GRAPHENE AND 2DM VIRTUAL CONFERENCE & EXPO

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CHARACTERIZATION OF THE BARRIER AND ELECTROCHEMICAL PROPERTIES OF CVD GRAPHENE ON METALLIC SUBTRATES

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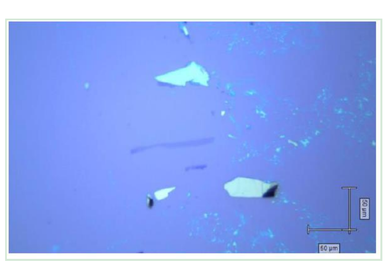
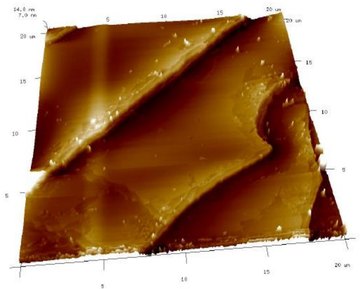
Introduction

Growth of graphene using the CVD method (so-called CVD graphene) on mono- and polycrystalline copper surfaces give the possibility to obtain large-area graphene coatings [1]. The CVD graphene can be also transferred onto other metallic or non-metallic substrates. The results of many investigations indicate that graphene can provide a barrier substantially reduce the corrosion rate (e.g.[2,3]), however, the tightness of real graphene coating is a fundamental feature of barrier protection [1-4]. The experimental investigations of barrier properties of graphene layers included the development of methodical bases for characterization of obtained layers (optical microscopy, μ-Raman Spectroscopy and AFM).

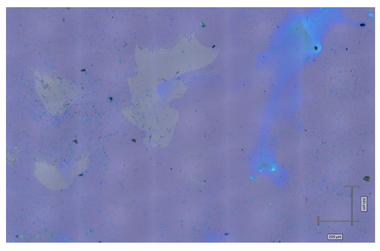
Different techniques to obtain graphene films (examples)



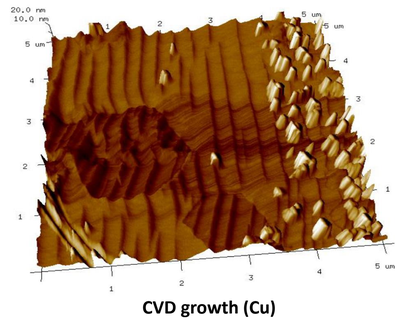
Mechanical exfoliation (Si/SiO_2)



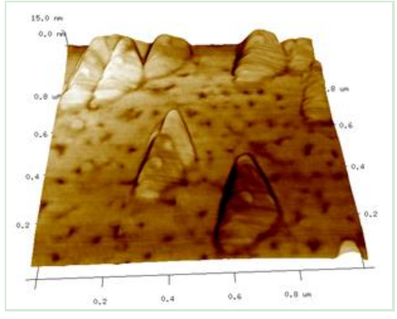
Epitaxial growth (SiC)



HSMG - (transferred on the Si/SiO2 (grown on liquid metal CuNi)



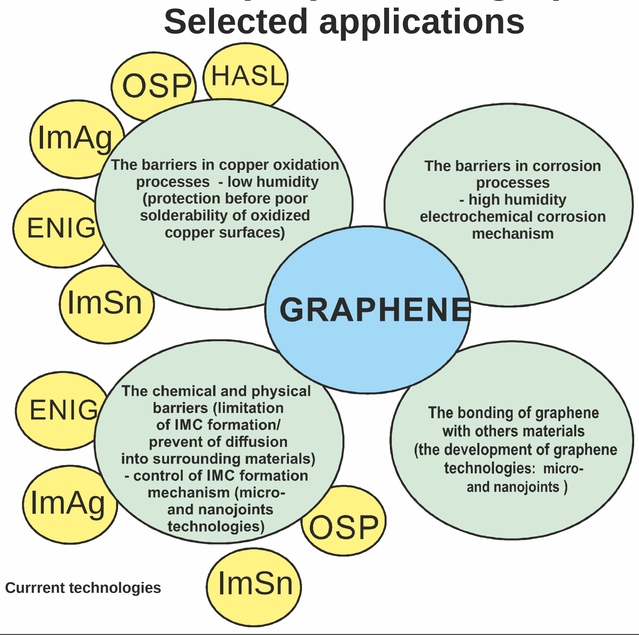
CVD growth (Cu)



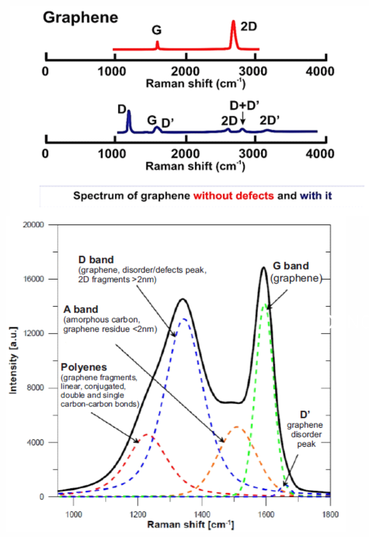
CVD growth (Cu)

The barier properties of CVD graphene

The barrier propeties of graphene
Selected applications



The characterization of barrier properties of graphene
Raman Spectroscopy



D/G band region of spectrum

2D band FWHM
LAYER NUMBER
·24-32 cm-1 – single-layer graphene
·50-54 cm-1 – bi-layer graphene
·55-58 cm-1 – three-layer graphene
·62-65 cm-1 – four-layer graphene
·65-68 cm-1 – five-layer graphene
·70-80 cm-1 – multi-layer graphene

Intensity ratio of 2D to G band – I(2D)/I(G)
LAYER NUMBER
·3-4 – single-layer graphene
·0.5-3 – multi-layer graphene

2D band position
LAYER NUMBER
·2640 cm-1 – single-layer graphene
·2650 cm-1 – bi-layer graphene
·2680 cm-1 – five-layer graphene (multilayered)
·2690 cm-1 – ten-layer graphene (graphite)

FWHM of G band
Charge doping
- 5-9 cm-1 – high level of charge doping of graphene
- 12-18 cm-1 – low level of charge doping of

FWHM of G band
Determination of La value of graphene/graphite
>32 cm-1 – the fragmentation for La less than 10 nm
16-32 cm-1 – the fragmentation for La more than 10 nm

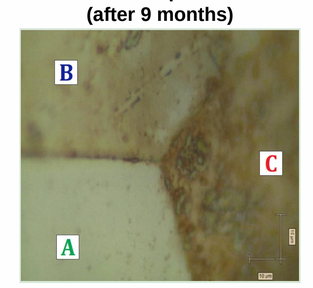
Intensity ratio of D to G band – I(D)/I(G) – (the ranges of ratio depend on wavelength of excitation laser)
DEFECTS
for graphene – 2D structure (one to only several layers) – characterized by Ld – mean distance between two defects (nm) :
o I(D)/I(G) < 1 and FWHM of G band < 32 cm-1 – large distance between defects (slightly defected structure, Ld ≥ 12nm);
o I(D)/I(G) ≥ 1 : small distance between defects (defected structure, 1.5nm <Ld <12nm);
o I(D)/I(G) <1 and FWHM of G band > 32 cm-1): very small distance between defects (strongly defected structure, Ld ≤ 1.5 nm).

G band position
DEFORMATION/STRESSES
·shifts towards higher frequencies – compression of graphene layer (tensile stresses in the layer of graphene)
·shifts towards lower frequencies – stretching the graphene layer (compressive stresses in the layer of graphene)

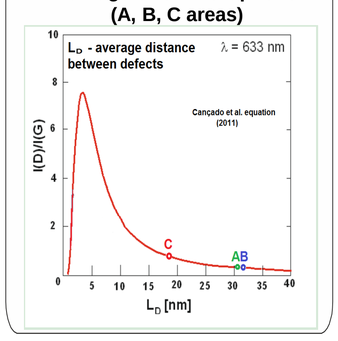
Intensity ratio of D to D' band – I(D)/I(D')
TYPE OF DEFECTS
· 3.5 – grain boundaries
· 7 – vacancies
· 13 – sp3

2D band position
DEFORMATION/STRESSES
·shifts to higher frequencies – compression of graphene layer (tensile stresses in the layer of graphene)
·shifts to lower frequencies – tensile of graphene layer (compressive stresses in the layer of graphene)

Oxidation of copper under CVD Graphene (after 9 months)

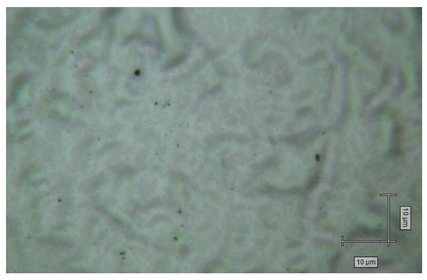


Damage of CVD Graphene (A, B, C areas)

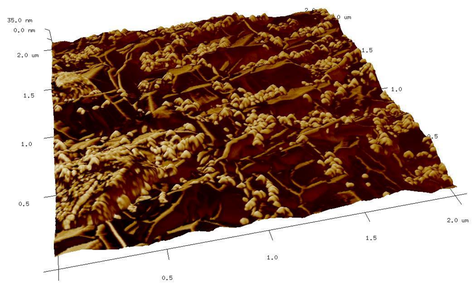


The electrochemical properties of CVD graphene

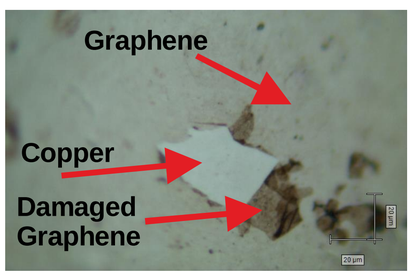
CVD Graphene on the copper substrate (optical microscopy)

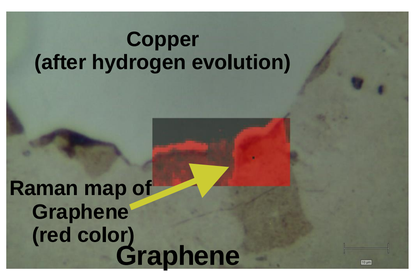


CVD Graphene on the copper substrate (AFM)



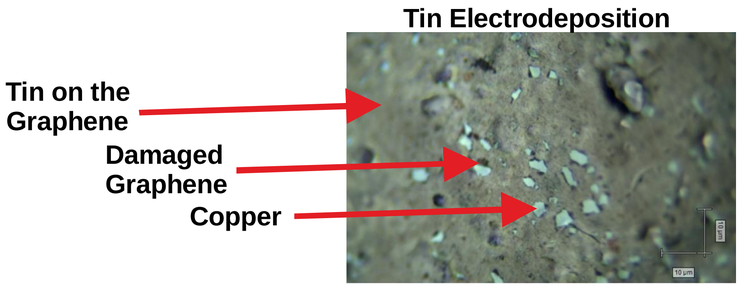
Hydrogen evolution on the CVD Graphene (damaged of Graphene film)

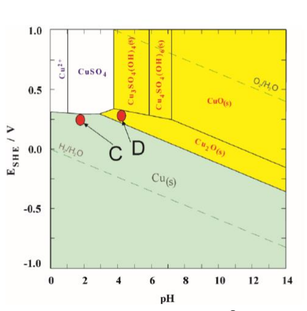




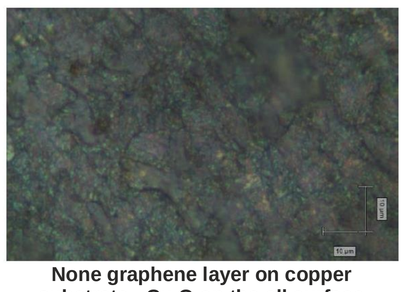
Selective electrodeposition of metals on CVD Graphene/Cu after hydrogen evolution

Tin Electrodeposition

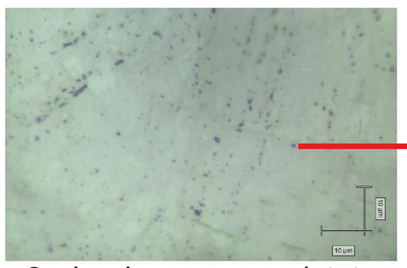




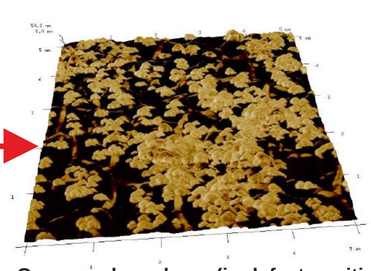
E-pH, Cu-SO_4^{2-}-H_2O



None graphene layer on copper substrate - Cu_2O on the all surface
pH=4.1, E=+300 mV/SHE, (D)

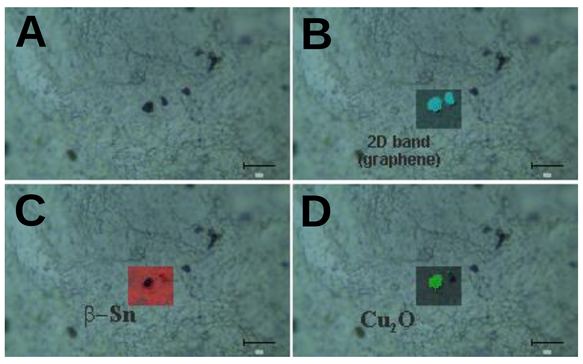


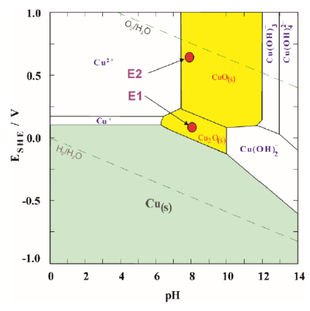
Graphene layer on copper substrate
Cu_2O - only in dark positions
pH=4.1, E=+300 mV, (D)



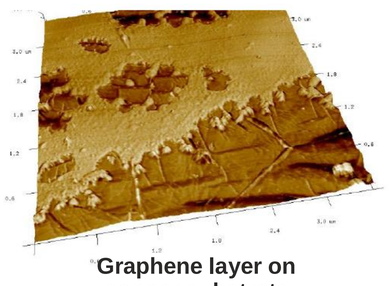
Cu_2O on graphene layer (in defect positions)
AFM image (tapping mode, phase contrast)
(place in dark position)

Electrodeposited tin layer (substrate: CVD graphene on the copper) :
A) Optical image - black places in tin layer;
B) Raman map of 2D band of Graphene (2840 cm^{-1}) - blue;
C) Raman map of beta-Sn band (127 cm^{-1}) - red;
D) Raman map of Cu_2O band (450-680 cm^{-1}) - green.
(black places: defective Cu_2O-graphene places on the copper/graphene substrate)





E-pH, Cu-H_2O



Graphene layer on copper substrate
(borate buffer, passive layer Cu_2O/B_2O_3)
(pH=8, E=150 mV/SHE, E1)

Conclusions :

- The obtained results indicate a strong influence of defects in CVD graphene materials (types, density), an important role of substrate preparation (topography, roughness, oxidation) and corrosion products as well as an influence of electrodeposition conditions on the barrier properties of graphene layers.
- The damages of graphene coatings by copper substrate and improper electrodeposition conditions can be analysed by μ-Raman Spectroscopy (μ-RS), Atomic Force Microscopy (AFM) and Optical Microscopy (OM).

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