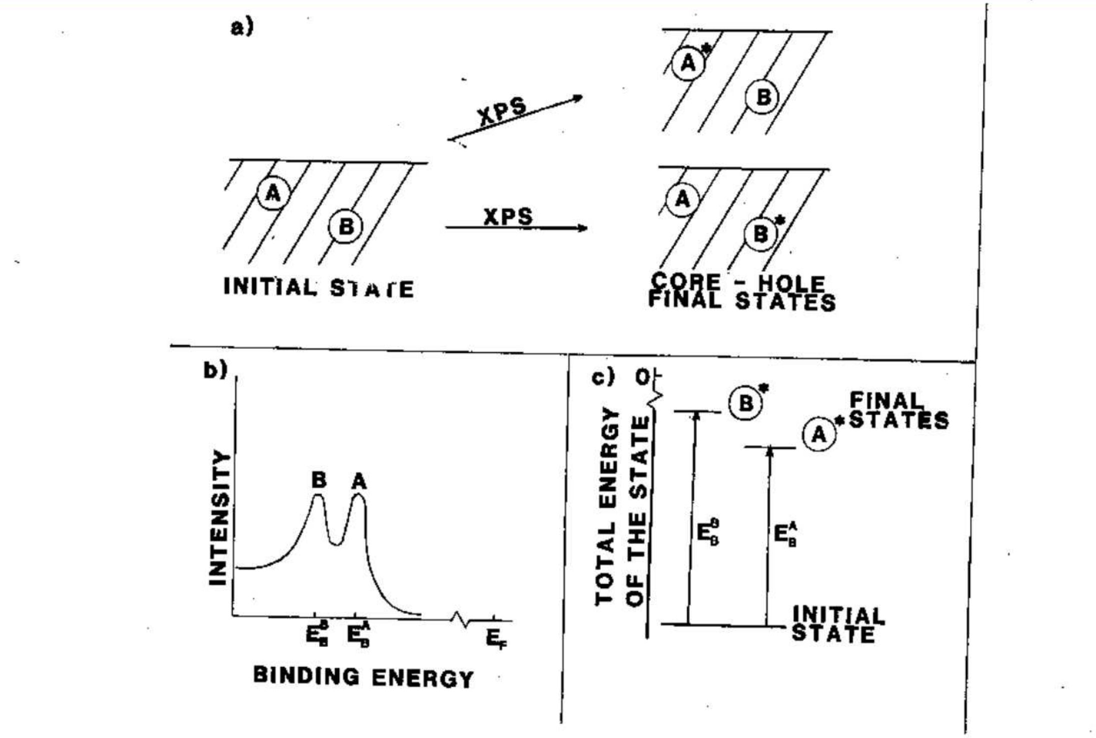


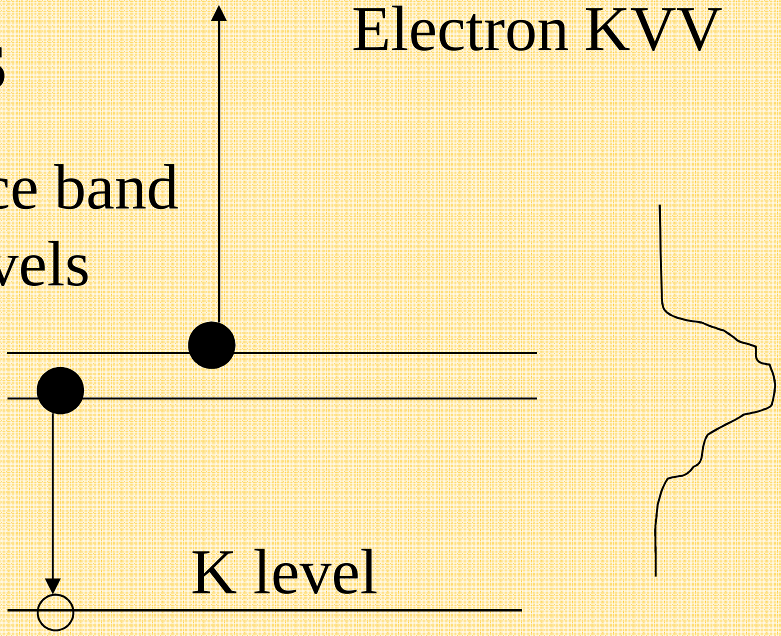
Fig. 2. Illustration of the shift in core-level binding energy for the same element in two different environments, A and B. The initial and final states in a total-energy differences framework are illustrated in (a), the core-level peaks in (b) and total energies of the states in (c). Final states of the type in (c) will be referred to throughout this review with A* described as the state of lower total energy and B* described as the state of higher total energy.

XPS : environ +1 eV entre C-C (graphitique, 284,6eV) et C-C (diamant, 285,5 eV) due à effet d'état final et niveau de Fermi du diamant

Ecrantage du niveau de coeur vacant par électrons π délocalisés > électrons σ très localisés

AES du carbone (KVV)

AES



Electron KVV

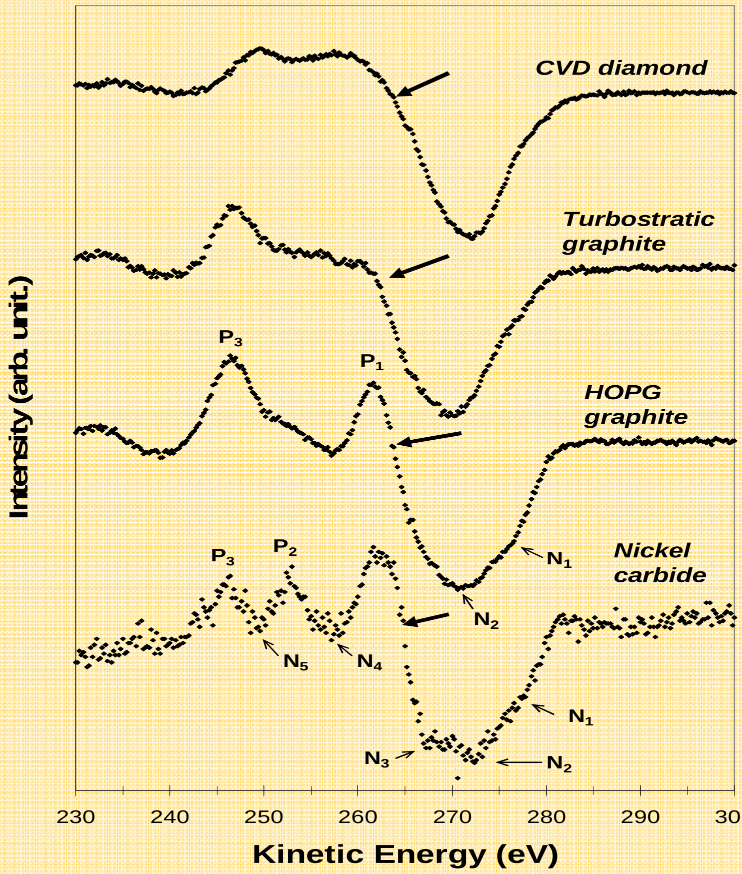
Valence band levels

K level

Double convolution de la densité des états de valence DOS o DOS*

Grande sensibilité à l’ état d’hybridation du carbone

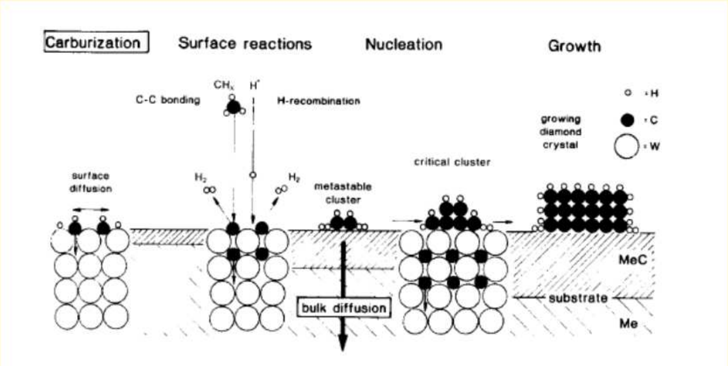
Mode dérivé



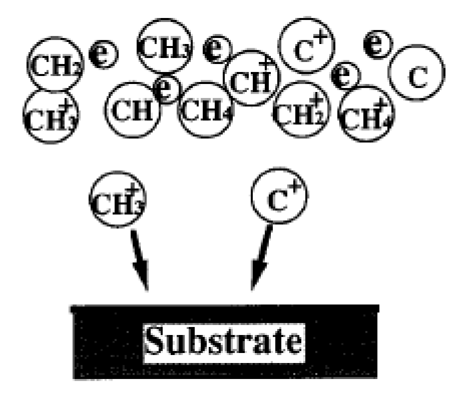
Our reference data base

Nucléation hétérogène du diamant CVD (métastable)

Nucléation classique : très faible densité



Nucléation assistée par polarisation (BEN-CVD)



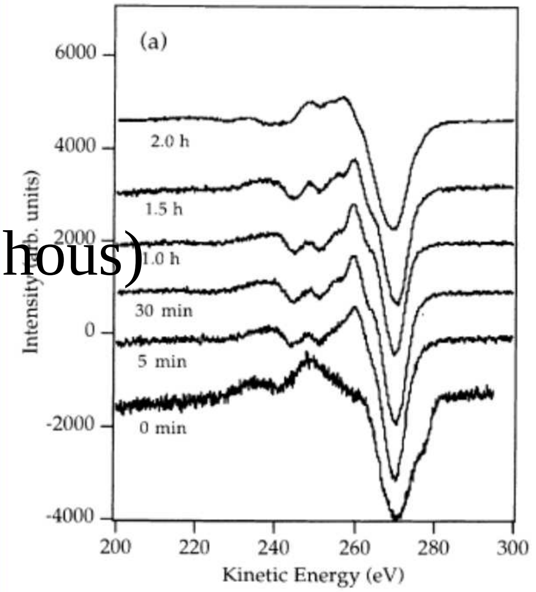
Bias Enhanced Nucleation-Micro-Wave Assisted CVD du diamant sur Si(100)

- Many reports in the literature about the nature of the **diamond precursor:**

- Graphitic fragments parallel or perpendicular to the surface
- Diamond like carbon (amorphous)
- Silicon carbide

Two mechanisms

- Surface nucleation
- Subimplantation



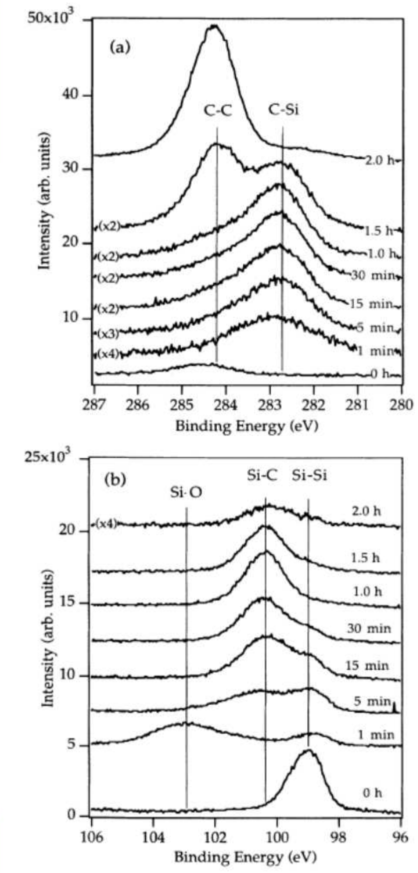
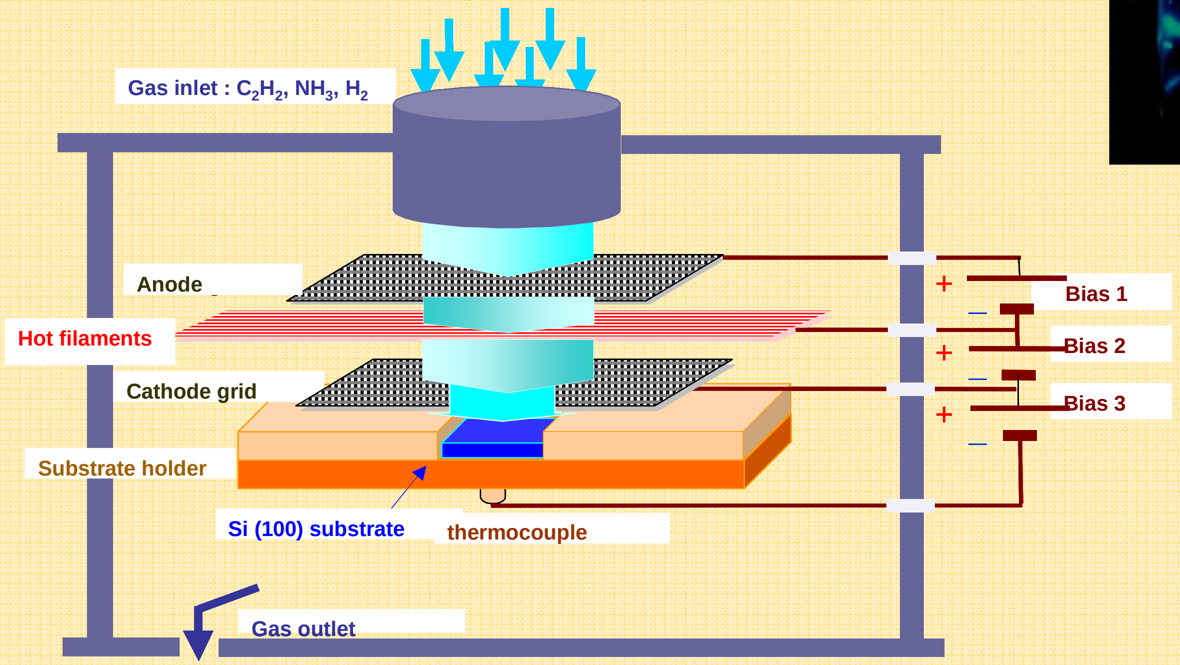


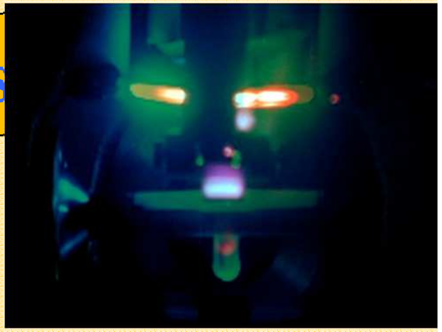
FIG. 5. XPS analysis as a function of bias-pretreatment time: (a) carbon 1*s* and (b) silicon 2*p* peak progressions.

Formation de carbure de silicium

Wolter et al, PhysRev B, 45, (1992) 11067

Procédé CVD assisté par radicaux et par ions





XPS, AES chamber

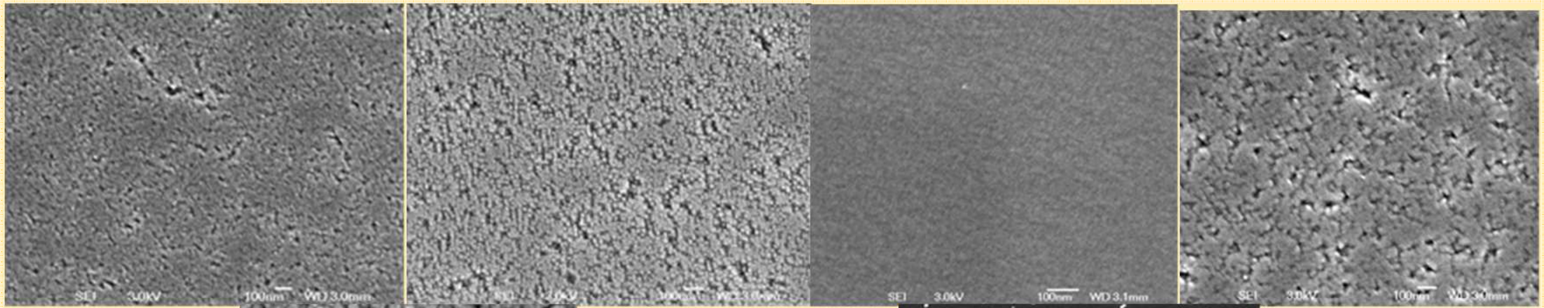
Polarisation between electrodes → ions

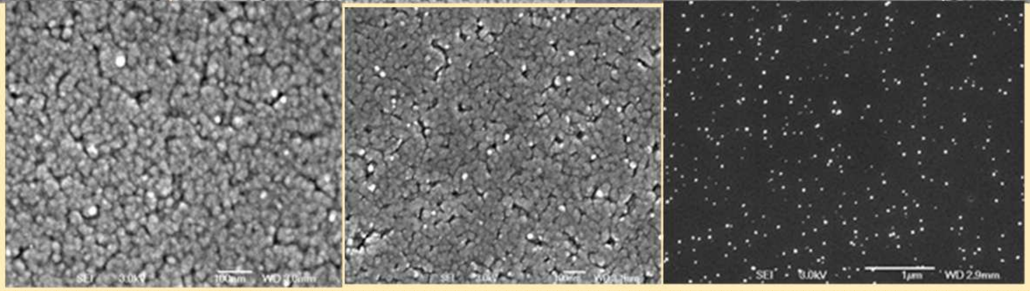
Hot filaments → radicals

- Bias 1 + Bias 2 : Plasma control (150-400V)
- Bias 3 : Control of the ions flux onto the substrate (0-60V)
- Nucléation : Bias + HF; Croissance : HF

SEM, AES et courant de polarisation
Nucleation BIAS –HF CVD on Si(100)

Temps(mn) 2 5 7 9

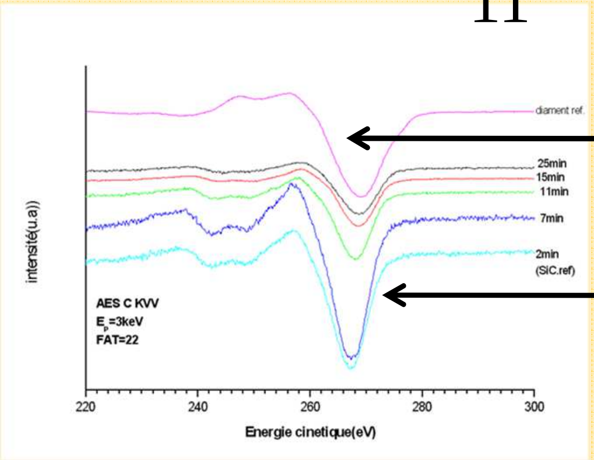




11 15 25

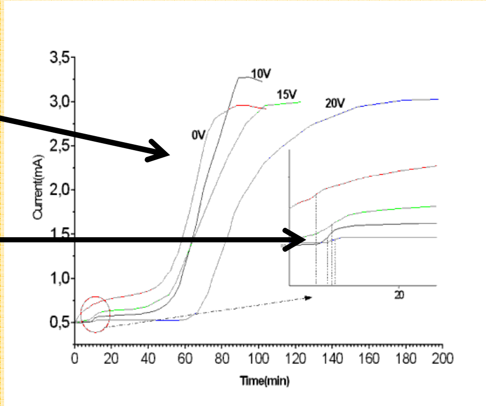
Le courant de polarisation évolue suite à l'apparition de diamant en surface (émission secondaire intense)

C KVV



Diamant

SiC

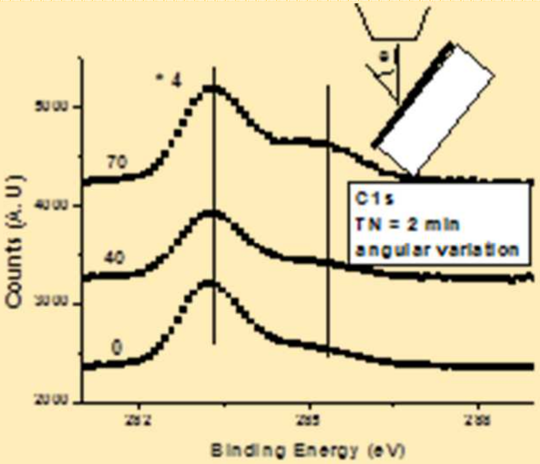


Analyse angulaire XPS C1s et Si 2p
Nucleation BIAS –HF CVD on Si(100)

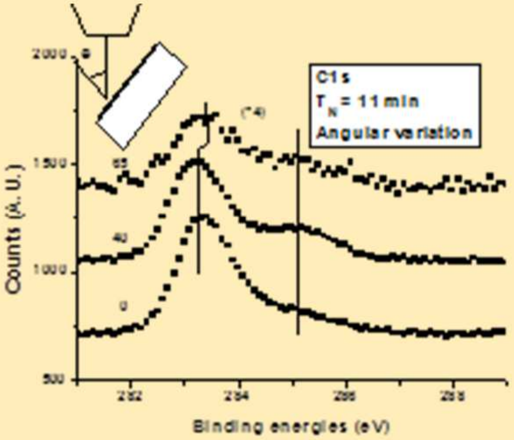
(T = 700°C; 4% CH4)

t = 2 min

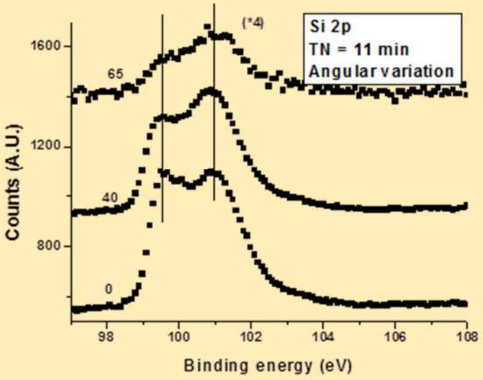
t = 11 min



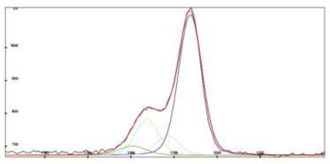
C1s

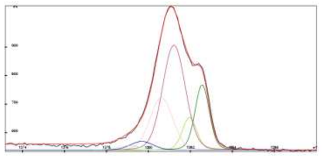


C1s



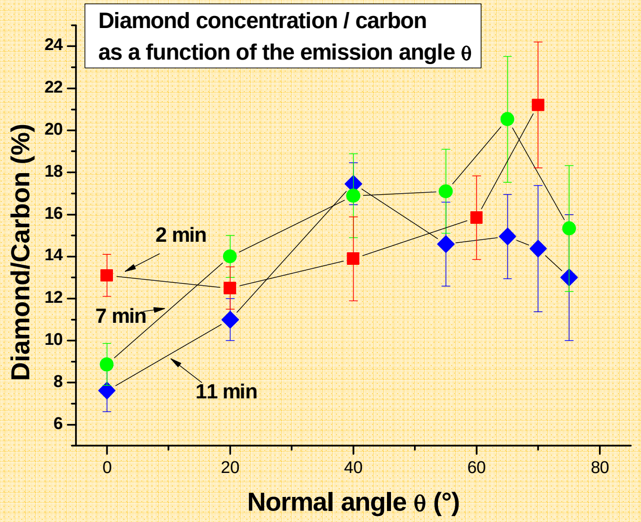
Si 2p

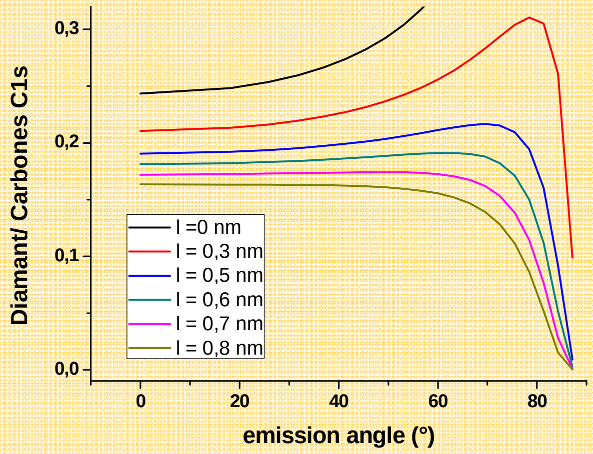




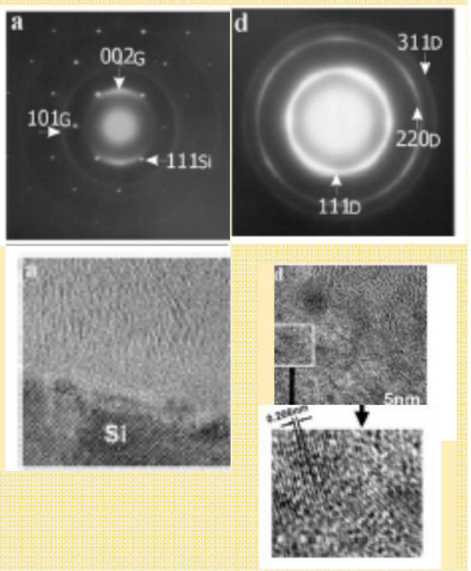
BEN –HF CVD on Si(100)

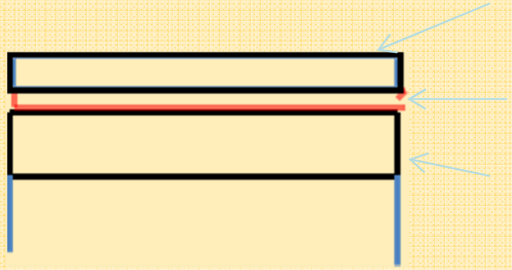
(T = 700°C; 4% CH4)





Lifschitz et al, Phys Rev Letters, 93 (2004) 056101





G ou DLC

D

SiC

- Mécanisme d'implantation superficielle
- Par contre on ne peut trancher sur la nature du précurseur

$$I_D = 2*A * n_D * \lambda_{CSi} * \cos\theta * \exp[-L/(\lambda_{CSi} * \cos\theta)] * sh[c/(2*\lambda_{CSi} * \cos\theta)]$$

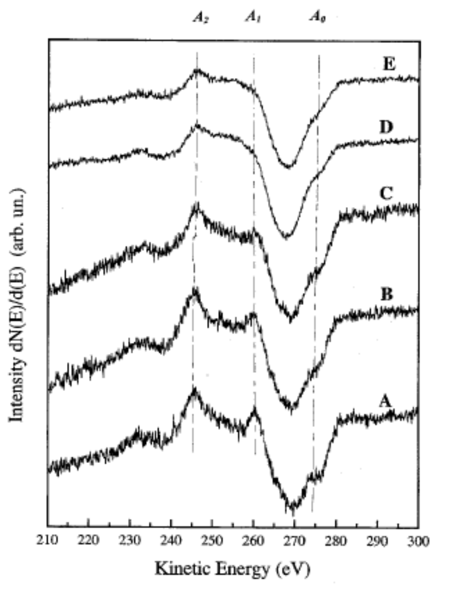
HF CVD sur Cu(111)

C KVV

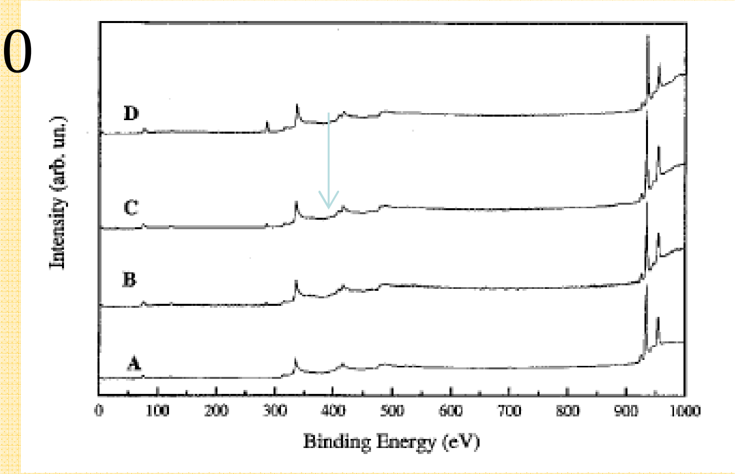
L. Constant, et al, Surface Science, 387, (1997), 28-43

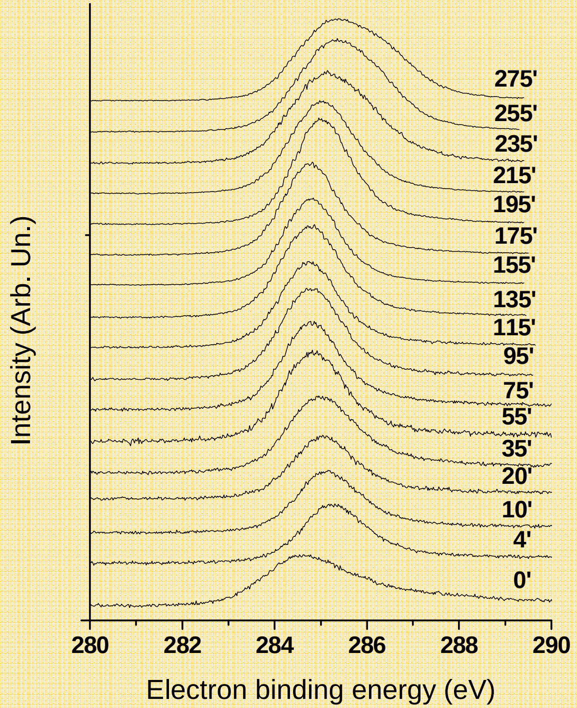
C 1s

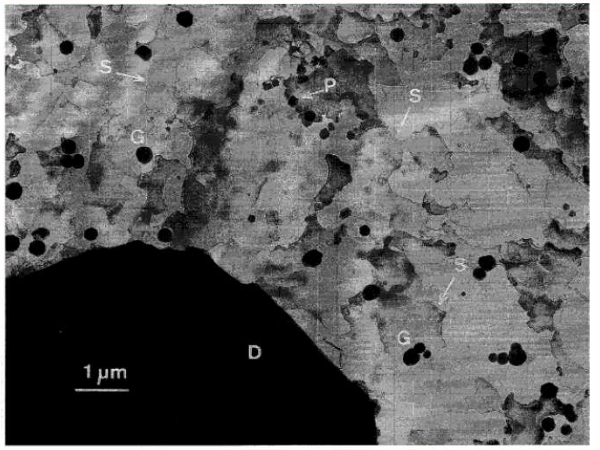
XPS wide scan

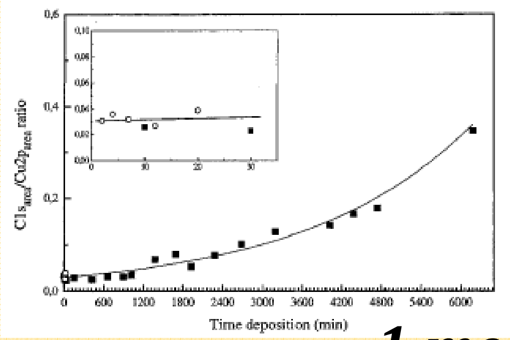


4020
900
100
10
0





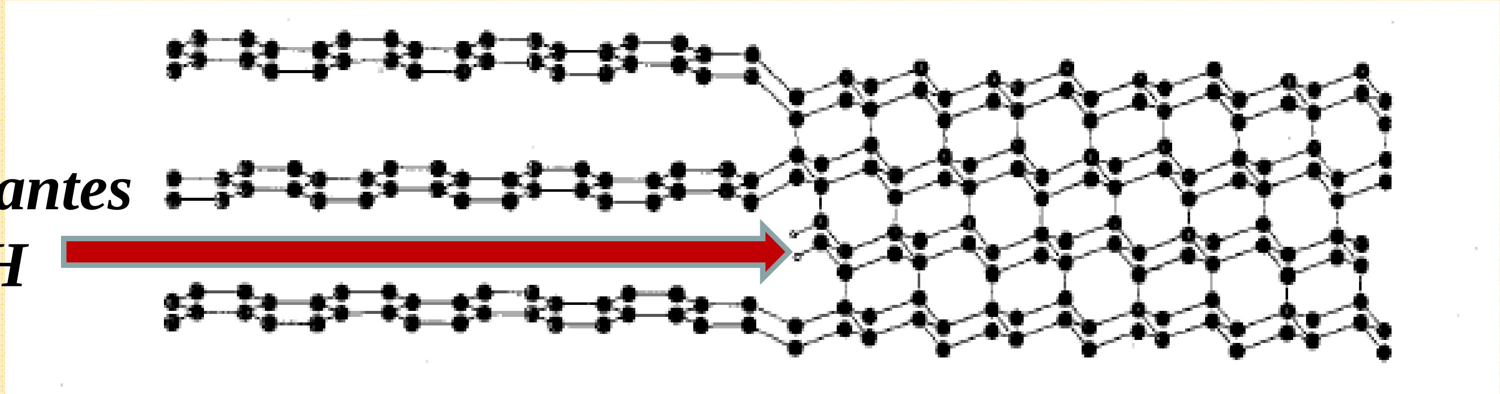




1 monocouche équivalente de graphite (graphène) à t= 0 min

Croissance de diamant sur cuivre

from the edge of graphitic fragments



2 liaisons pendantes comblées par H radicalaire

Séquence d’empilement G(00.1)//D(111) : 2//3

Lambrecht W.R.L. et al., Nature, 364, 607, (1993)

Thin graphene layers (TGL) sur Diamond like carbon (DLC)

DLC (ta:C)

- Surface non polaire
- Faible rugosité
- Faible densité de piégeage des charges
- Inerte chimiquement
- Procédé simple
- Stable thermiquement

Mais transfert de graphène (CVD cuivre)

Graphène sur DLC (transistor RF)

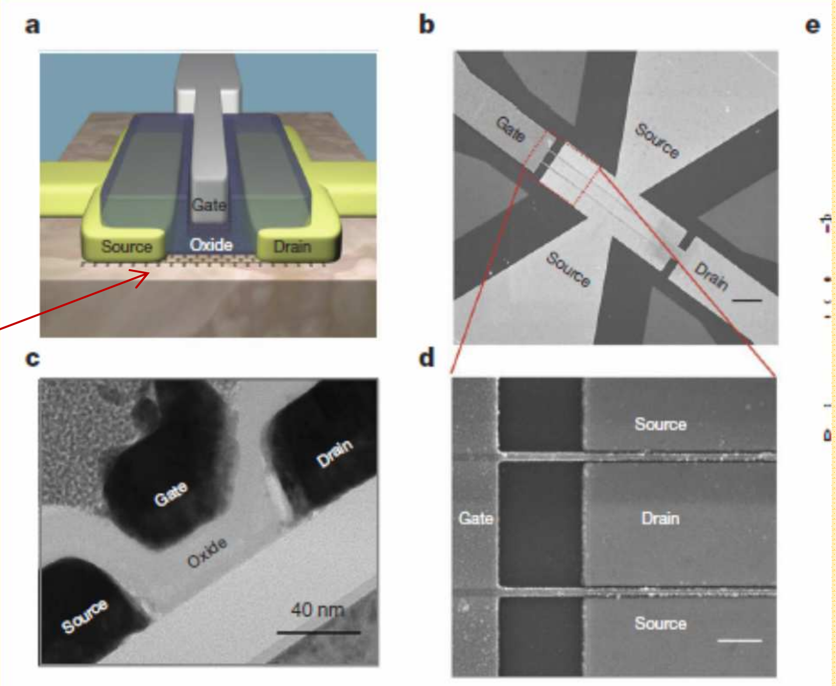
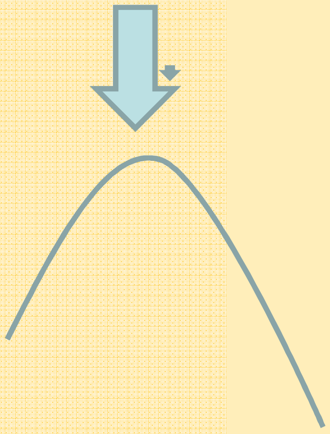


Figure 1 | Fabrication and output characteristics for graphene r.f. transistors. **a**, Schematic view of a top-gated graphene r.f. transistor on DLC substrate. **b**, SEM image of a typical top-gated dual-channel r.f. device. Scale bar, 3 μm. **c**, Cross-section TEM image of a graphene transistor with a gate

Wu Y.Q.. Et al, Nature, ***472*** *(2011) 74-78*

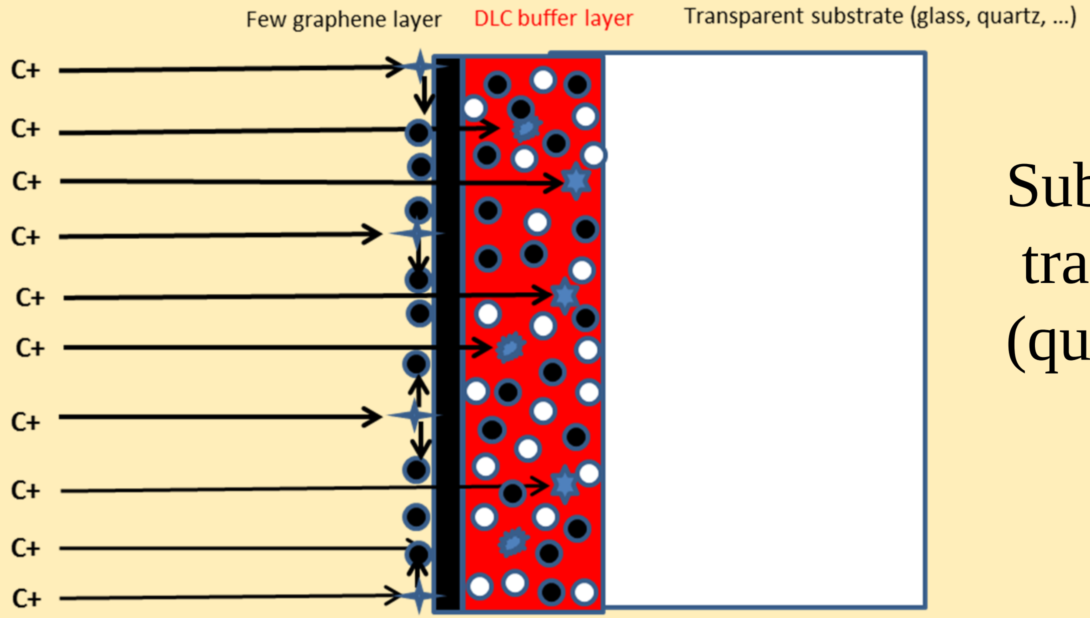
Croissance de DLC

~ 100 eV



Distribution d'énergie des ions

A scheme of continuous growth of few graphene layers
on top of DLC growing film by pulse laser ablation of carbon



✦ Surface impinging and diffusion at low C^+ energy with sp^2 carbon formation

✹ Subplantation with stress (without relaxation) at medium C^+ energy with sp^3 carbon formation

✡ Subplantation without stress (with relaxation) at high C^+ energy with sp^2 carbon formation

Substrat
transparent
(quartz, verre,)

D'après D.R. MacKenzie et al., Phys rev. Letters, 67 (1991) 773

Etude surface DLC

S. Rey et al, Applied Physics A, 71 (2000) 433-439.

C1s core level XPS on DLC films with variable fluences after a thermal annealing at 923K (left); angular resolved for a DLC film at 10 J/cm2 post-annealed at 923K (right)

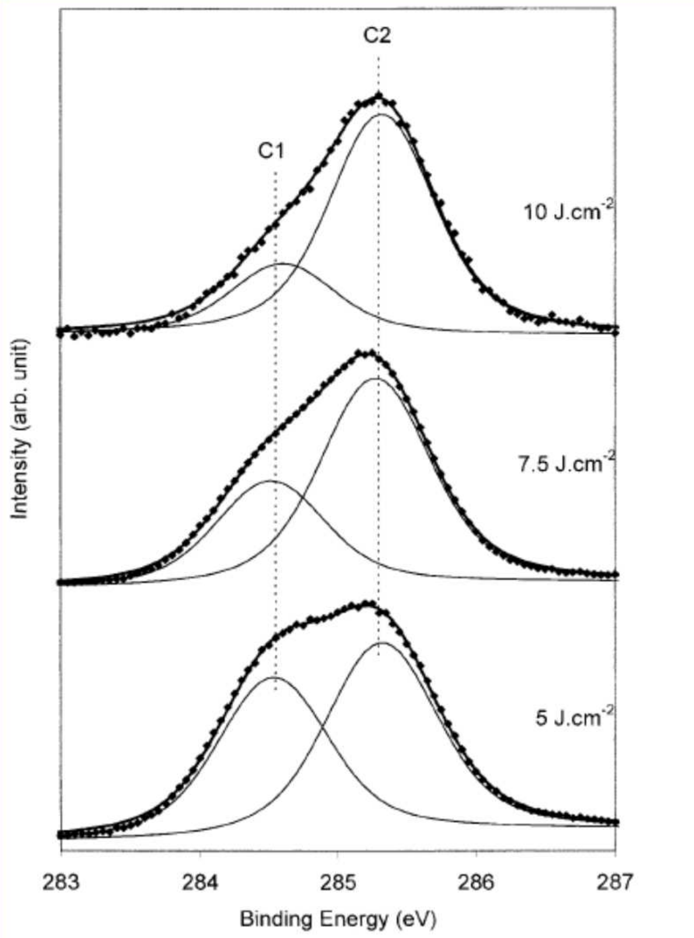


Fig. 1. XPS C 1*s* spectra obtained on ns($X-923$)-type samples as a function of the laser fluence X

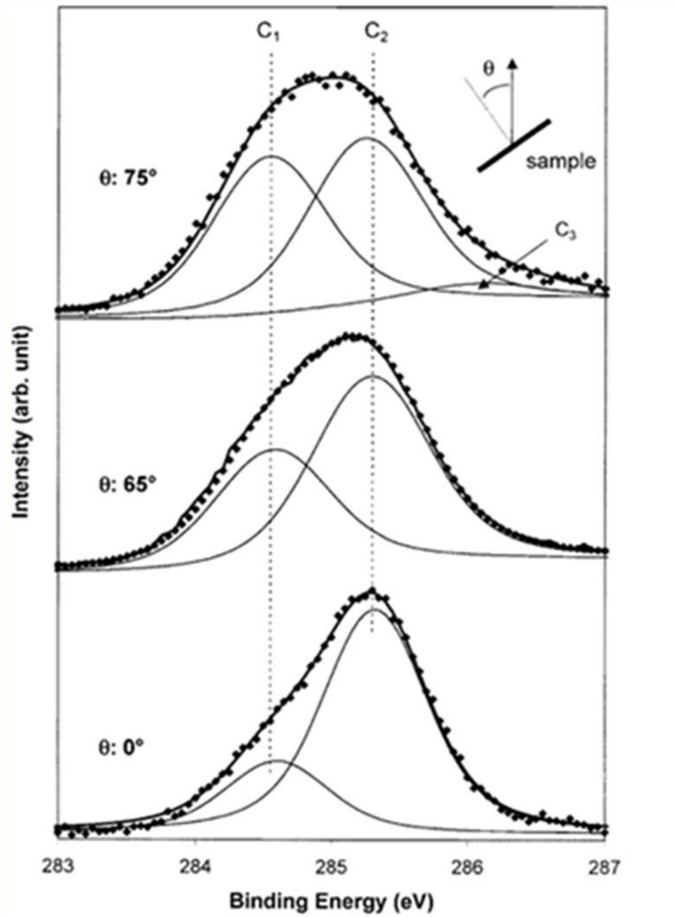
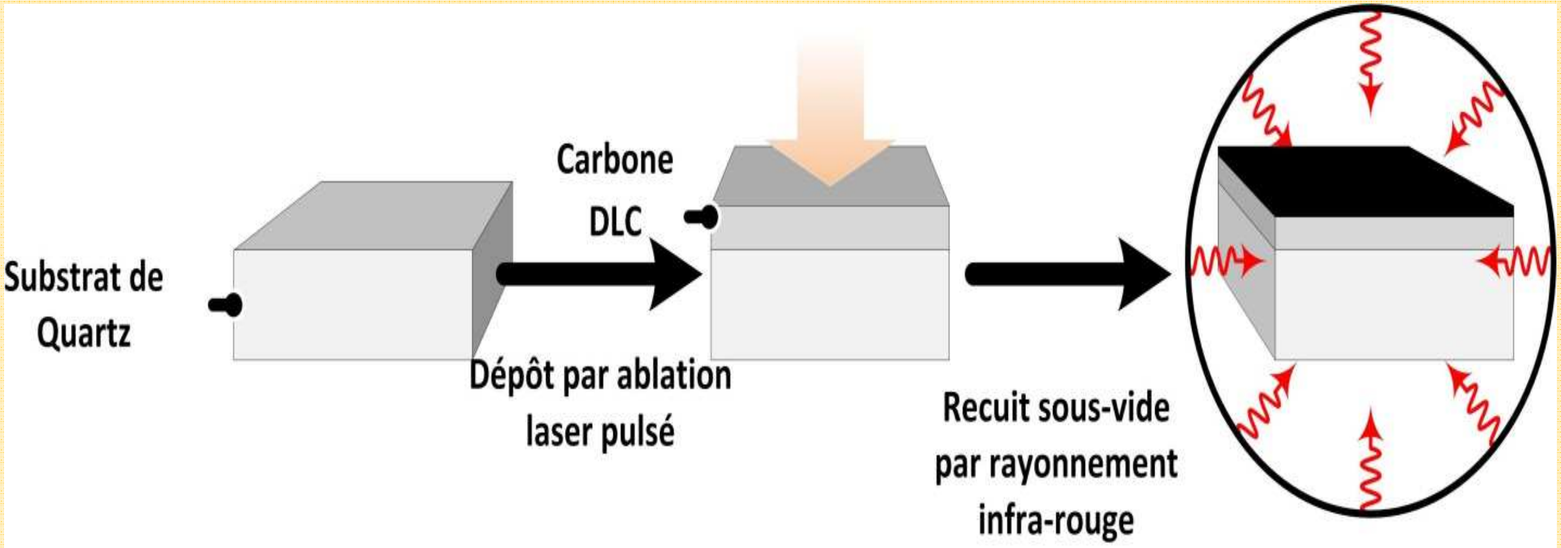
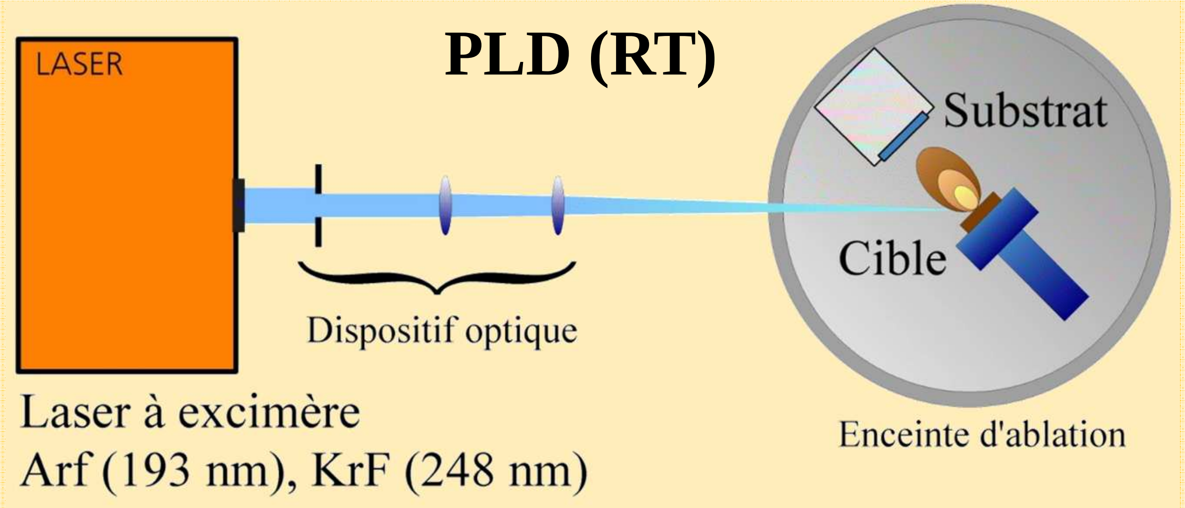


Fig. 2. Angular XPS analysis of the C 1*s* core level obtained on the ns($10.0-923$) sample. θ is the angle between the normal of the sample surface and the direction of the emitted electrons

Procédure d'élaboration de Graphene/DLC/Quartz)



ou traitement laser

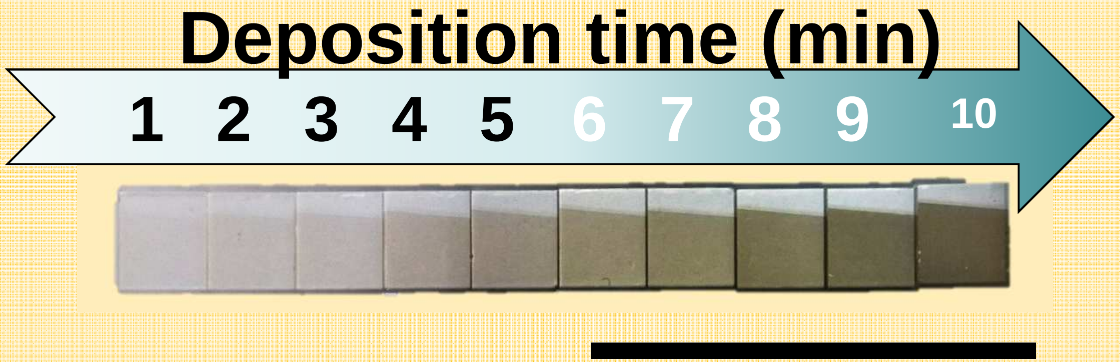


Conditions de Dépôts et traitements thermique

$1\ J/cm^2 < \text{Fluence} < 10\ J/cm^2$

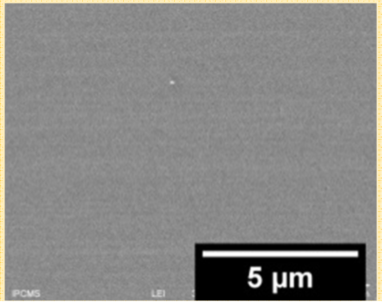
1 min < t < 10 min soit épaisseur DLC entre 3 et 30 nm

$600 < T_{recuit} < 1100°C$



5 cm

T = 800°C
F = 5,6 J/cm2



Très bonne uniformité
Rugosité < 1 nm

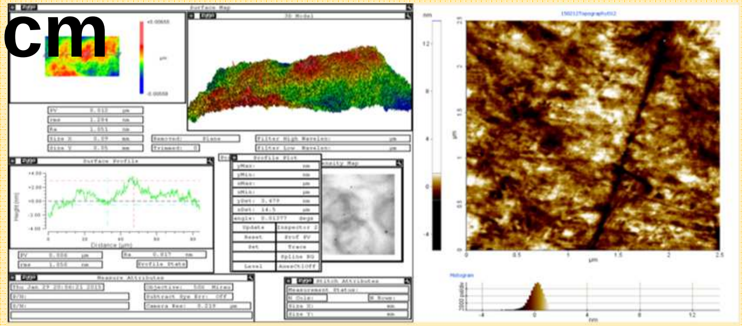
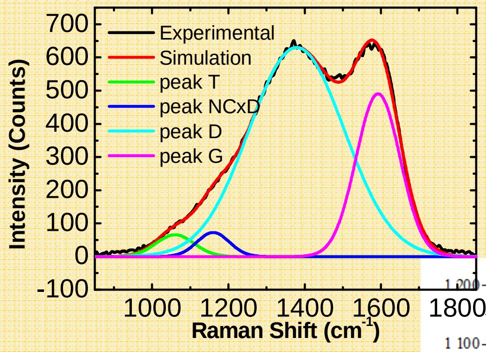


Figure Erreur ! Il n'y a pas de texte répondant à ce style dans ce document.**.1 On the left Interferometry measurements, on the right the AFM image in Non-contact mode of DLC_quartz_10**

Spectroscopie Raman : DLC sur Quartz

apres post-traitement thermique UHV



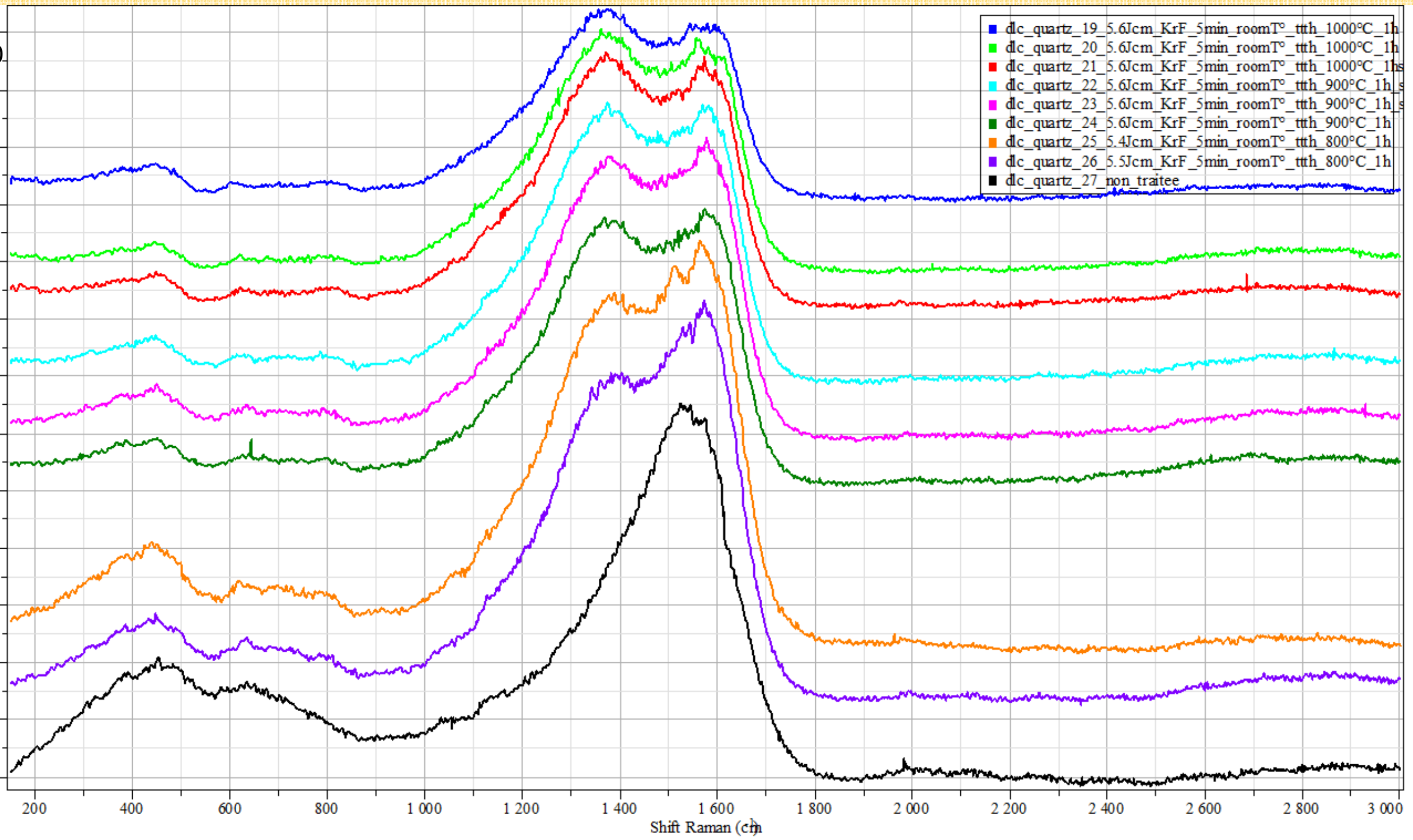
600°C < T < 1000°C

D G

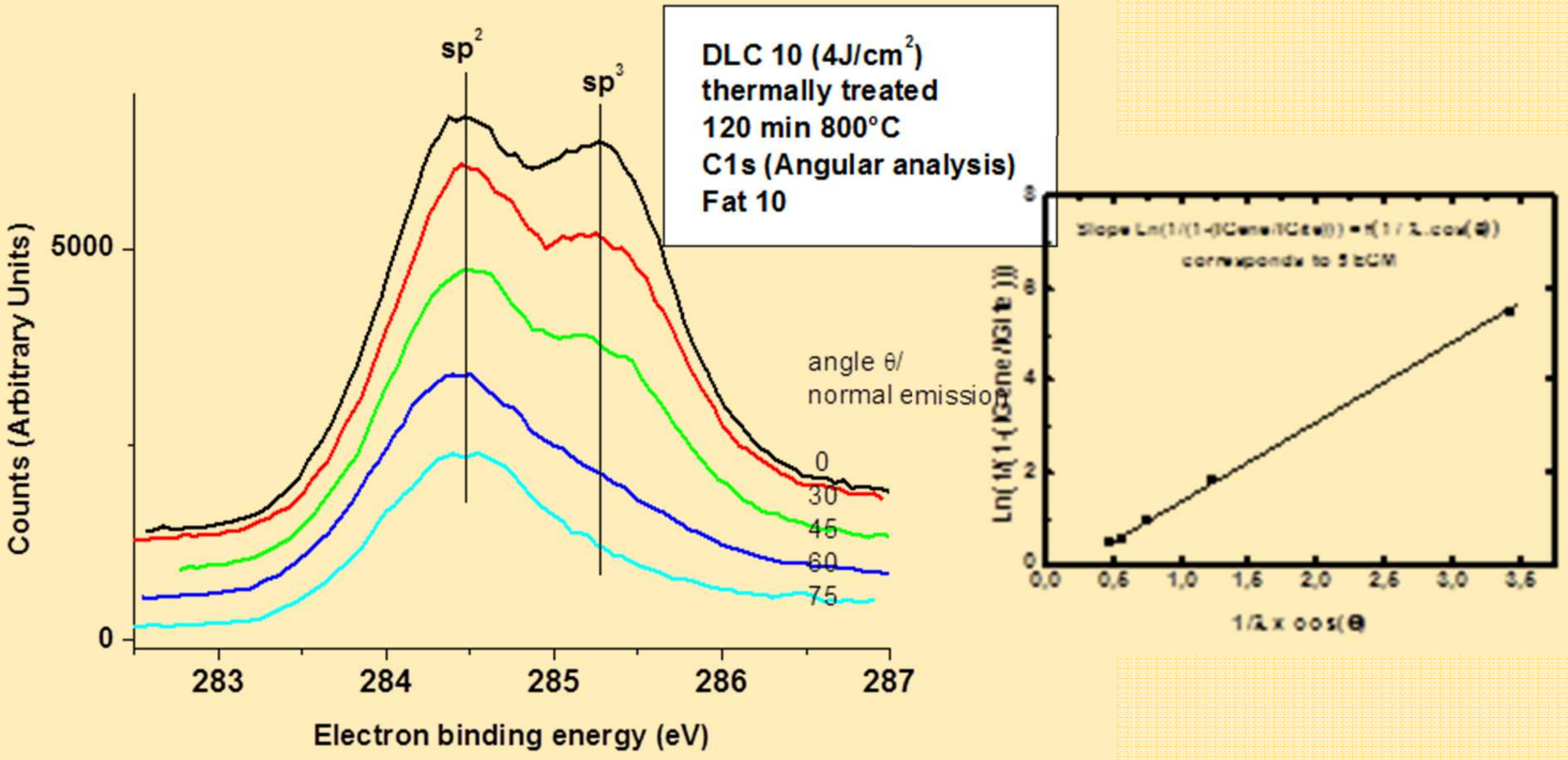
2D

Raman
non pertinent

,



XPS : a proof of the occurrence of a graphene layer on top of DLC

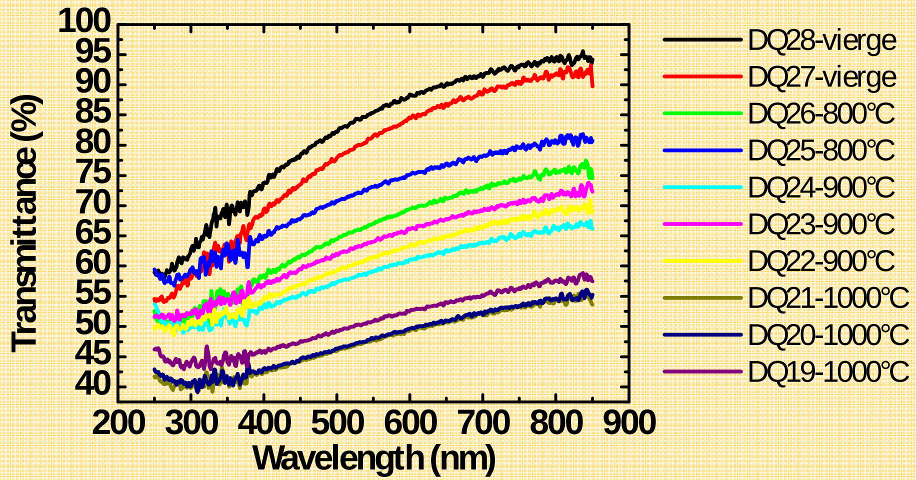


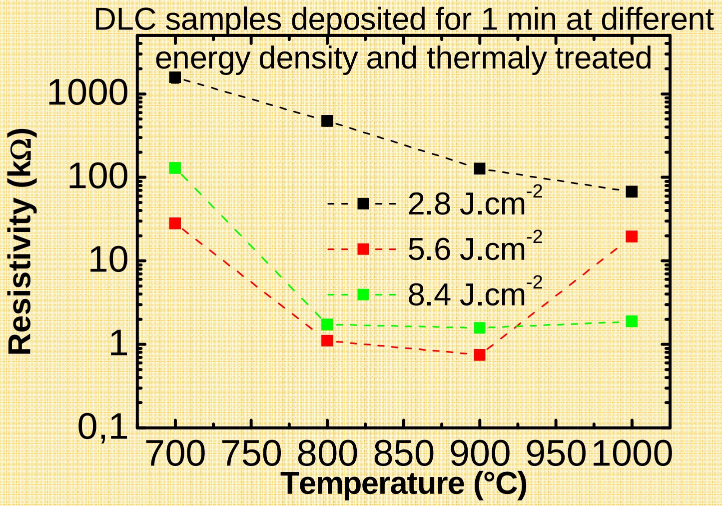
Mesure de l’épaisseur de la couche TLG

$e = \lambda_C * \cos\theta * \; Ln\{1 / [1- (I_{Gene}/ I_{Gite})]\}$

With λ_C = 2,1 nm e ~ 1,0 nm

Transmittance and sheet conductivity





Avec transmission environ 90% et
resistivités surfaciques ~ 1 kΩ/cm^2 la figure
de mérite des électrodes transparentes
« conductivity of transparency»
est du même ordre de grandeur que ITO

Diapositive 22

2ndF1 Fitsum AWEKE; 18/05/2015

Conclusions

- Le dépot de carbone par HF CVD conduit à des transformations de phase du carbone sur silicium et cuivre
- Le mécanisme de nucléation aussi bien que la nature des précurseurs varient suivant les conditions
- Les spectroscopies de surface apportent des informations importantes

- Production très simple de “thin layers graphenic layers” sur DLC par transformation de surface
- avec de bonnes performances pour des électrodes transparentes
- Quelle est la véritable nature de ces couches “graphéniques”?

Remerciements

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F. Antoni (ICube/MaCEPV, Strasbourg)

S. Zafeiratos (ICPEES, Strasbourg)

J. Faerber (IPCMS/GSI, Strasbourg)

J. Hommet (IPCMS/GSI, Strasbourg)