Development of near-field laser ablation inductively coupled plasma mass spectroscopy for sub-micrometric analysis of solid samples

C. Jabbour, J.-L. Lacour, M. Tabarant, A. Semerok, S. V. Fomichev, F. Chartier

DE LA RECHERCHE À L'INDUSTRIE

cea den

Development of near-field laser ablation inductively coupled plasma mass spectrometry for sub-micrometric analysis of solid samples.

C. JABBOUR[1], J-L. LACOUR[1], M. TABARANT[1], A. SEMEROK[1], S.V. FOMICHEV[2], F. CHARTIER[1]

1 CEA Saclay, DEN-DANS, Department of Physical Chemistry, Analytical Studies and Surface Reactivity Service, Nuclear Isotopic and Elemental Analytical development Laboratory, F-91191 Gif-sur-Yvette, France.

2 Kurchatov Institute, Moscow, Russia.

chirelle.jabbour@cea.fr

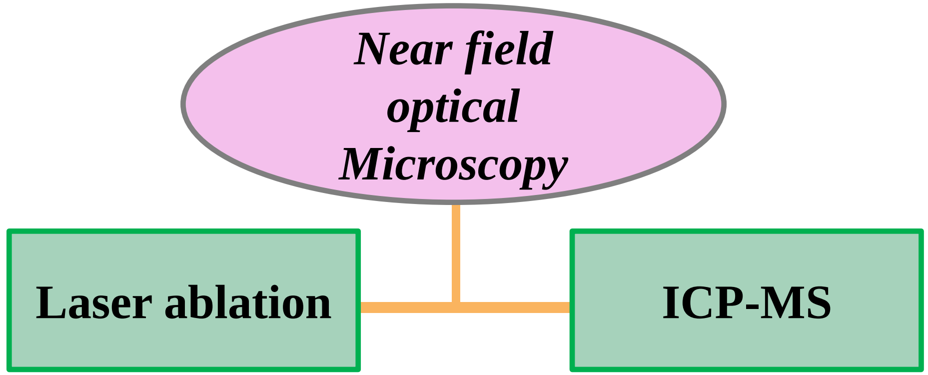
2016 Winter Conference on Plasma Spectrochemistry, January 10 - 16, 2016, Tucson, Arizona.

SUMMARY

- ***Objective***
- ***Near Field Laser Ablation***
- ***Experimental***
- ***Multiparametric study: Results and Modeling Code***
- ***Conclusions and Prospects***

OBJECTIVE

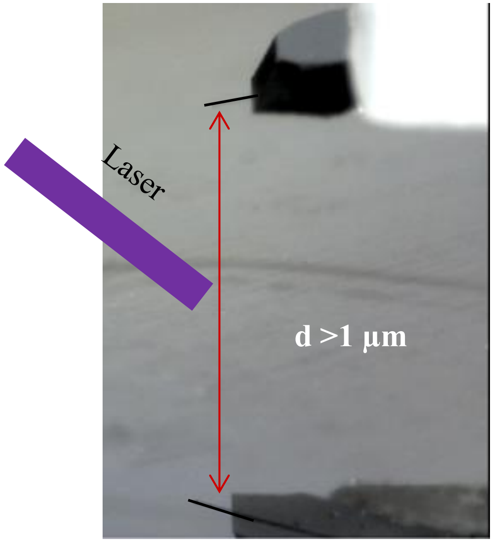
- Powerful analytical qualitative and quantitative method at ambient pressure.
- Optical diffraction limit ➡ Lateral resolution µm



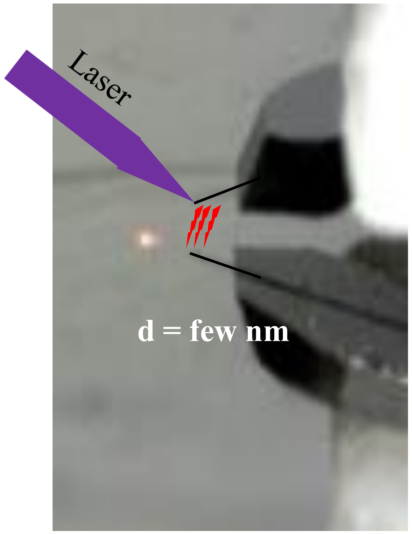
- Break the resolution limit ➡ Sub-micrometer scale:
- High-resolution surface analysis.

M.V.Zoriy, M. Kayser, J. Sabine Becker, Int. J. Mass Spectrom. ***273****, 151–155 (2008)*
V. Zorba, X.Mao, R.E.Russo, Anal Bioanal Chem ***396****, 173-180 (2010)*
T.A.Schimtz, G.Gamez, P.D.Setz, L.Zhu, R.Zenobi, Anal.Chem. ***80****, 6537-6544 (2008)*

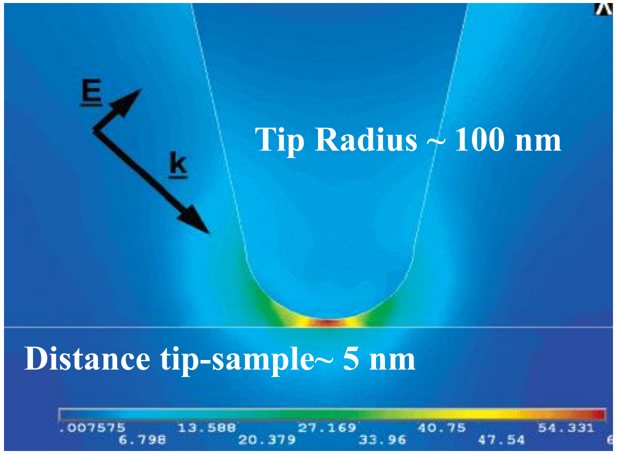
NEAR FIELD LASER ABLATION



No tip enhancement effect
(No ablation)

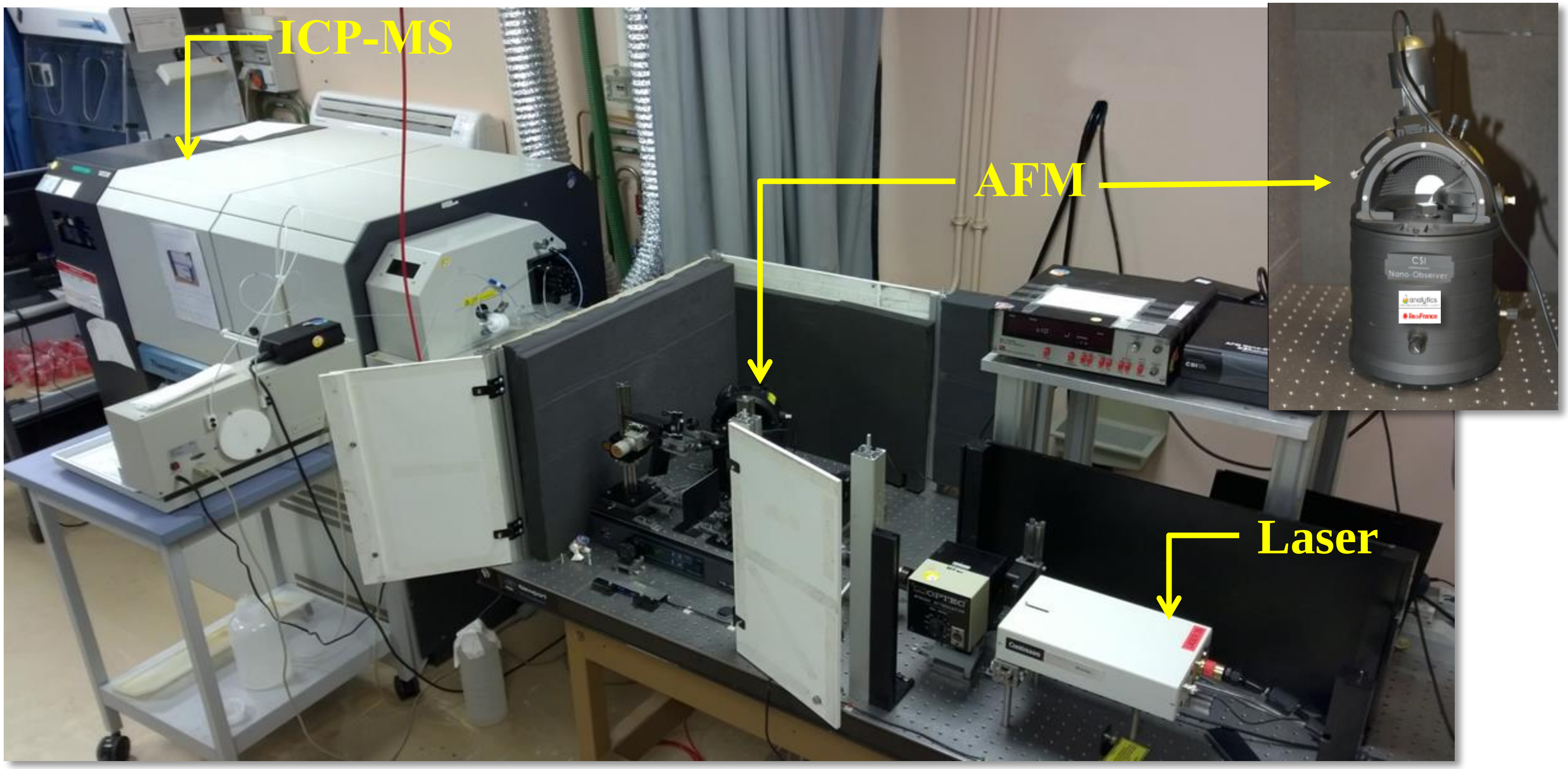


Laser energy enhancement
(Near field ablation)



Andrew Downes, Donald Salter, Alistair Elfick. J. Phys. Chem. B (2006), 110, 6692-6698

EXPERIMENTAL

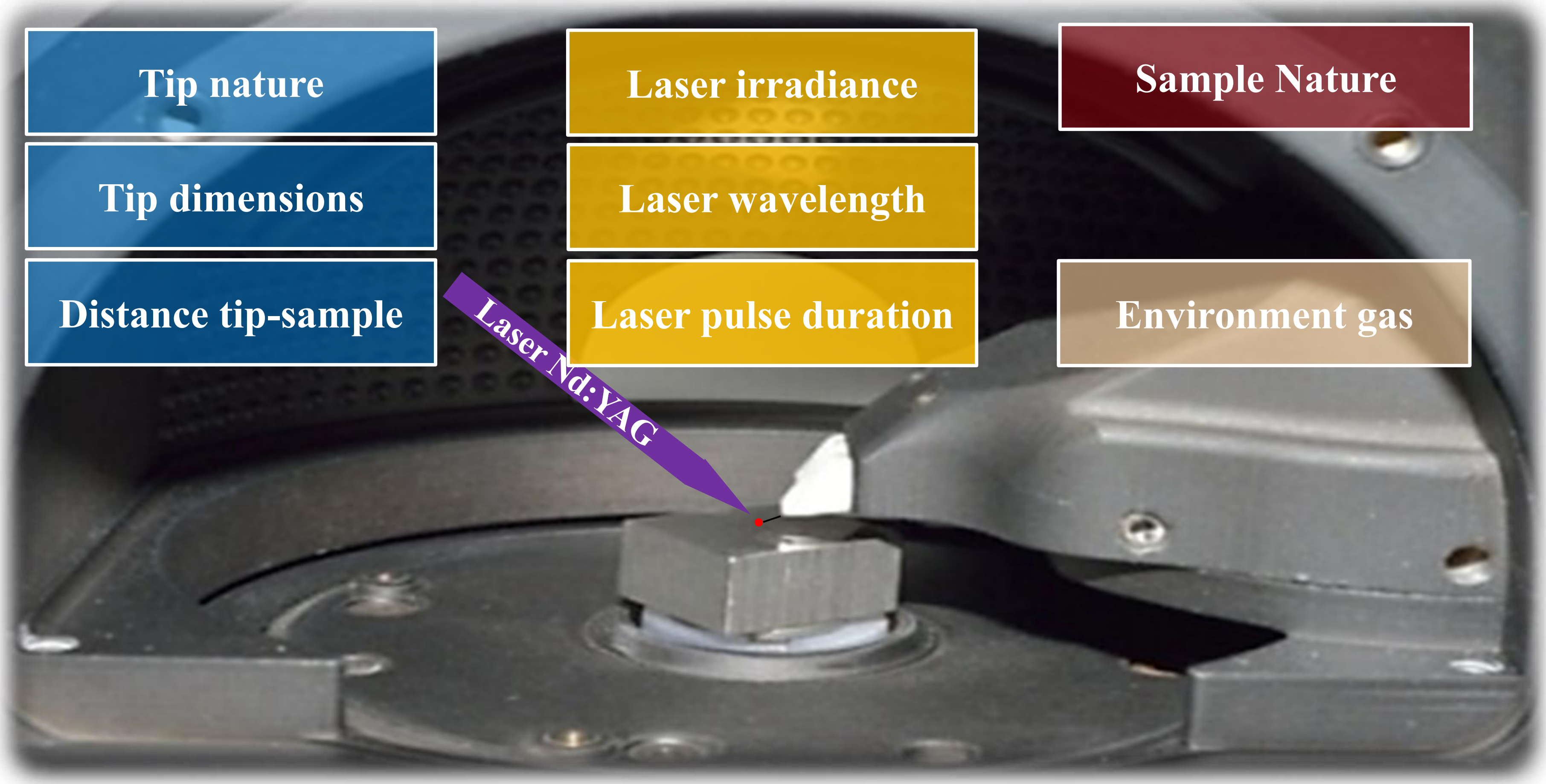


Laser Nd:YAG (266 nm) , pulse duration 4 ns.

***AFM**: **A**tomic **F**orce **M**icroscope.*

***ICP-MS**: **I**nductively **C**oupled **P**lasma - **M**ass **S**pectrometry : double focusing sector field*

MULTIPARAMETRIC STUDY



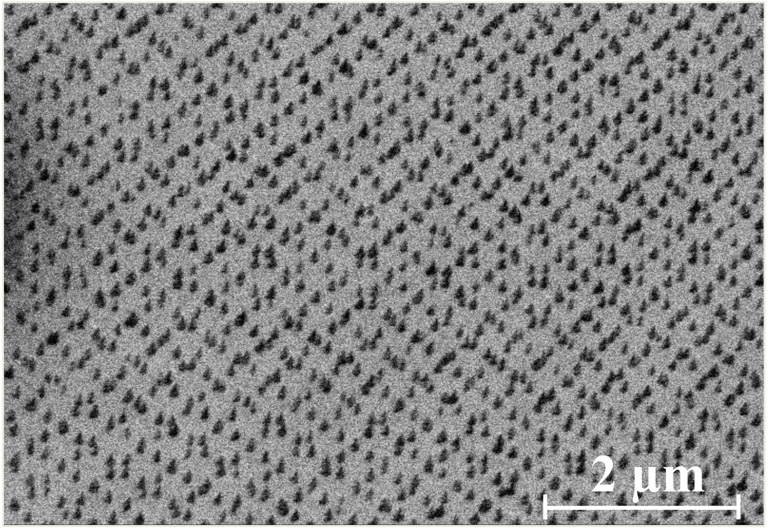
Parameters influencing the near field ablation efficiency, resolution, craters dimensions (amount of ablated mass)

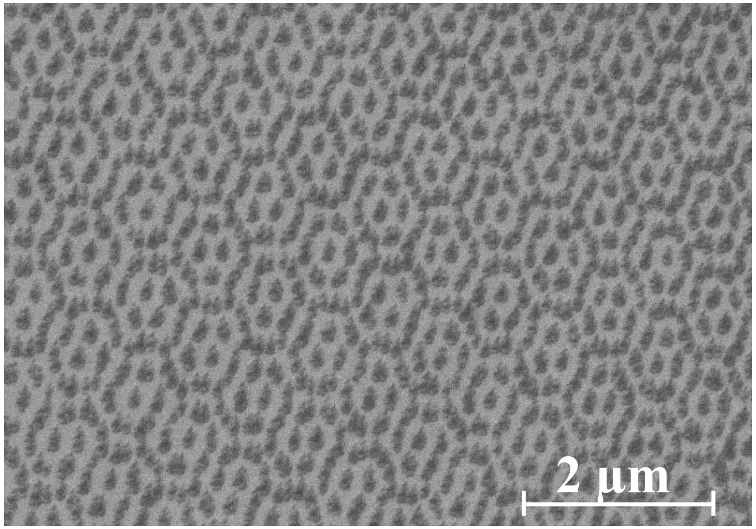
RESULTS

Tip effect on the measurement resolution

λ_{laser} = 266 nm ; τ = 4 ns

- *Different tip natures and dimensions (diameter 10 - 30 nm ⟶ NO VISIBLE CRATERS).*
- **Observed craters only with the conductive diamond coated tip** *(Si + Diamond coating doped with B (diameter ~ 200 - 250 nm).*





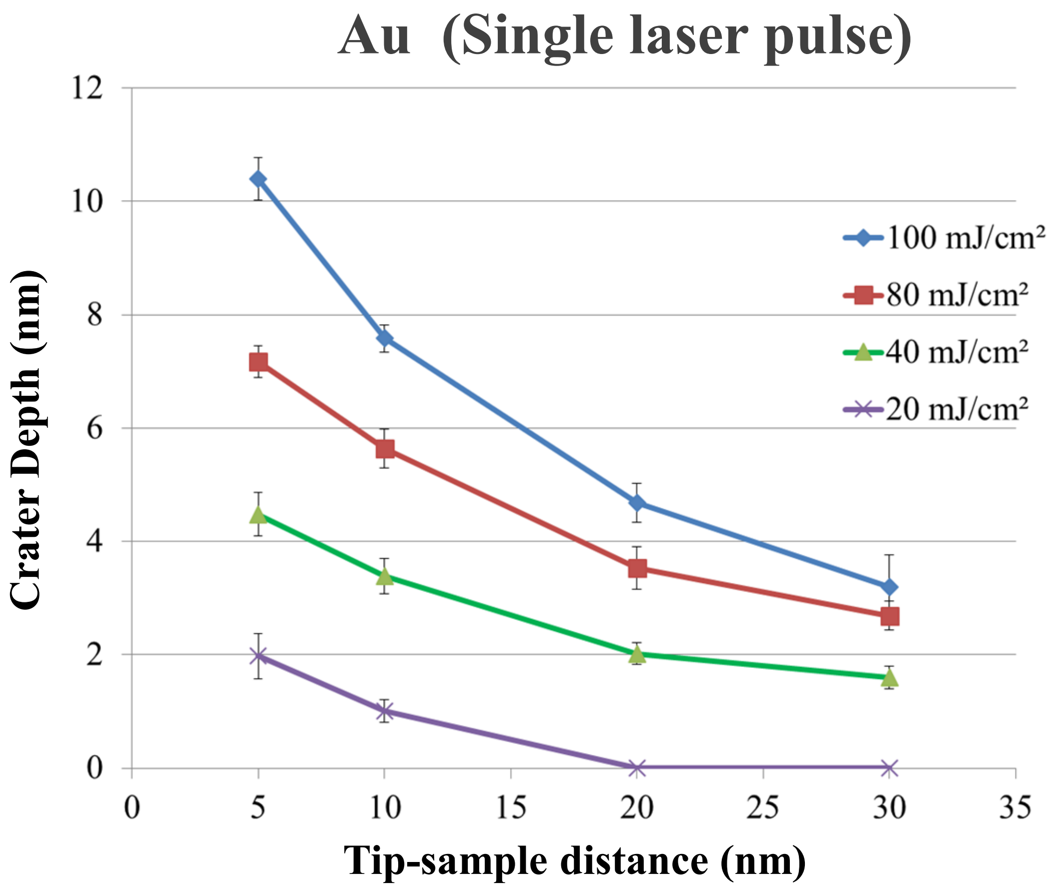
The diameter of the obtained craters ranged from 100 to 120 nm using a single laser pulse.

RESULTS

Tip-sample distance and laser irradiance effects on the craters dimensions

λ_{laser} = 266 nm ; τ = 4 ns

- **Tip-sample distance**
  - Crater diameter ~
  - Crater Depth
  - **Ablated mass**
- **Laser Irradiance**
  - Crater diameter ~
  - Crater Depth
  - **Ablated mass**



RESULTS

Sample nature and multiple laser pulses effects on the craters dimensions

λ_{laser} = 266 nm ; τ = 4 ns

➢ Sample Nature

Samples: Gold / Silicon

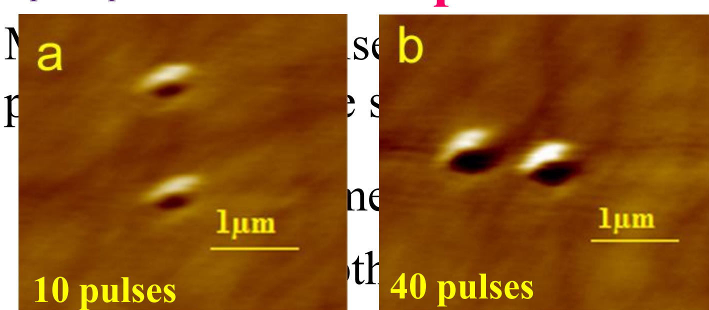
- Crater diameter ~ ⟹
- Crater depth : Au > Si

⇨ **Ablated mass**: Au > Si

Number of laser pulses \ Ablated mass	Au	Si
1	2 E+06 Atoms	6 E+05 Atoms
10	~ 4 fg	~ 0.3 fg
40	~ 12 fg	~ 1 fg
200	2 E+08 Atoms	4 E+07 Atoms

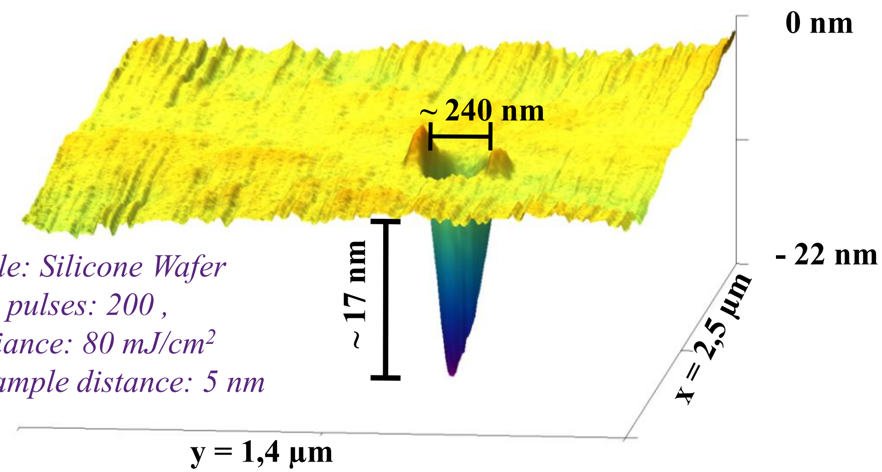
Sample: Gold
Irradiance: 80 mJ/cm²
Tip-sample distance: 5 nm

➢ Number of laser pulses



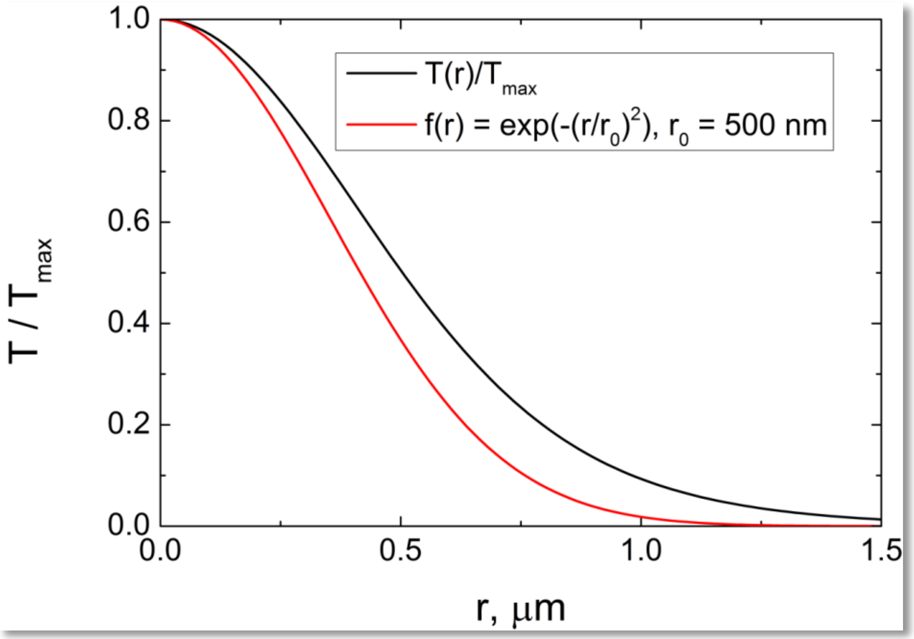
⇨ **Ablated mass** ↗

Sample: Silicone Wafer
Laser pulses: 200 ,
Irradiance: 80 mJ/cm²
Tip-sample distance: 5 nm

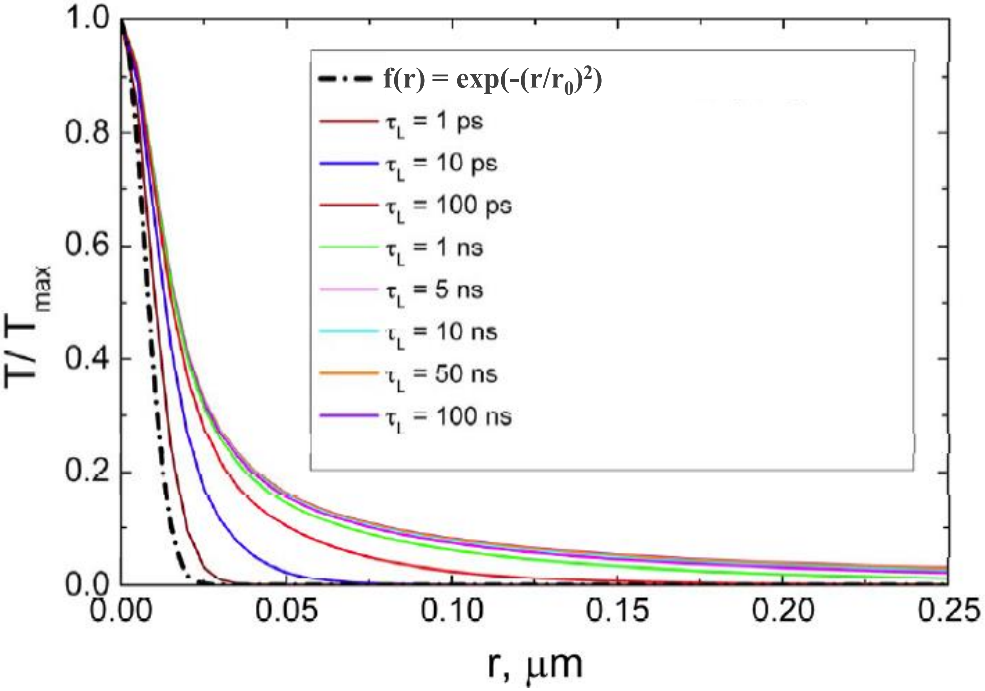


MODELING OF THE SURFACE HEATING

Si, 266 nm, α^{-1} = 5 nm, τ = 4 ns, 2r$_0$ = 1 µm



Si, 266 nm, α^{-1} = 5 nm, τ = 4 ns, 2r$_0$ = 20 nm



T= f(r) pour z = 0 et t = τ_{laser}

τ : laser pulse duration

α^{-1}: sample absorption coefficient

2r$_0$: interaction size at the surface

Si (266nm): α^{-1} = *5 nm*
D_t = *0,8 cm²/s*
L_t = *1,2 µm*

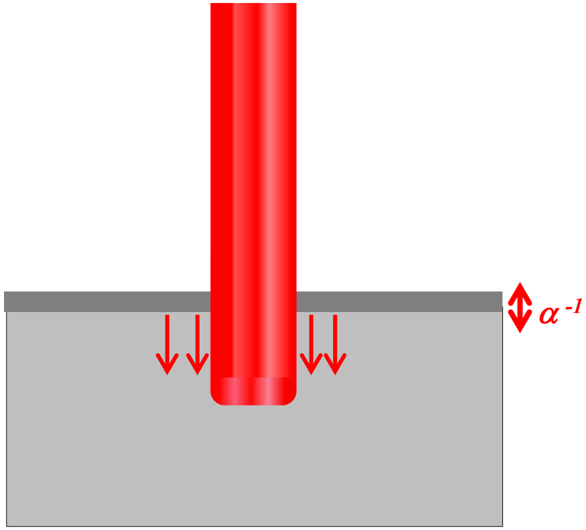
Au (266nm): α^{-1} = *11 nm*
D_t = *1,3 cm²/s*
L_t = *1,4 µm*

MODELING OF THE SURFACE HEATING

Laser ablation on a large surface of interaction

Laser ablation on a very small area of interaction (near field)

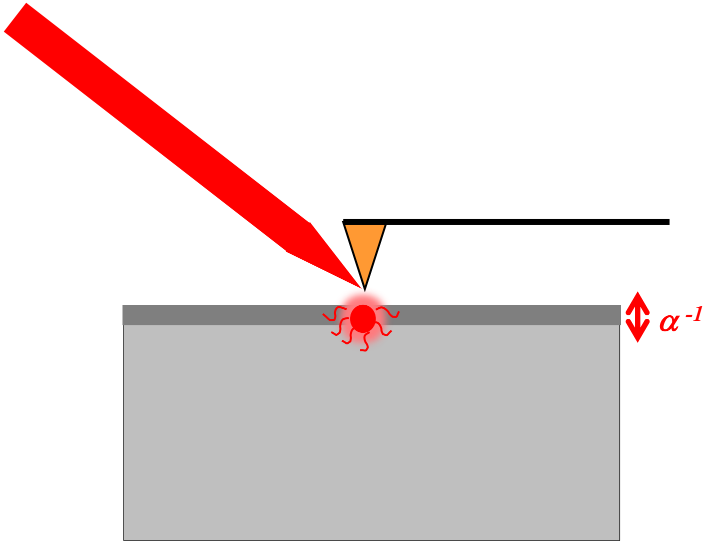
Si, 266 nm, α^{-1} = 5 nm, τ = 4 ns, <u>$2r_0 > 1$ µm</u>



Ablation dominated by 1D sample thermal diffusion related to the pulse duration

<u>Si</u> <u>(266nm)</u>: α^{-1} = *5 nm*
D_t = *0,8 cm²/s*
L_t = *1,2 µm*

Si, 266 nm, α^{-1} = 5 nm, τ = 4 ns, <u>$2r_0$ = 20 nm</u>

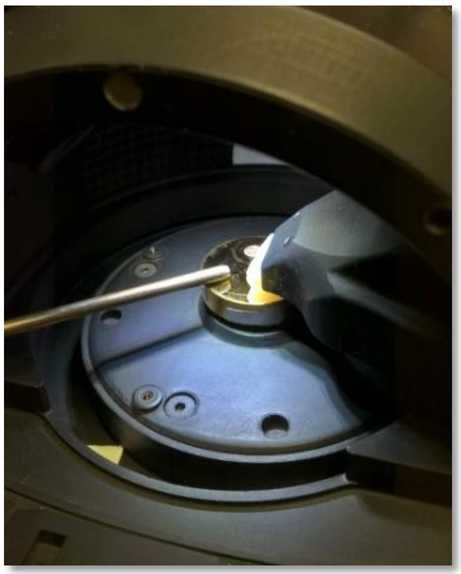


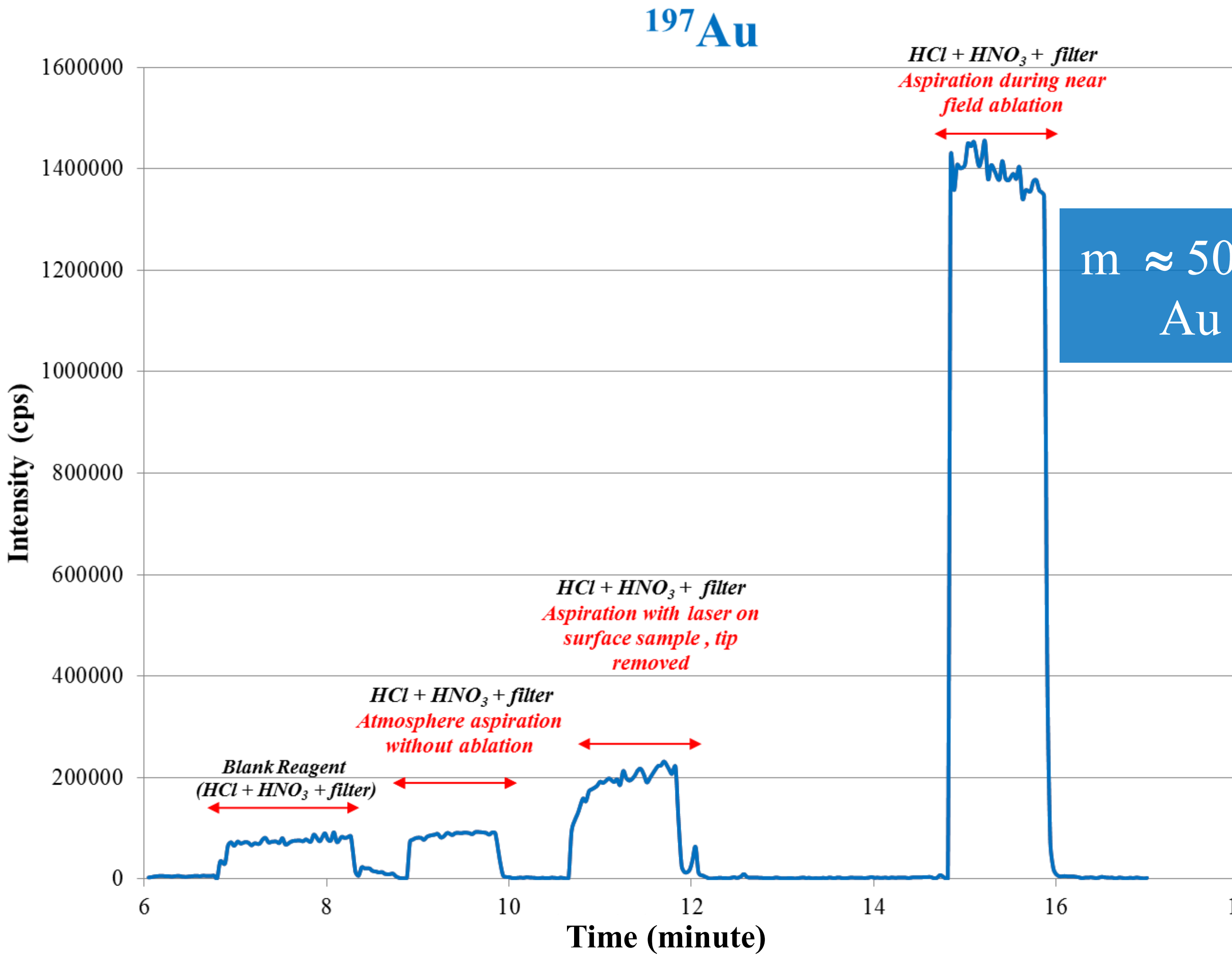
Ablation dominated by 3D sample thermal diffusion and absorption coefficient

<u>Au</u> <u>(266nm)</u>: α^{-1} = *11 nm*
D_t = *1,3 cm²/s*
L_t = *1,4 µm*

FIRST TESTS WITH ICP-MS

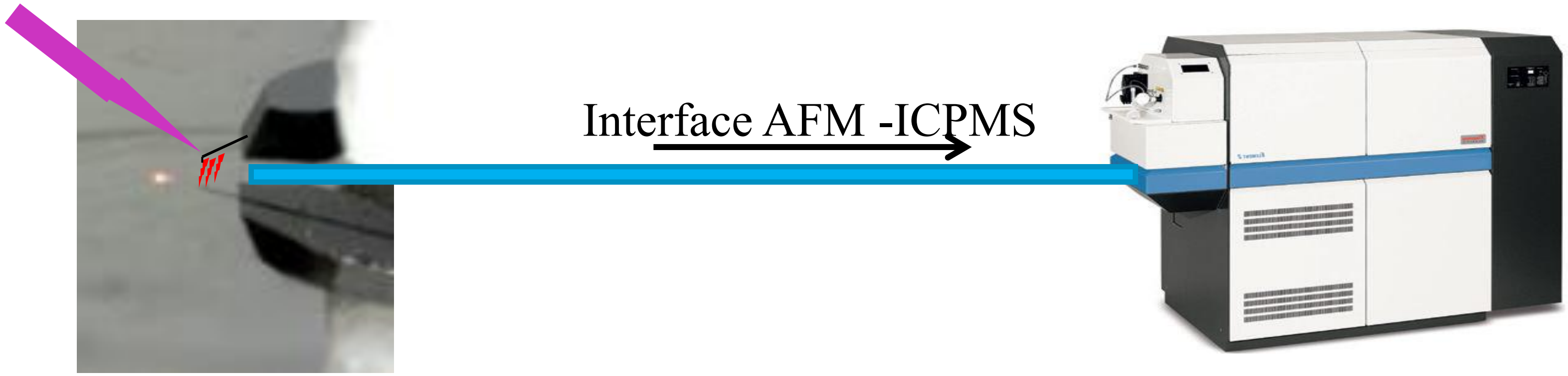
Ablated gold particles were collected on a filter using a simple aspiration tube set at a few mm from the tip before being analyzed by ICP-MS (25 000 craters /single laser pulse)





m ≈ 50 pg Au

CONCLUSIONS AND PROSPECTS



- Near field laser ablation on gold sample and silicone wafer.
- Completion the multi-parametric study (wavelength, laser pulse duration…).

- Development of the AFM-ICP-MS interface (on-going).
- Particle characterization: particle size, mass, shape ... (on-going).
- Development of the elemental analysis method by ICP-MS.

Thank you for your attention

MAY THE ATOMIC FORCE BE WITH ME !!

Commissariat à l'énergie atomique et aux énergies alternatives
Centre de Saclay | 91191 Gif-sur-Yvette Cedex
T. +33 (0)1 69 08 26 29 |
Etablissement public à caractère industriel et commercial | R.C.S Paris B 775 685 019

DEN-DANS
DPC
SEARS