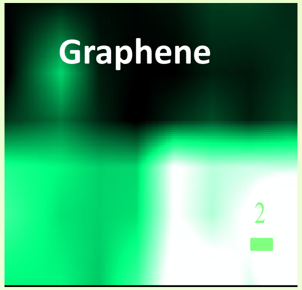
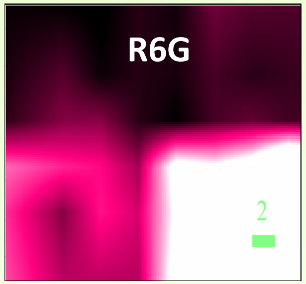
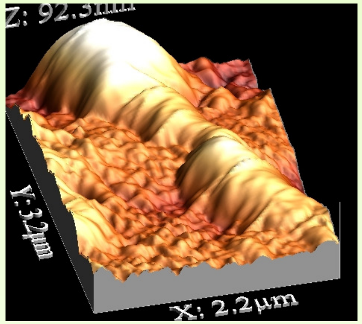
Efficient Combination of Interference and Plasmon Resonance Raman Amplifications by Optimized Heterostructures for Optical microscopy and Molecule Detection





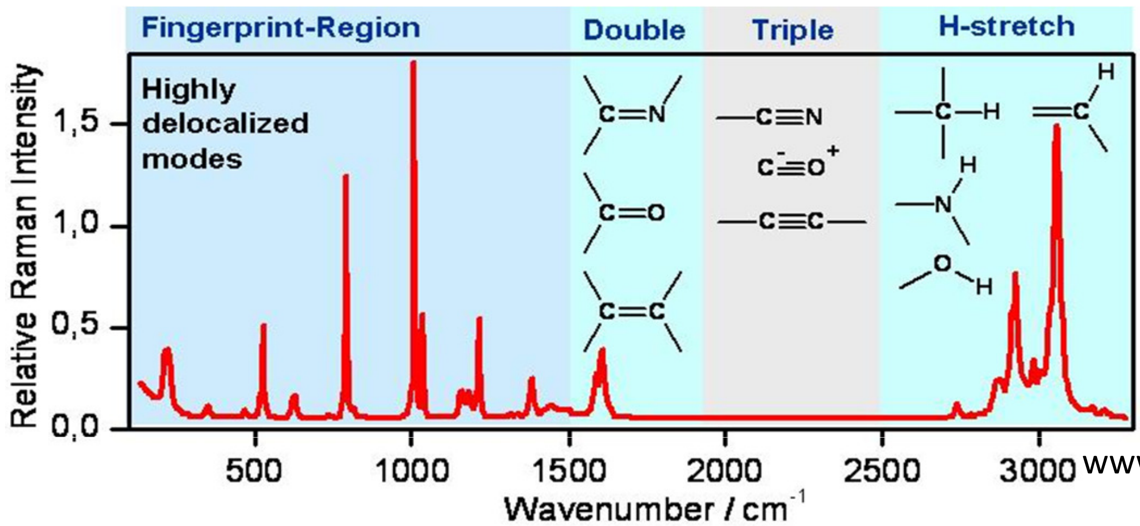
Montse Aguilar-Pujol
Leo Álvarez-Fraga
Esteban Climent-Pascual
Félix Jiménez-Villacorta
Carlos Prieto
Rafael Ramírez-Jiménez UC3

Alicia de Andrés
Instituto de Ciencia de Materiales de Madrid
CSIC



Why Raman spectroscopy?

* It is specific – the vibration spectrum is a finger print of each molecule



www.fisi.polimi.it/en/research

* Non destructive
* Sub-micron resolution, down to 10 nm for special configuration (TERS)
* Quite high penetration depth
* Label-free imaging method

BUT Very low cross section. About 10^{10} to 10^{12} lower than IR absorption cross section

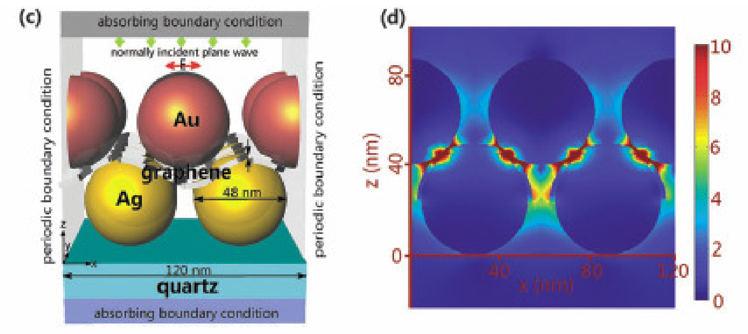
How can Raman signal be increased ?

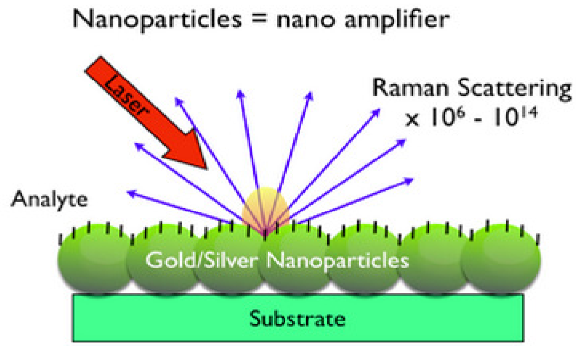
Resonant Raman scattering

Choose the adequate excitation wavelength (at absorption wavelengths of the analyte). When the energy of the incident laser light coincides with an electronic transition the Raman intensity increases orders of magnitude.

Surface Enhanced Raman Spectroscopy - SERS

Enhancement related to localized **surface plasmon resonance** from metal NPs and to "**hot spots**"





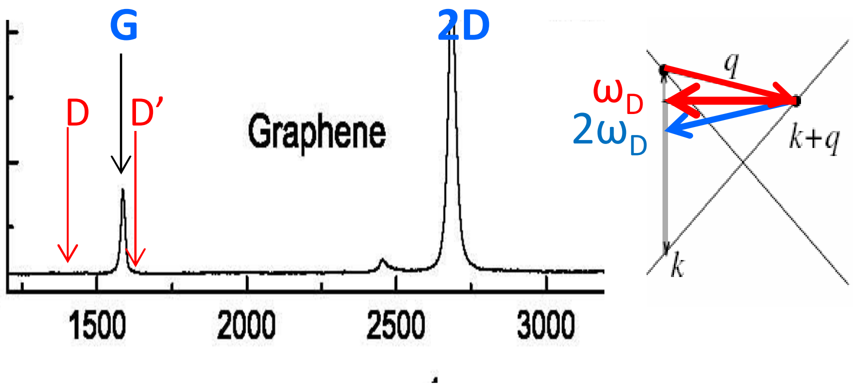
http://research.chem.psu.edu/lxjgroup

Interference Enhanced Raman Spectroscopy - IERS

See later….

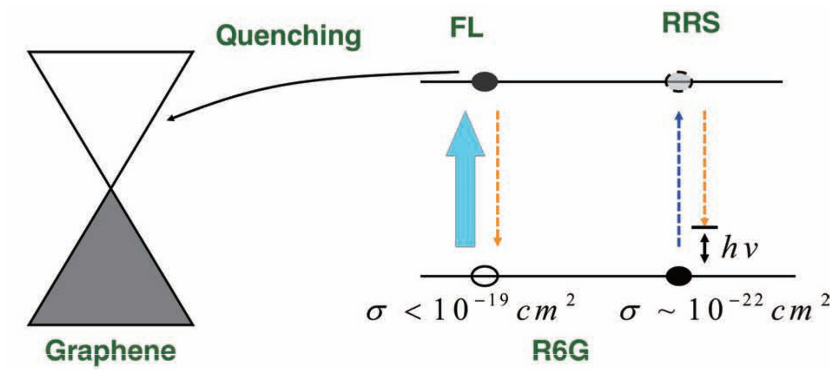
The role of Graphene in SERS

Raman of graphene is **resonant** and very sensitive to changes in electronic structure, presence of defects, strain,…useful **to probe its environment**



GERS: Chemical enhancement related to **graphene**.

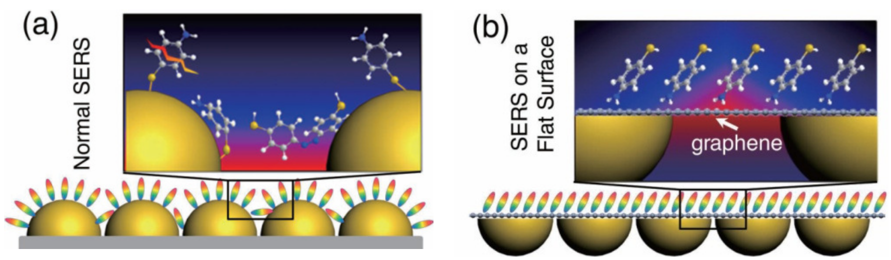
Graphene as a substrate: **fluorescence quenching** for molecules, especially limiting in resonant conditions



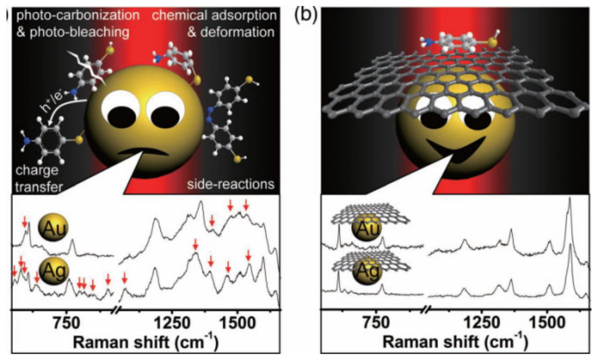
Xie et al. *J. Am. Chem. Soc.* 2009 , *131*

Good **compatibility** of graphene with biological material.
Graphene creates uniform electrical field distribution

Provides a flat bio-compatible surface



Protects and stabilizes the NPs

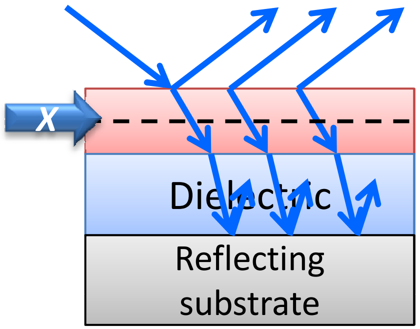


Xu J. Kong , et al . PNAS ***2012***

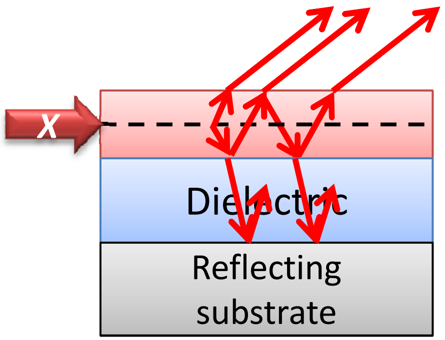
Interference Enhanced Raman Spectroscopy - IERS

Multiple reflections at the interfaces induce interference effect for:

Absorbed incident light



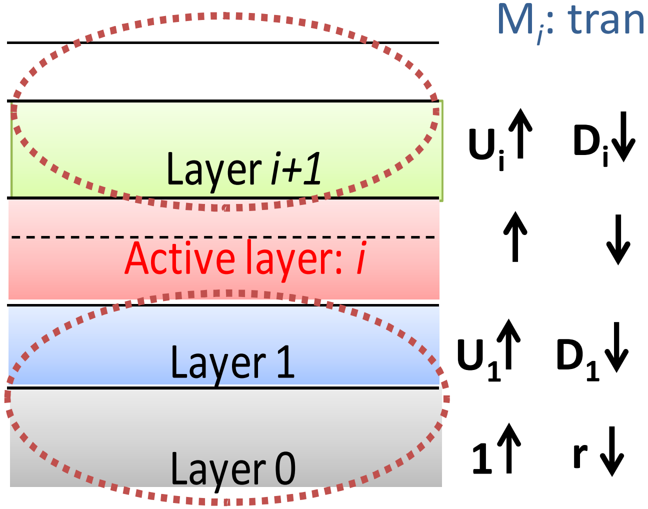
Raman scattered light



Multiple layers: Transfer matrix method

U_1: Amplitud of Upwards travelling wave

D_1: Amplitud of Downwards travelling wave



M_i: transforms amplitudes $i+1 \rightarrow i$

$$\begin{pmatrix} U_i \\ D_i \end{pmatrix} = M_i \begin{pmatrix} U_{i+1} \\ D_{i+1} \end{pmatrix}$$

$$M^U = M_i M_{i+1} \ldots M_{n-1}$$

$$M^L = M_0 M_1 \ldots M_{i-1}$$

$$M = \begin{pmatrix} M_{00} & M_{01} \\ M_{10} & M_{11} \end{pmatrix}$$

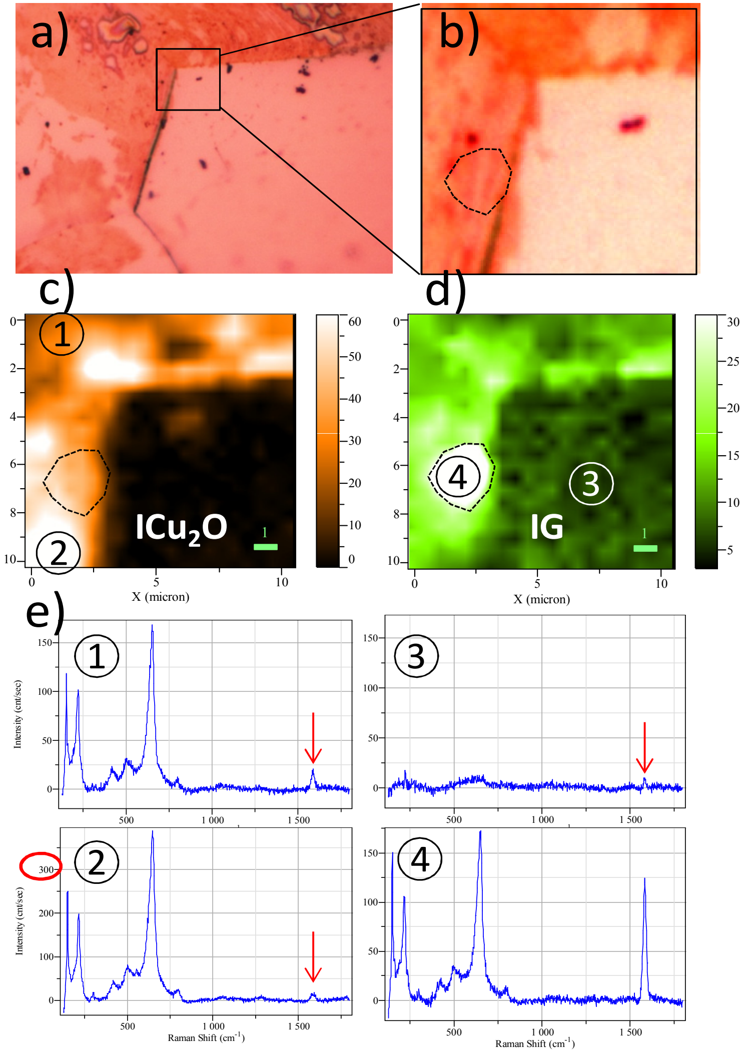
$$\boxed{F_{sc} = F_{ab}(M^L_{00}M^L_{11} - M^L_{10}M^L_{01})}$$

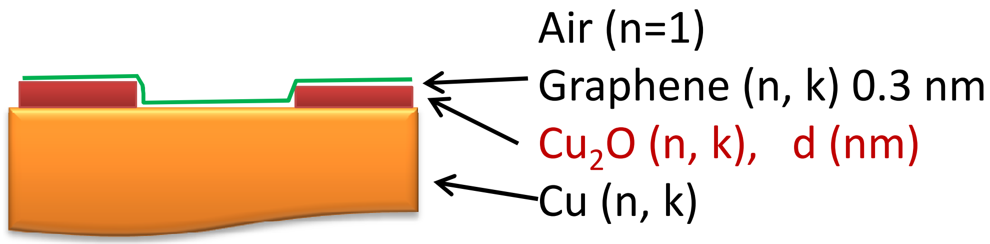
$$\boxed{F_{ab} = \frac{e^{-i\delta x}M^U_{00} + e^{i\delta x}M^U_{10}}{e^{-i\delta}M^U_{00}M^L_{00} + e^{i\delta}M^U_{10}M^L_{01}}}$$

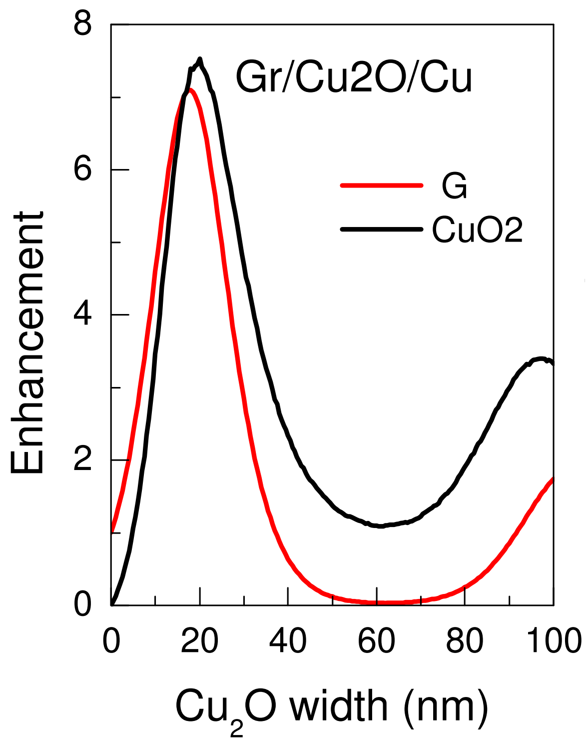
R. Ramírez-Jiménez et al. **Carbon** 105, 556 (2016)

1- Raman Enhancement by Interference in graphene

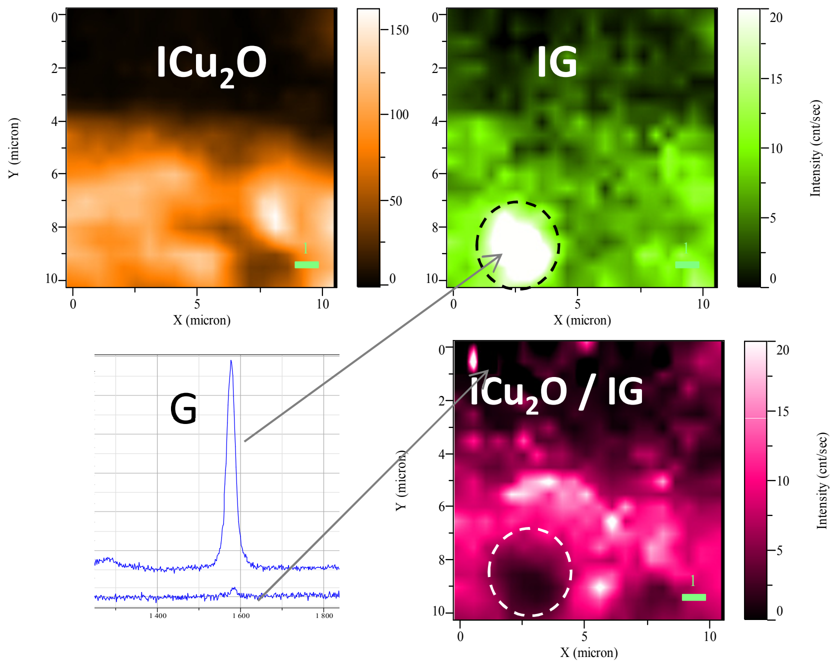
Graphene on Cu foil after several months

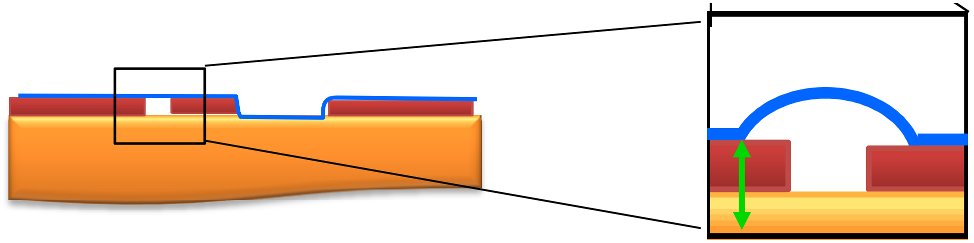






Interference in graphene bubbles

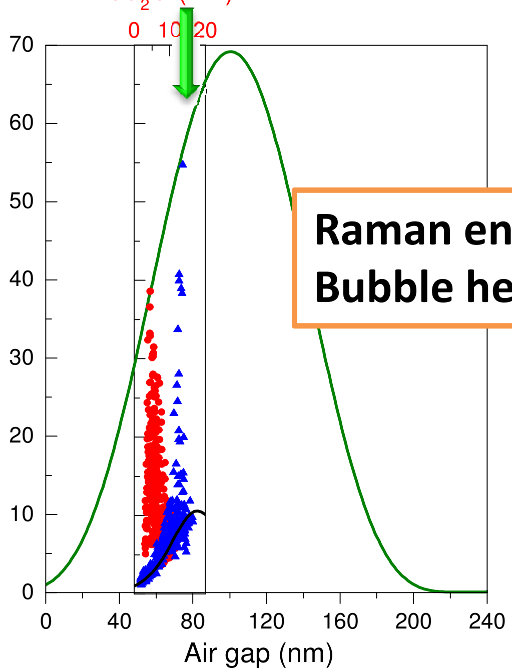




Graphene bubbles:

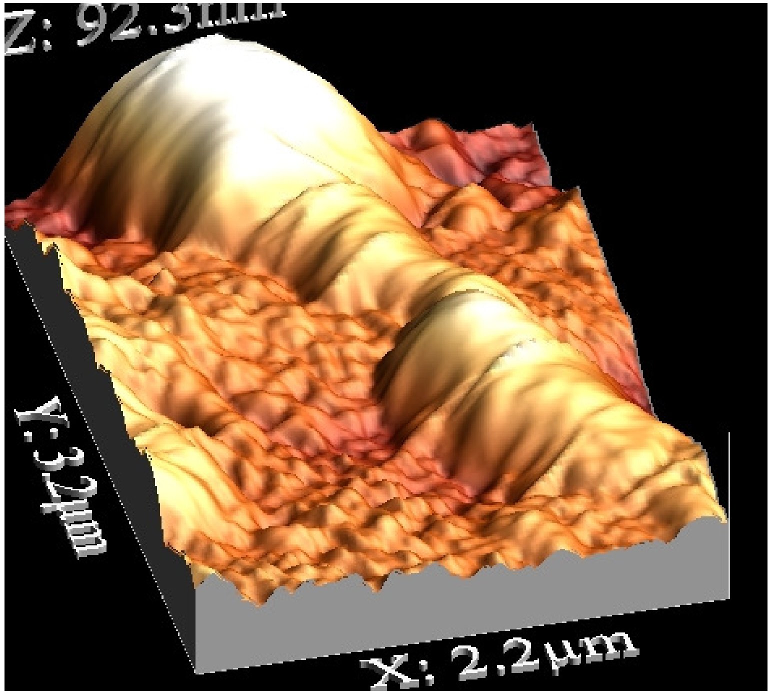
Raman characteristics of

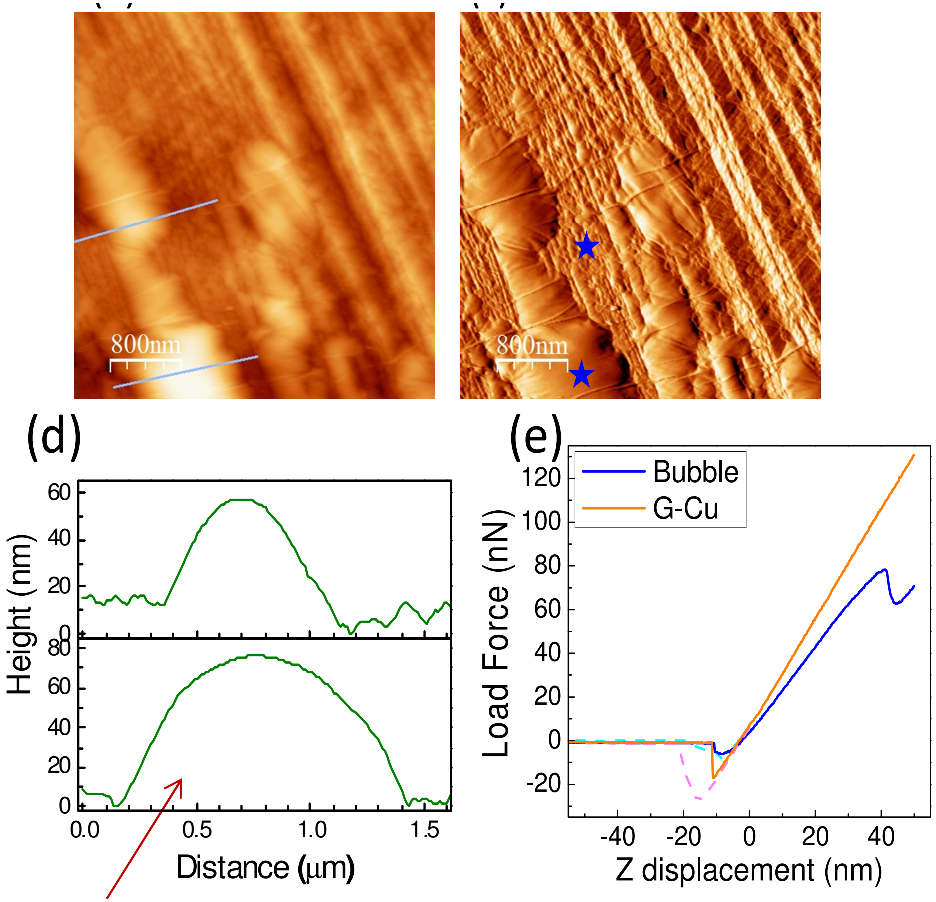
free-standing graphene



Raman enhancement: 60
Bubble height70 nm

Interference enhancement by graphene bubbles

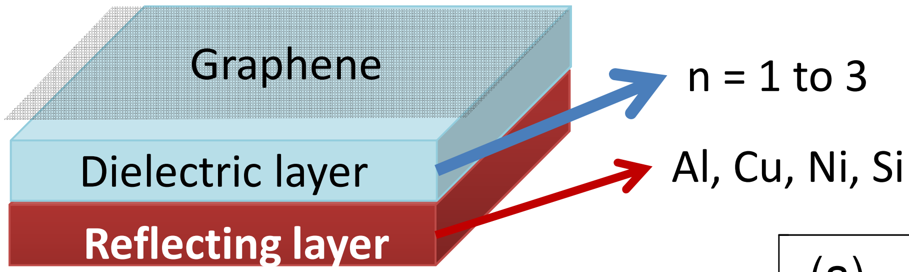


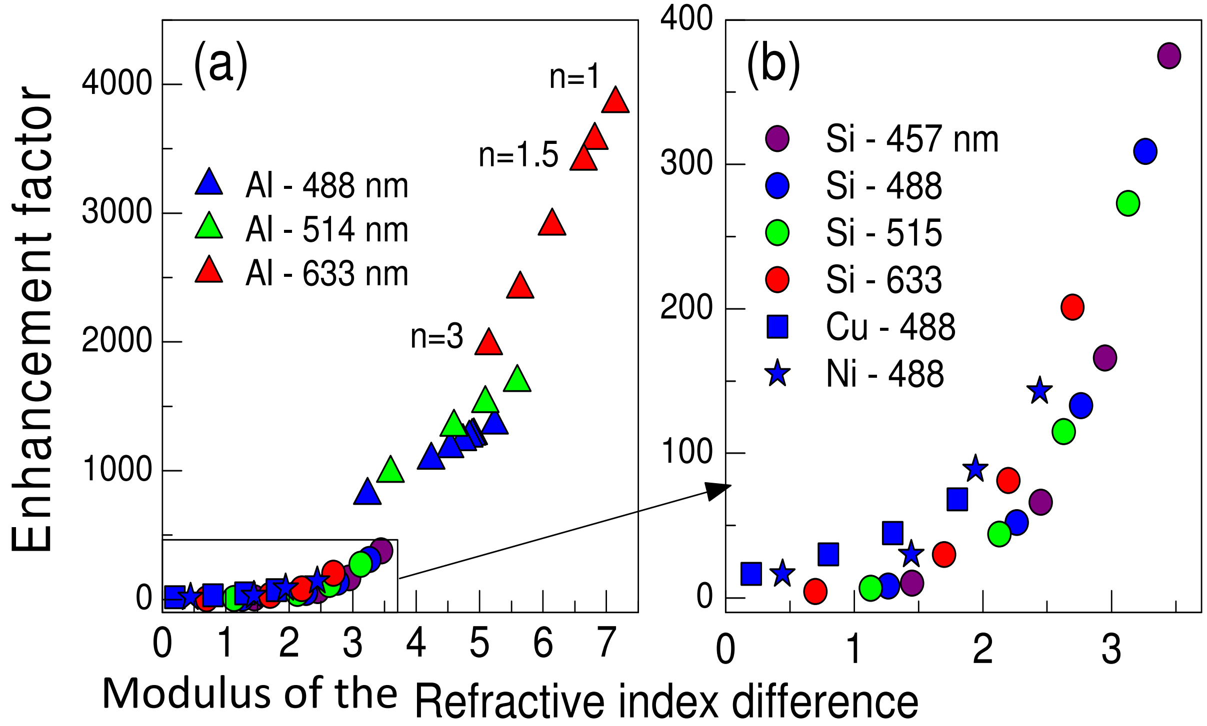


Bubbles: lateral size around few microns
height -70 nm

R. Ramírez-Jiménez et al. **Carbon 105,** 556 (2016)

General behavior of IERS

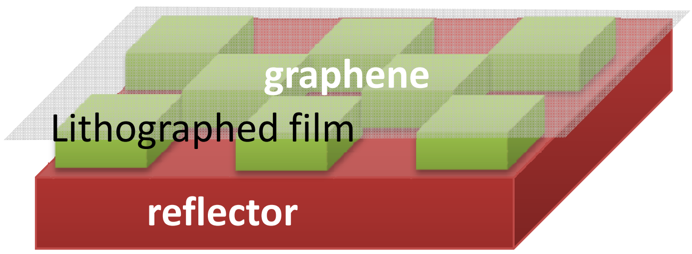




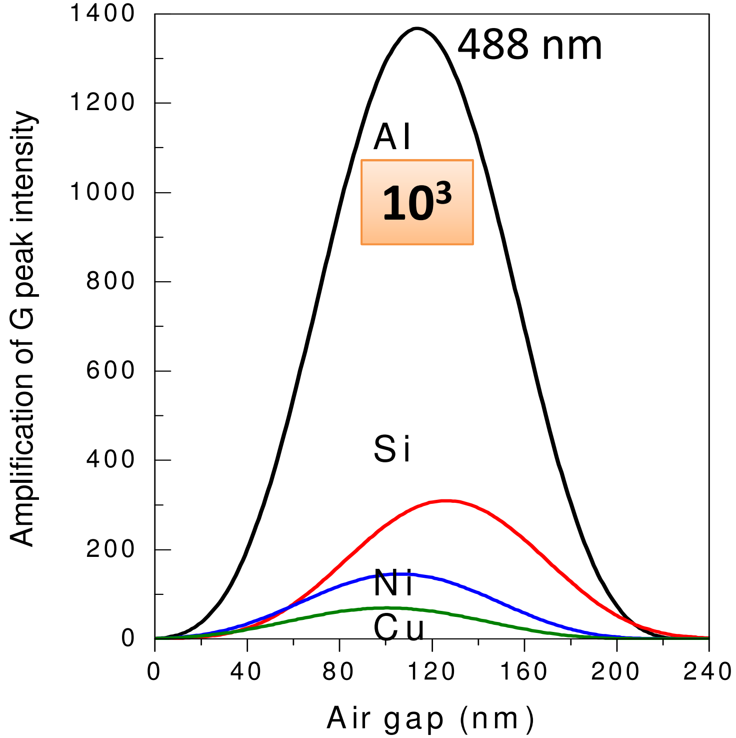
Low refractive index of the dielectric layer

High refractive index of the reflecting layer

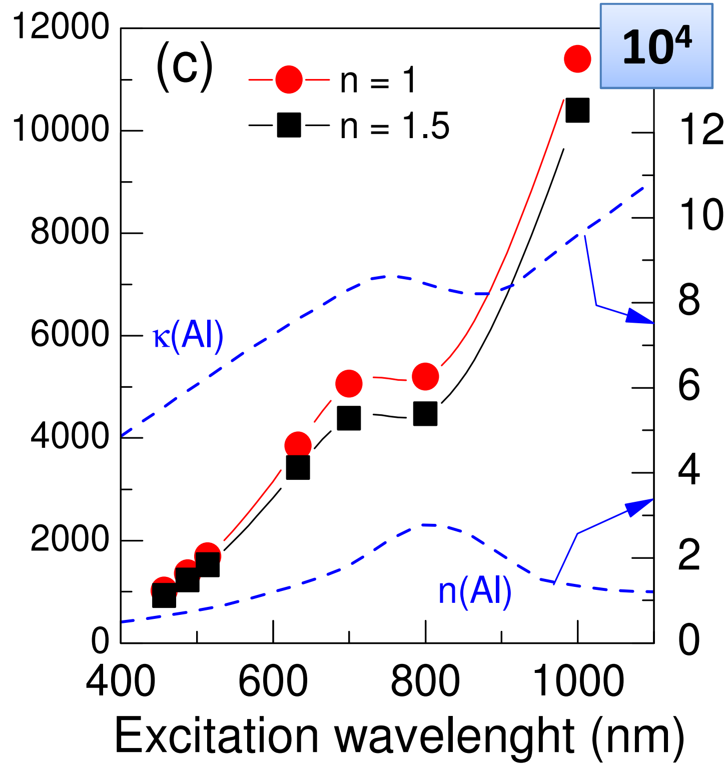
Interference in Graphene/dielectric/Aluminium



Graphene/air/Substrate



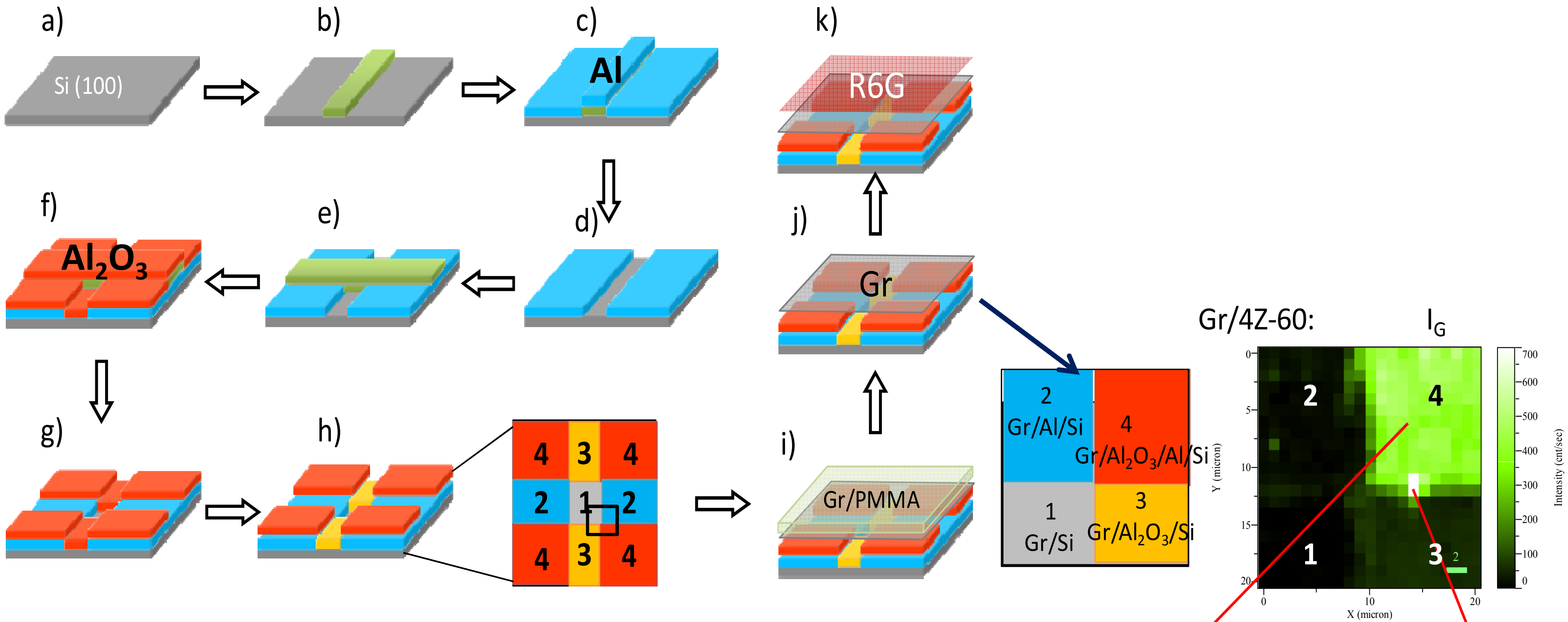
Graphene/dielectric/Al

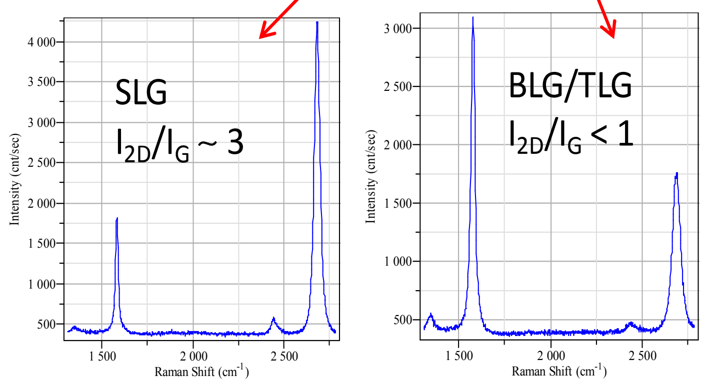


Raman enhancement up to **1400** is predicted for the system Al/air/graphene at 488 nm laser excitation

and up to **12000** for 1000 nm

2- Heterostructures for interference : Si/Al/Al_2O_3





1: Si

2: Si/Al (Al: 90 nm)

3: Si/Al_2O_3 (Al_2O_3: 50, 60, 70 nm)

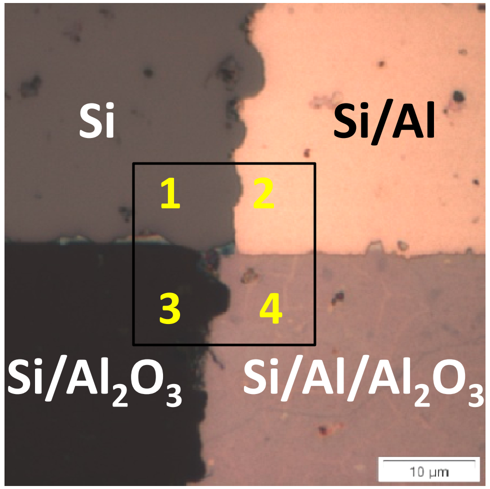
4: Si/Al/Al_2O_3

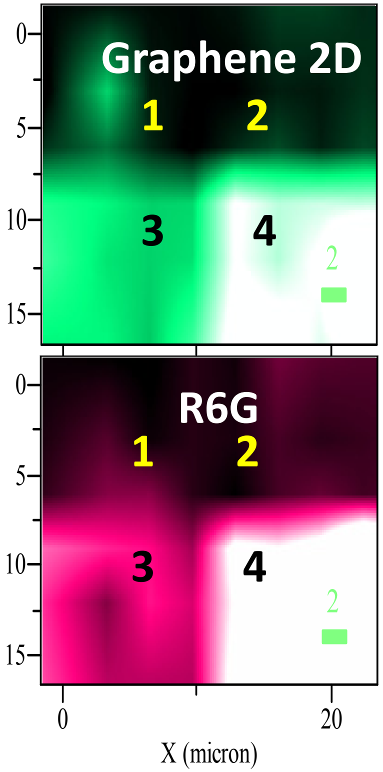
+ Graphene + Rhodamine 6G

L. Alvarez-Fraga, et al. " **ACS Appl. Mat. & Interfaces 9**, 4119 (2017)

Si/Al/Al_2O_3 / Graphene / R6G

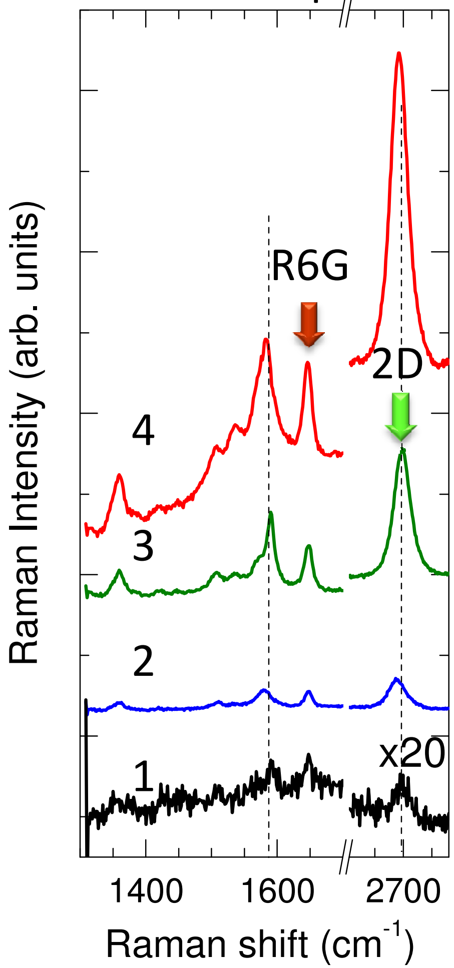
70 nm Al_2O_3



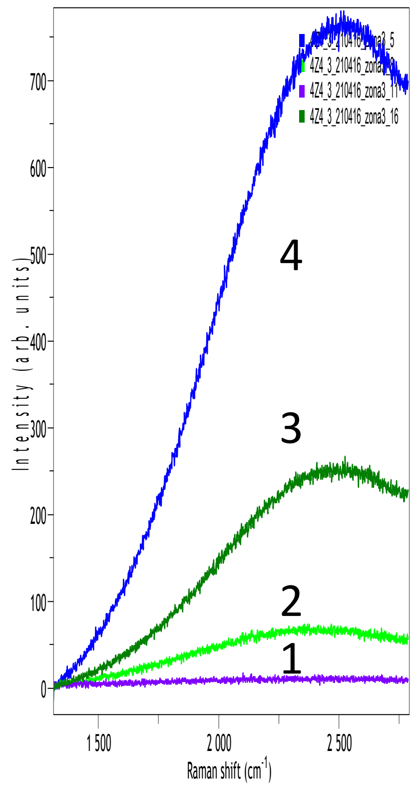


Al_2O_3 (nm)	IERS 2D Calc	IERS 2D	IERS R6G
50	950	550	
60	1140	670	
70	820	350	150

R6G on Graphene



R6G without graphene



R6G surface density = $2x10^{13}$ molecules/cm^2 = 1ML

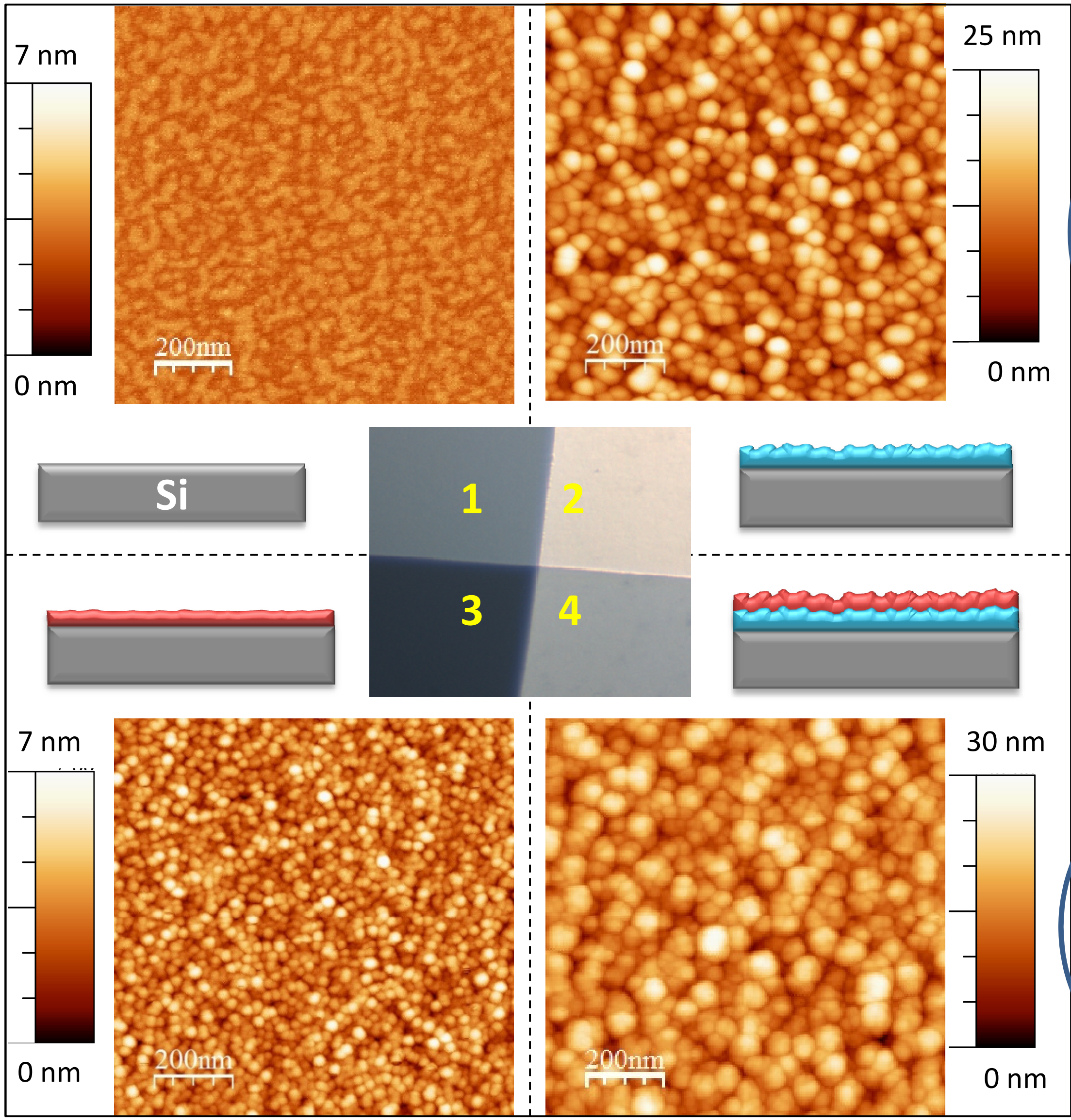
Factors limiting amplification

1: Si

0.43 nm RMS
FWHM=1.0 nm

2: Si/Al (90 nm)

3.9 nm RMS
FWHM= 9.1 nm



3: Si/Al_2O_3 (60 nm)

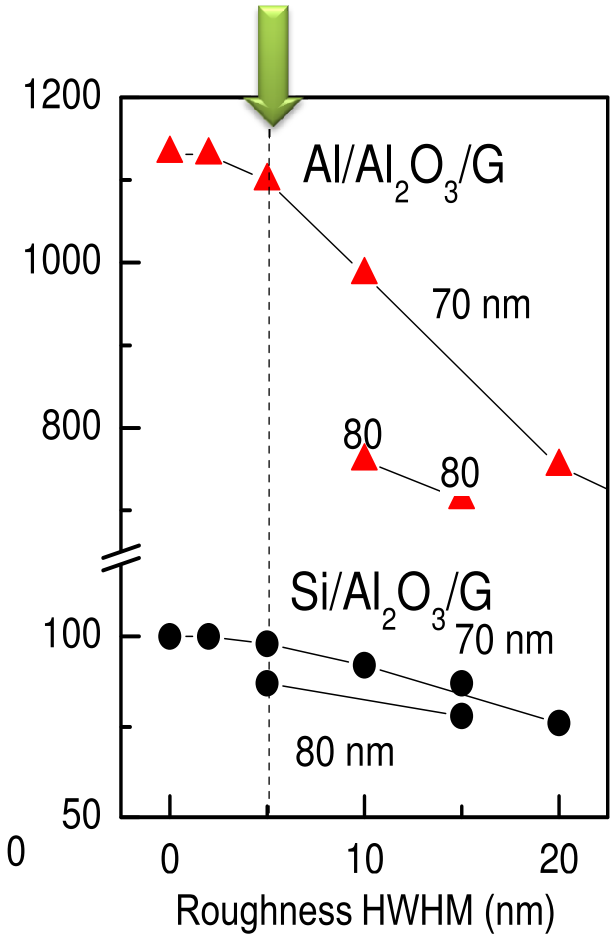
1.1 nm RMS
FWHM= 2.4 nm

4: $Si/Al/Al_2O_3$

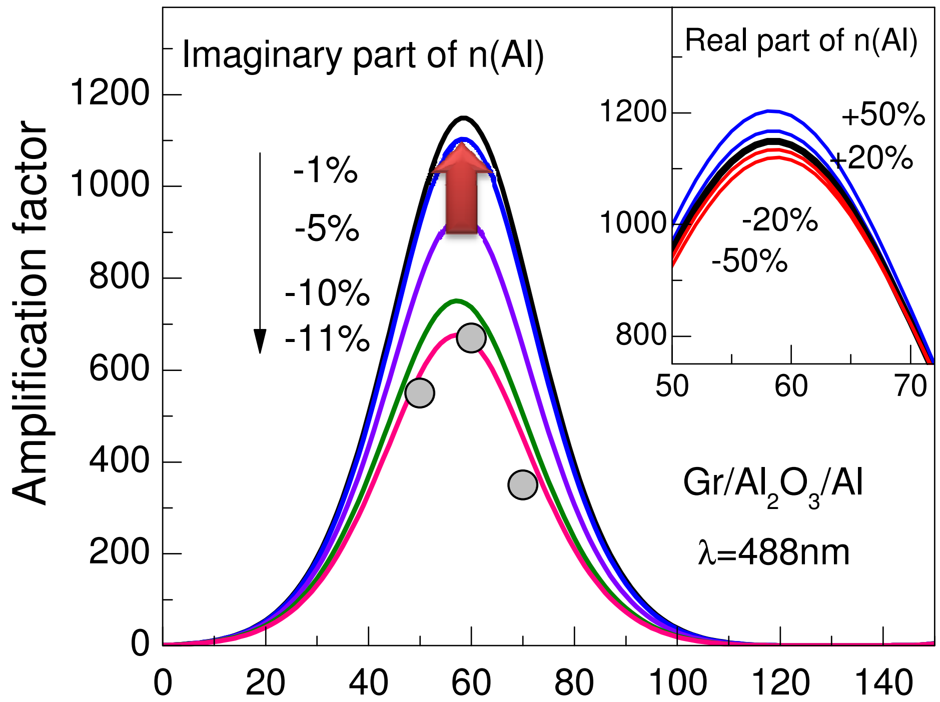
4.4 nm RMS
FWHM= 10.4 nm

Factors limiting amplification

Roughness of the heterostructure

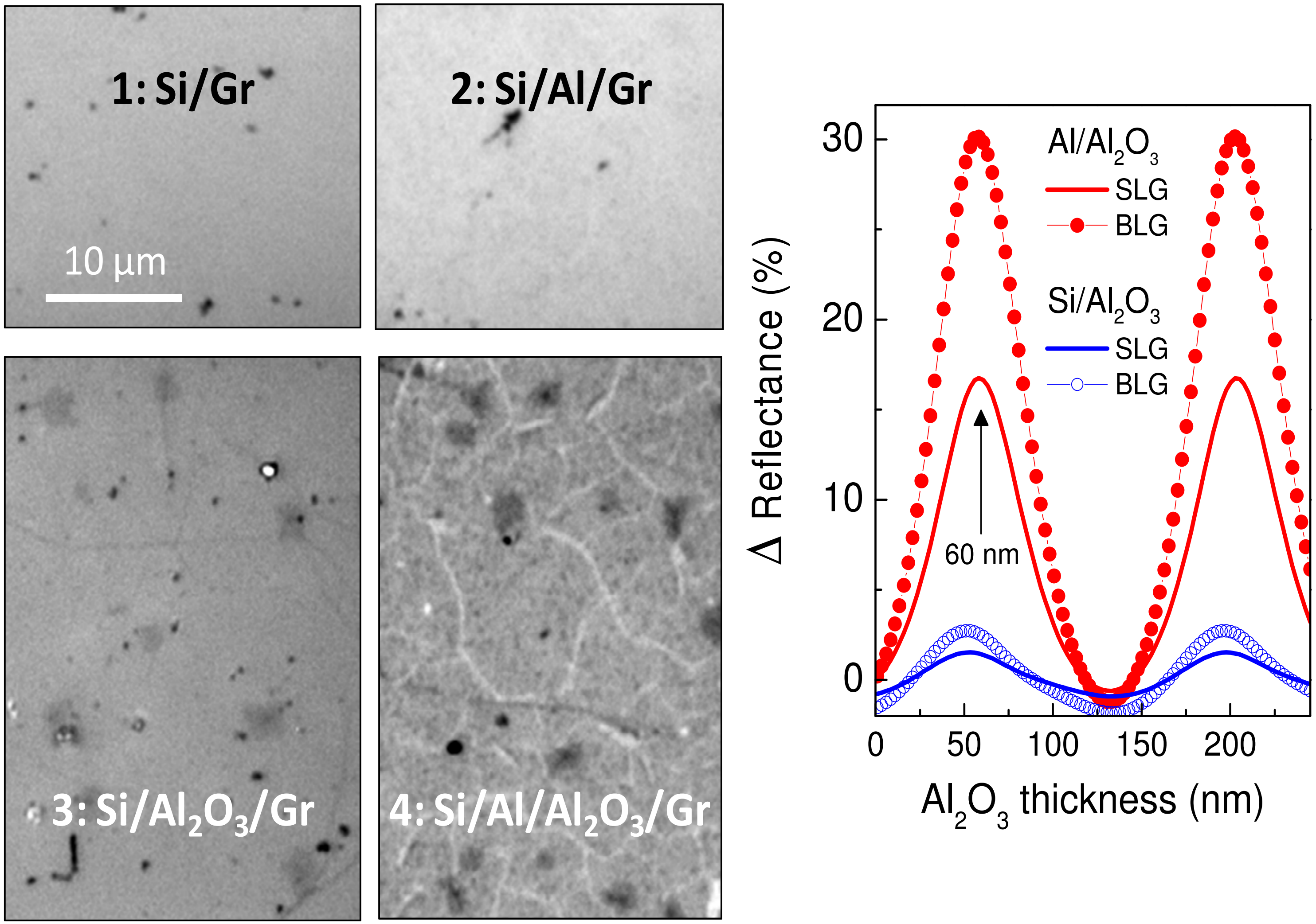


Refractive index of the Aluminum layer



Improve Aluminum layer quality:
Decrease roughness and **increase layer density**
-> e-beam deposition of Al

Interference amplification in white light images



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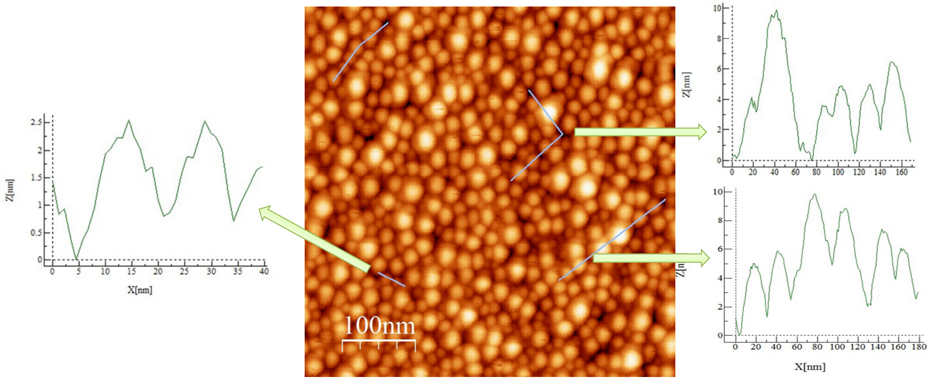
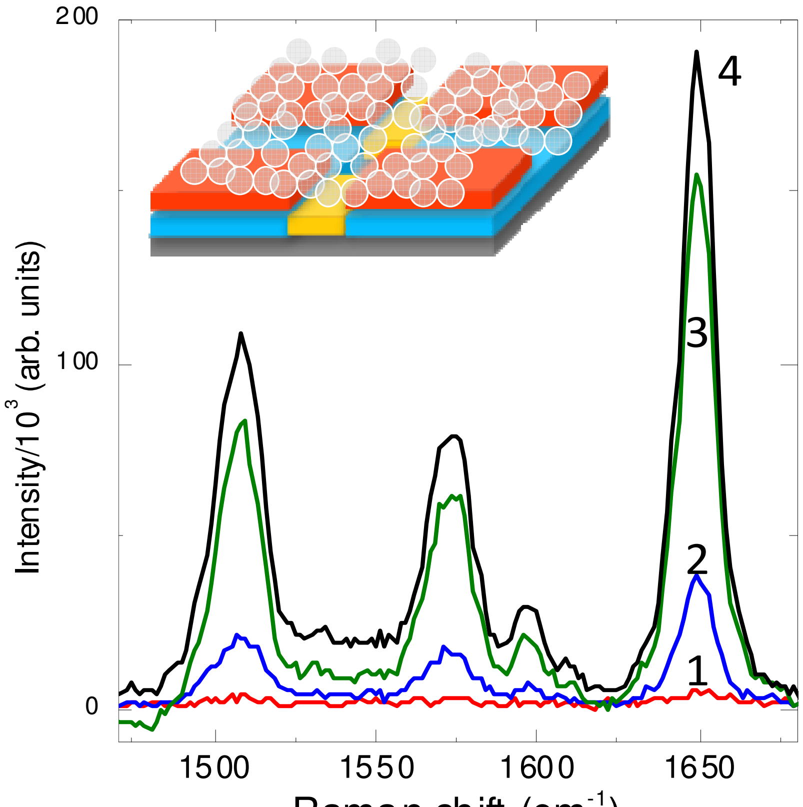
3- Combination of IERS and SERS



Ultrathin Ag film deposited on the IERS heterostructure

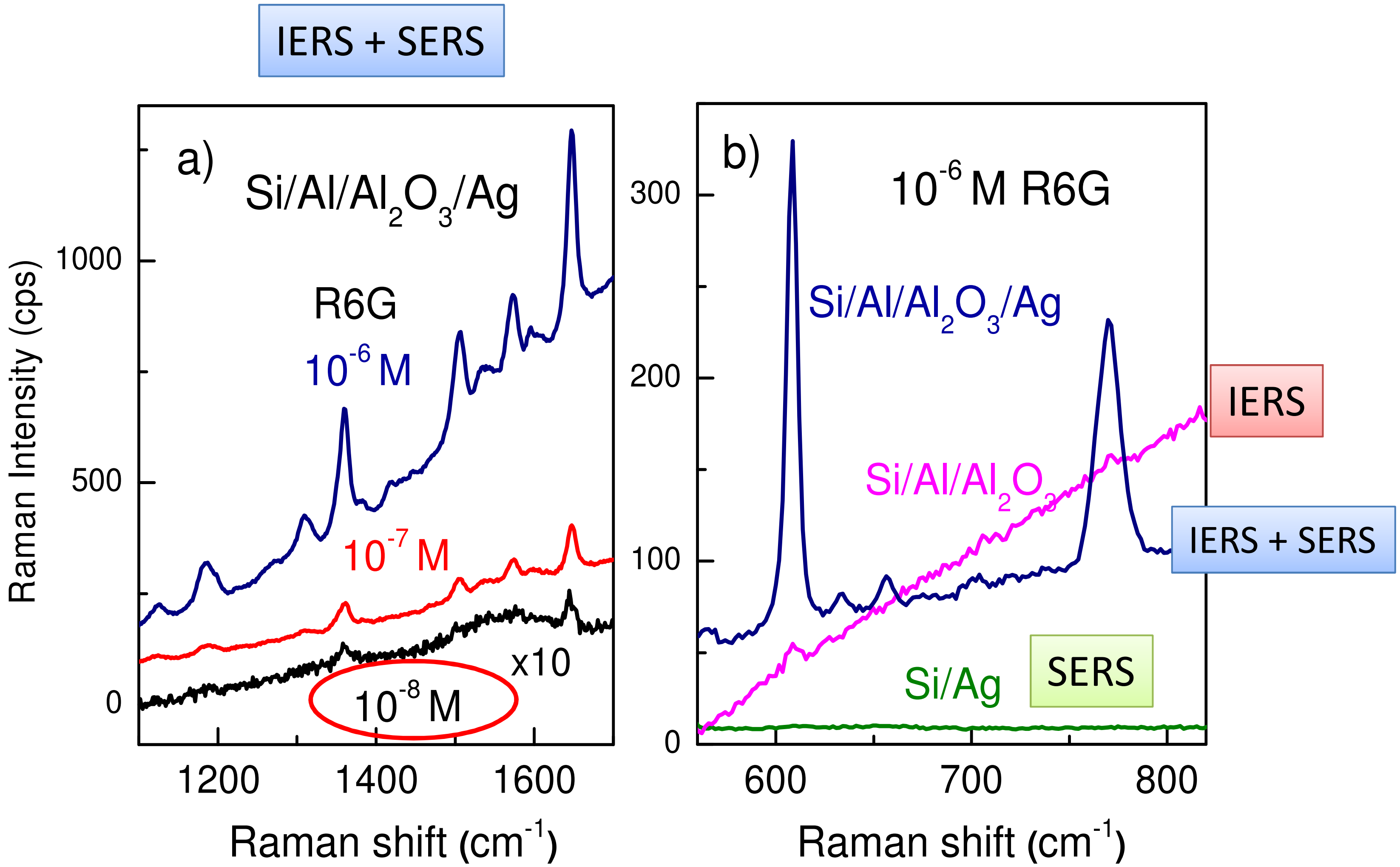
Ag film: bimodal size distribution:
big NPs ~ 40 nm ∅ ~ 10 nm height
small NPs ~ 20 nm ∅ ~ 3 - 5 nm height



IERS + SERS

4: $Si/Al/Al_2O_3$
3: Si/Al_2O_3
2: Si/Al
1: Si

+ Ag 1nm film
+1 ML R6G



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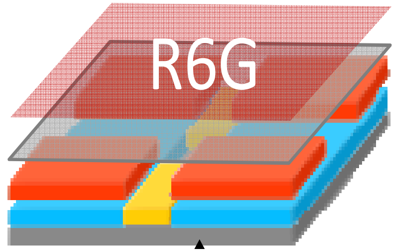
Conclusions

1- Interference enhancement:

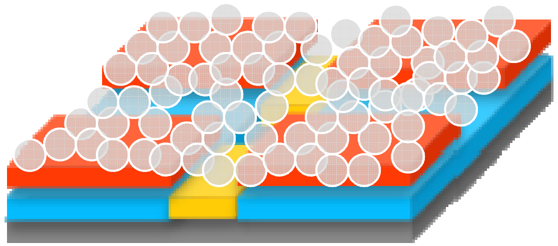
Optimum system: Al/air/Graphene -> RE = **1400 for 488 nm**
. **12000 for 1000 nm**



Si/Al/Al_2O_3/Gr-> RE ≅**700 for 488nm, limited by κ (Al)**

Amplification of Raman signal and of **fluorescence** of the analyte
Increased contrast in optical images: optimum por 60 nm Al2O3

2- Combided IERS + SERS



Amplification factor of combined **IERS + SERS** platforms: **10^5**
Detection of 10^{-8} M R6G

<u>On going:</u>
* Increase SERS amplification.
  Limitation: the Ag film has to be transparent enough
- Optimize Aluminum refractive index for IERS