Department of Physics
and Astronomy
“Galileo Galilei”

Department of
Chemical Sciences

INFN
Legnaro National Laboratory

University of Padova, Italy

PhD course: Science & Engineering of Materials and Nanostructures

Investigation of P Monolayer Doping in Germanium

Semiconductor and Advanced Crystals group

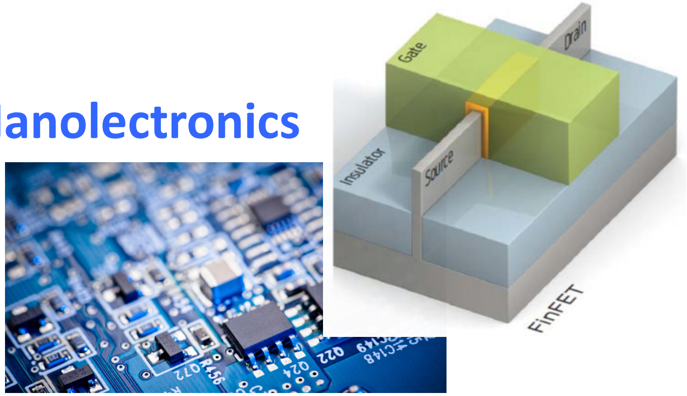
F. Sgarbossa, S. Carturan, V. Boldrini, G. Maggioni, E. Napolitani, G. Rizzi, G. Granozzi, D. R. Napoli, D. De Salvador

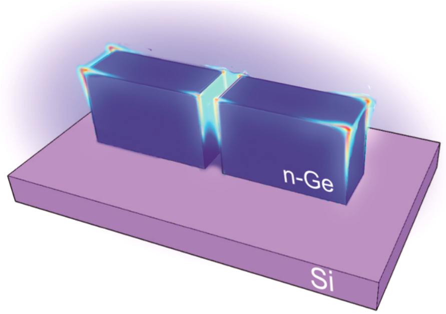
Talk scheme

- Introduction
- Monolayer Doping
- Molecular Precursors and Sample Synthesis
- Surface Characterizations
- Diffusion tests and bulk characterizations
- Laser Thermal Annealing from ML sources
- Conclusions

Ge devices

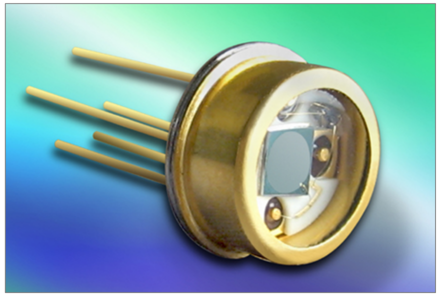
Nanolectronics

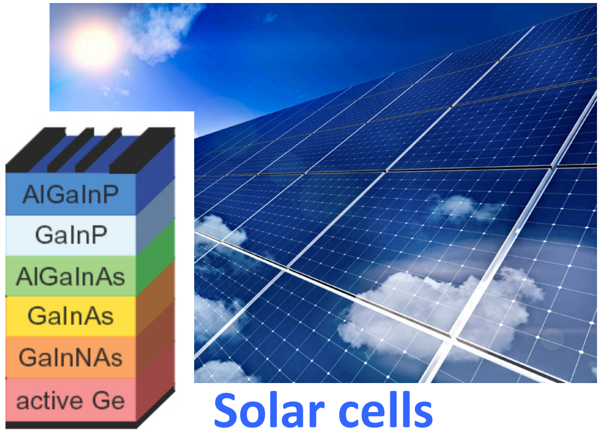




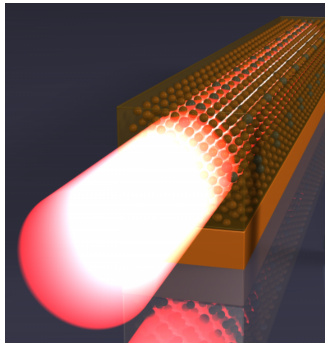
Plasmonic molecular sensors

Photodetectors



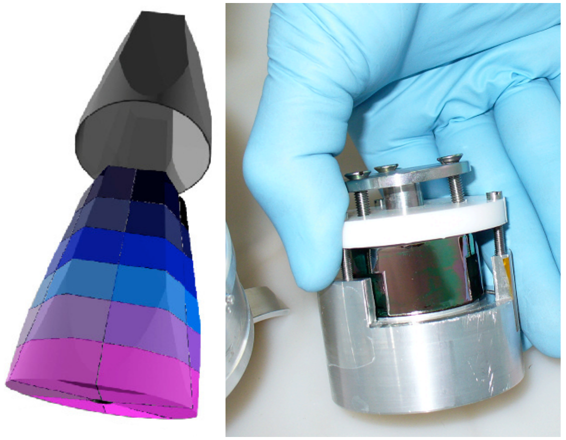


Solar cells



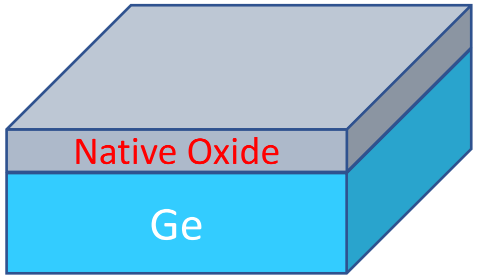
Lasers

γ-Ray detectors

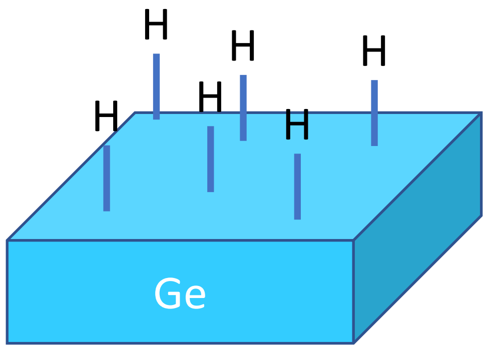


Monolayer Doping Technique on Ge

Substrate Preparation

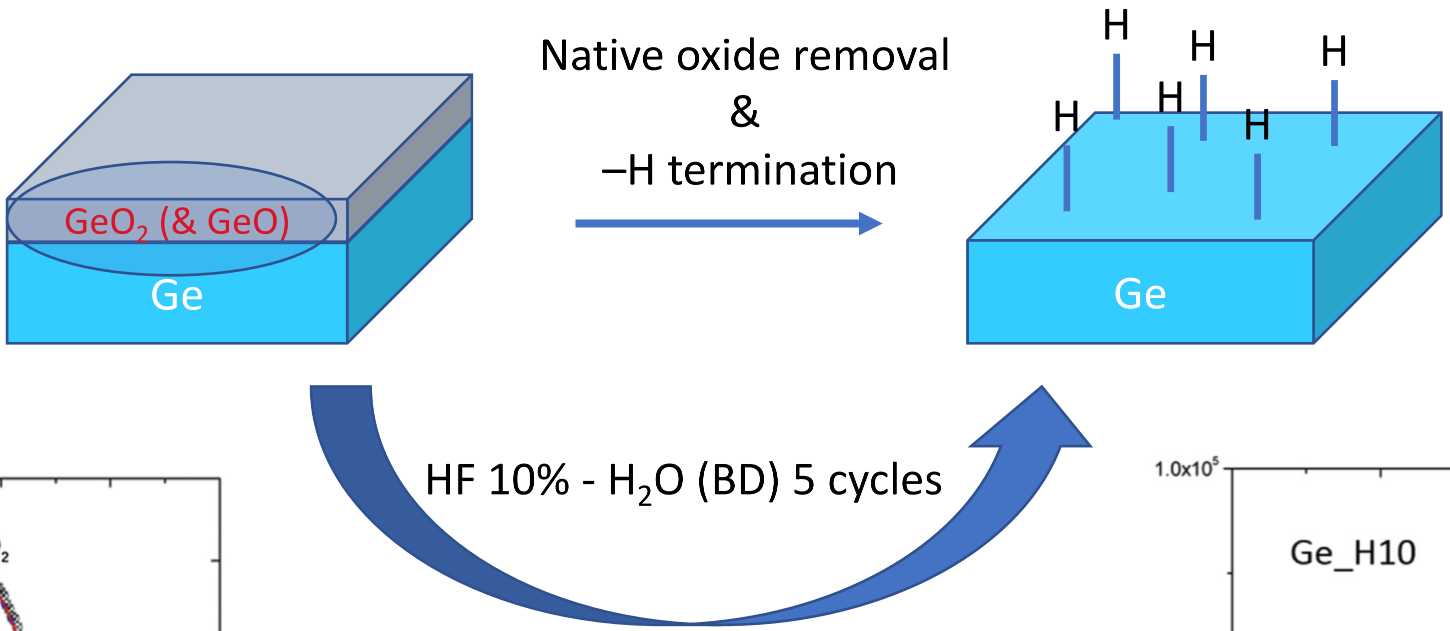


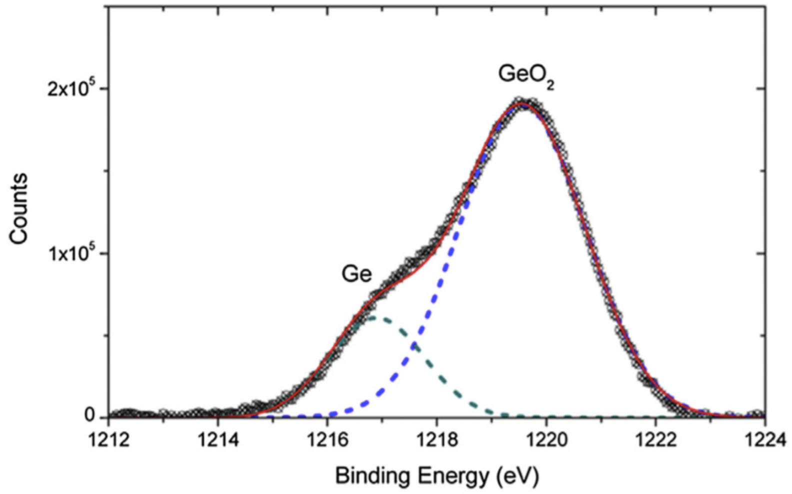
Native oxide removal
&
–H termination

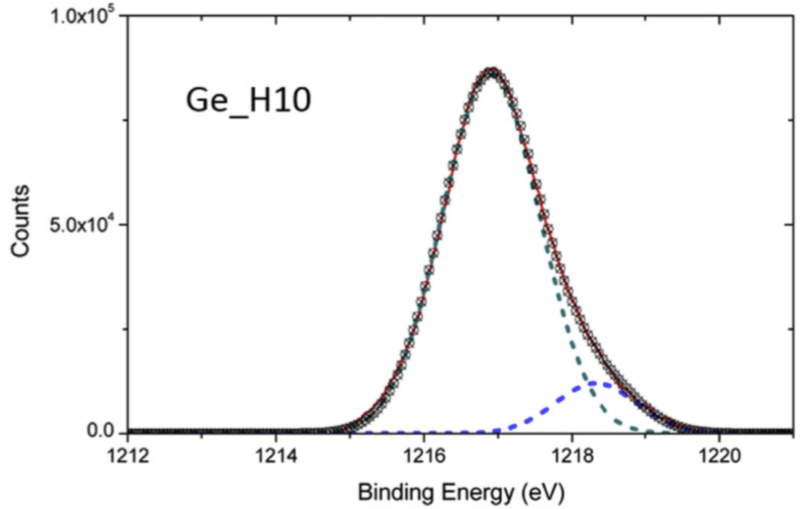


Monolayer Doping Technique on Ge: surface preparation

Substrate Preparation

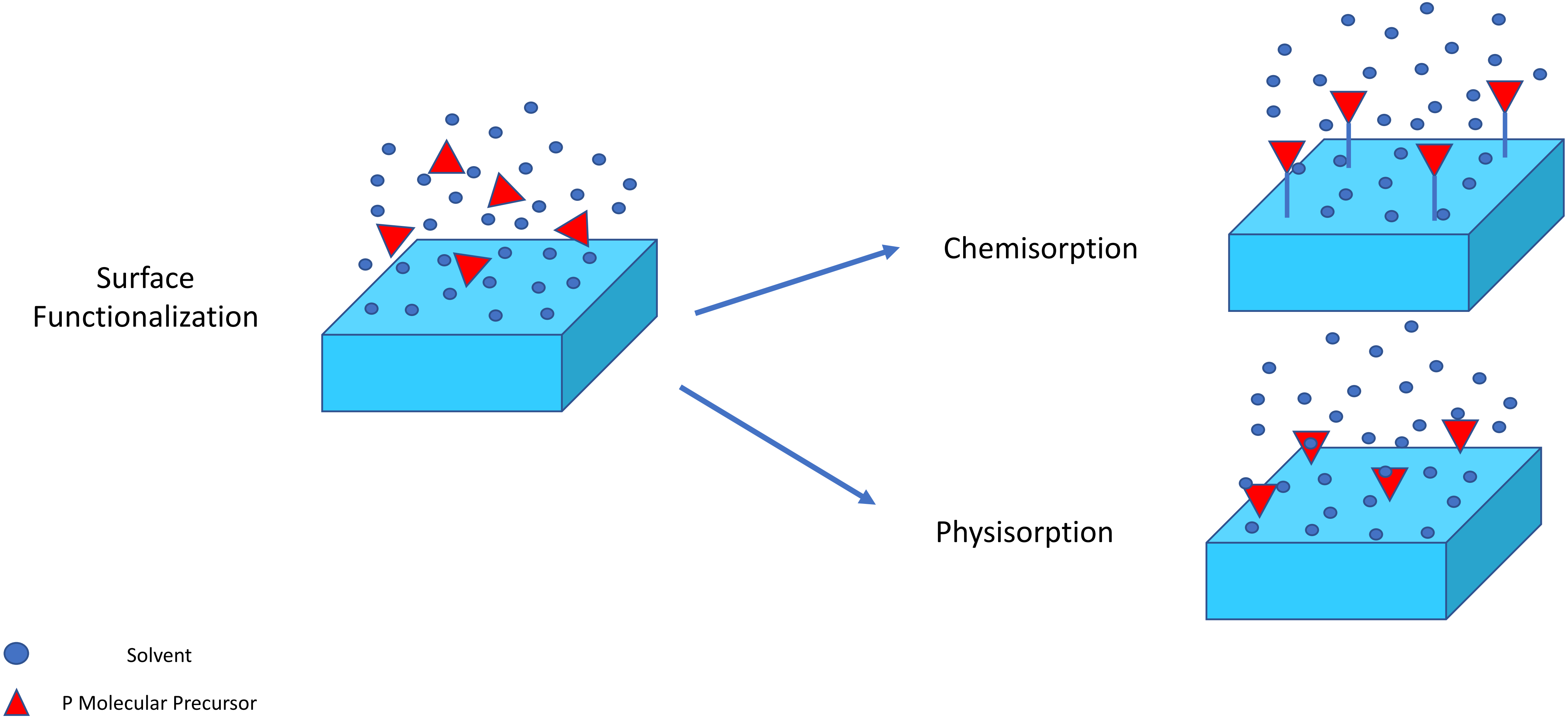




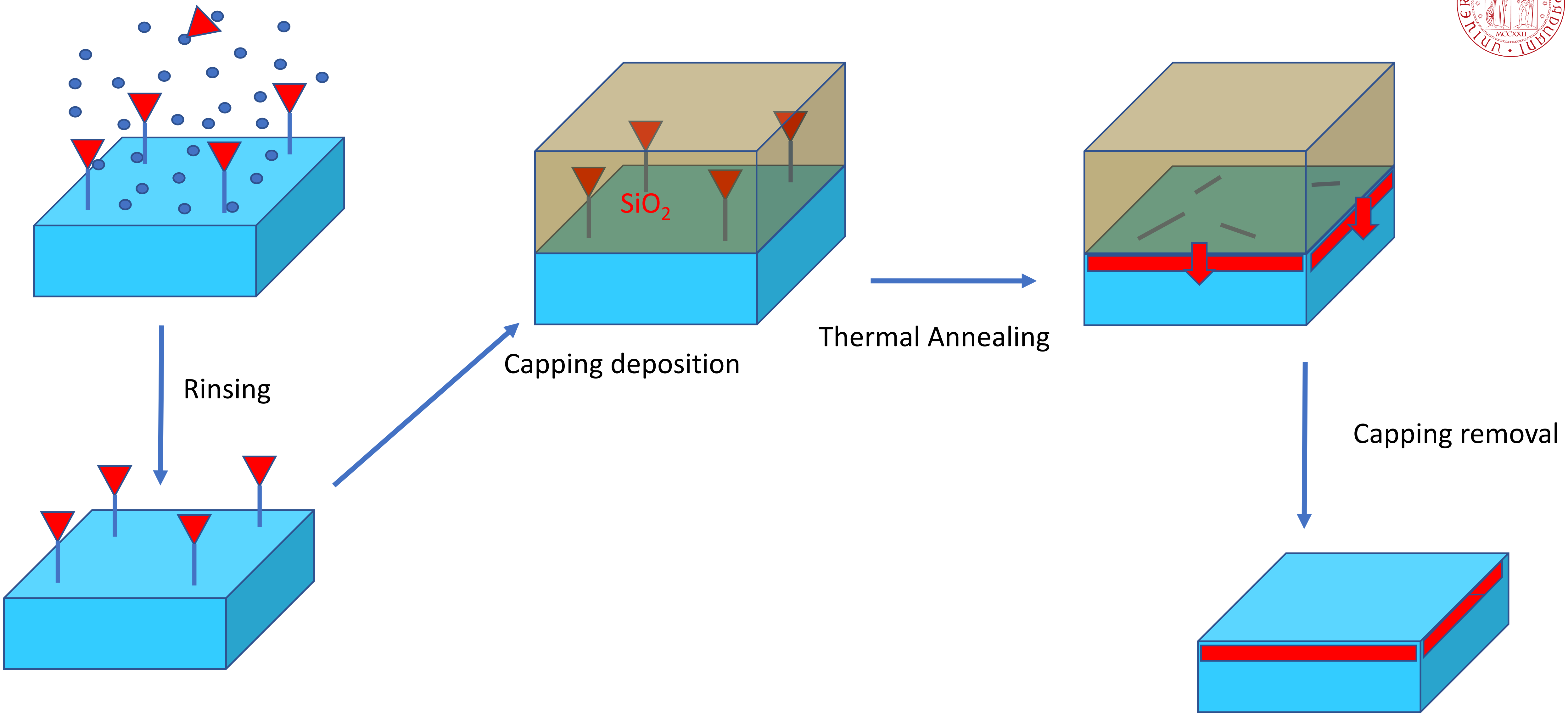


Carturan, S., et al *Materials Chemistry and Physics*, (2015) *161*, 116–122.

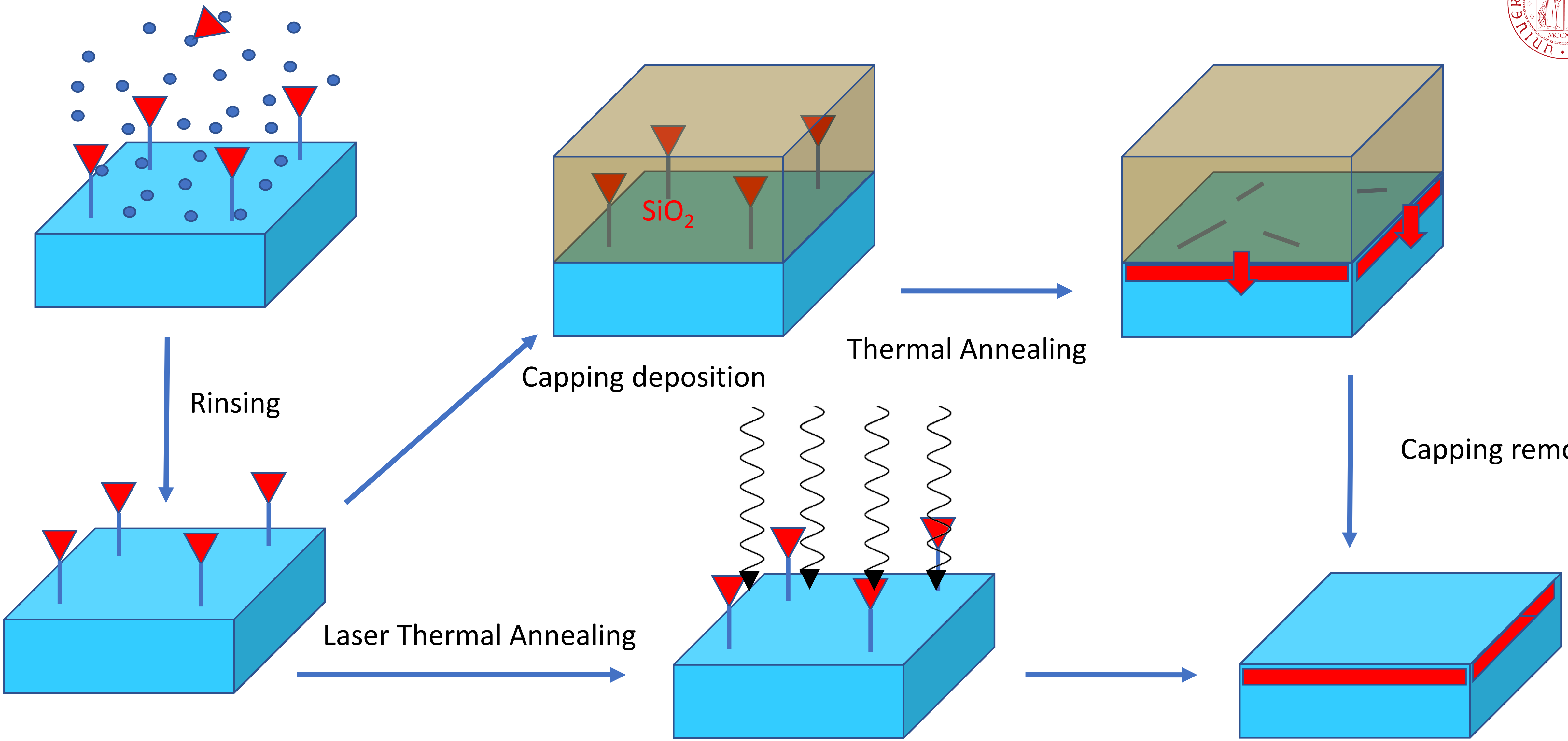
Monolayer Doping Technique on Ge



Monolayer Doping Technique on Ge

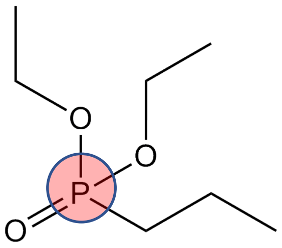


Monolayer Doping Technique on Ge



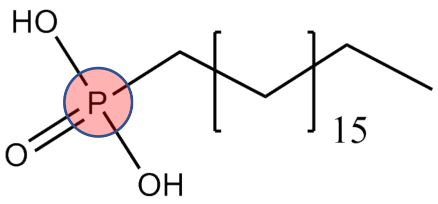
P Molecular precursors

DPP



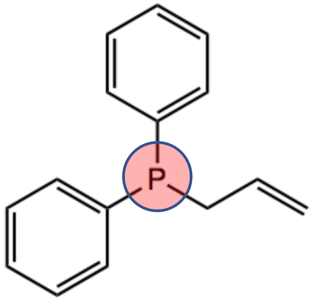
Diethyl 1-propylphosphonate (DPP)

ODPA



Octadecylphosphonic acid (OPDA)

ADPP



Allyl diphenil phosphine (ADPP)

Previous Si MLD works

Ho, J. C. et al. 2009. *Nano Letters (2009), 9*

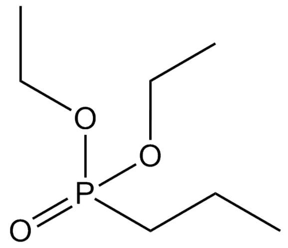
Arduca, E. et al. *Nanotechnology (2016), 27*

Longo, R. et al. *Advanced Functional Materials (2013), 23*

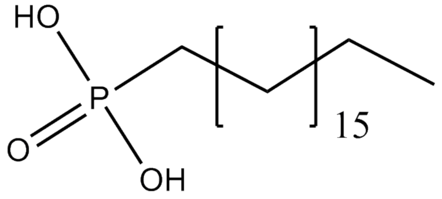
Other works & info: Connell, J. Et al. *Nanotechnology*

Molecular precursors: surface affinity and reactions

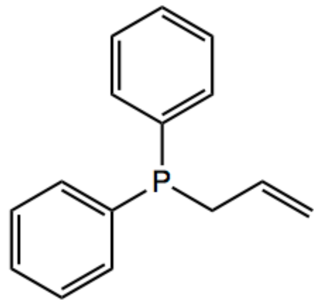
DPP

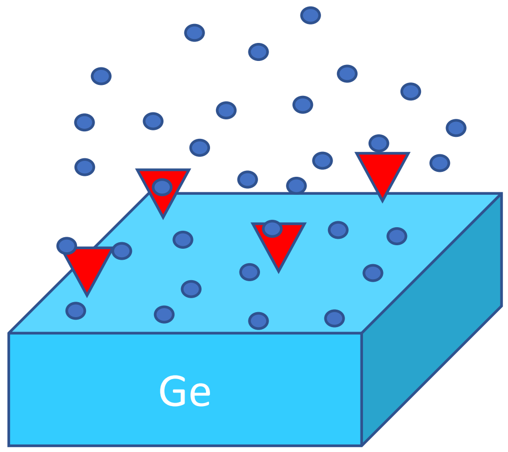


ODPA



ADPP





Molecular precursors: surface affinity and reactions

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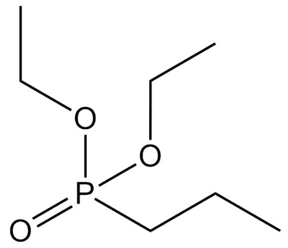
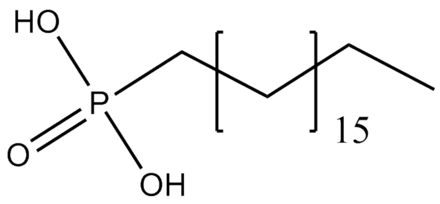
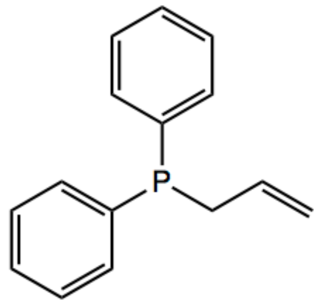
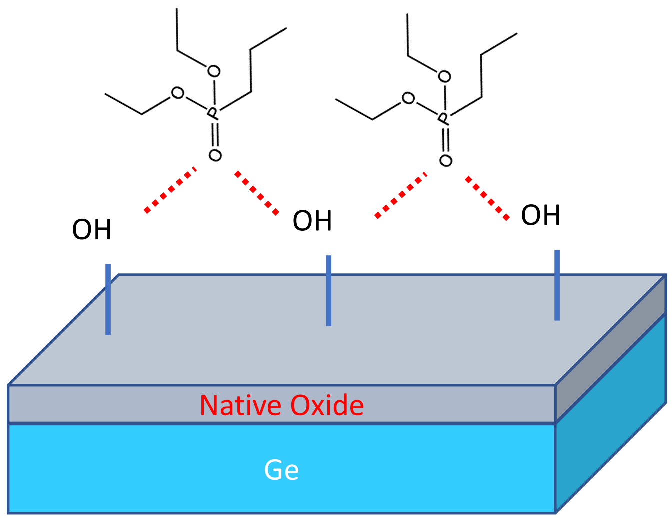


ODPA



ADPP

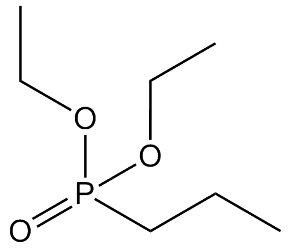




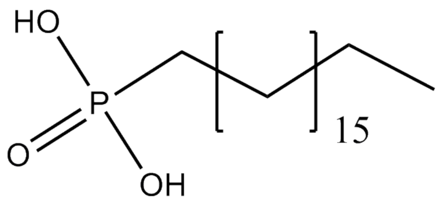
Other info: Yerushalmi, R Surfaces. *Angew. Chem. (2008), 120* (c)

Molecular precursors: surface affinity and reactions

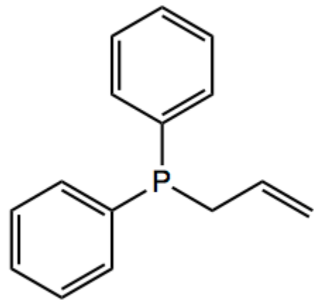
DPP

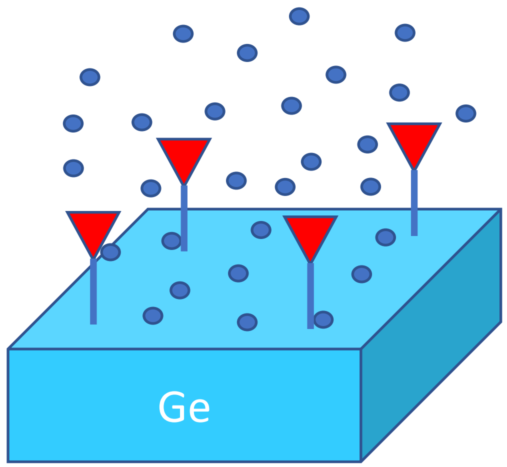


ODPA



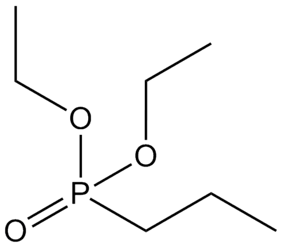
ADPP



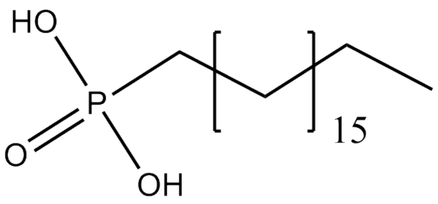


Molecular precursors: surface affinity and reactions

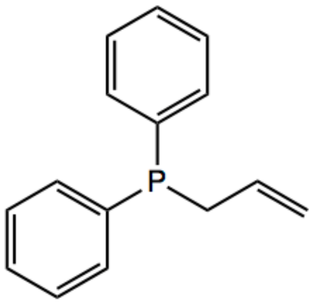
DPP

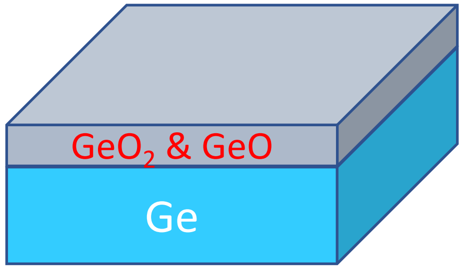


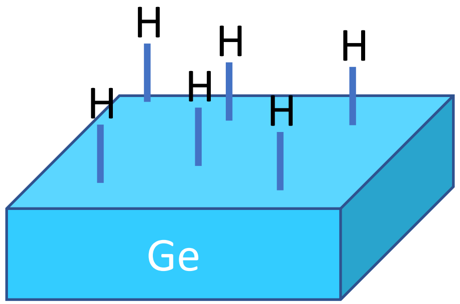
ODPA

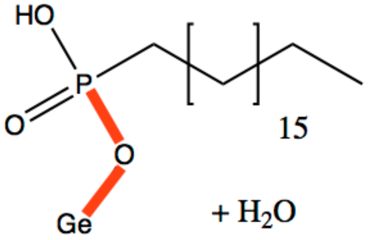


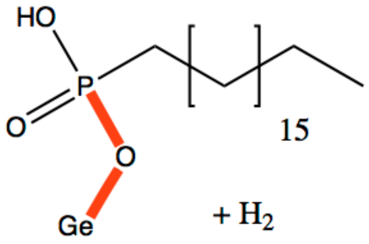
ADPP







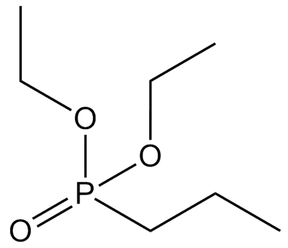




Buriak, J. M., *Chemical Reviews (2002), 102,* 5

Molecular precursors: surface affinity and reactions

DPP



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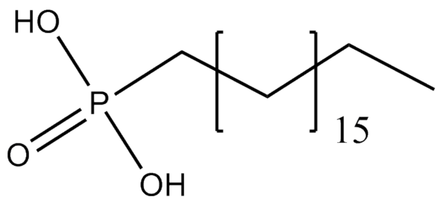
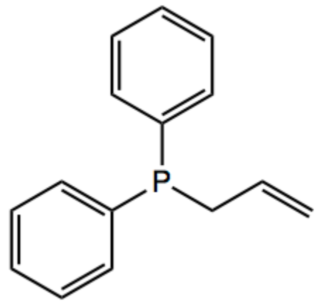
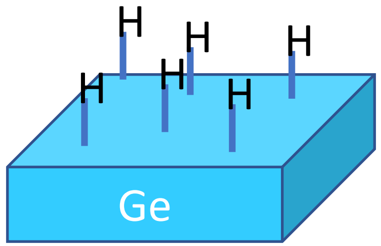
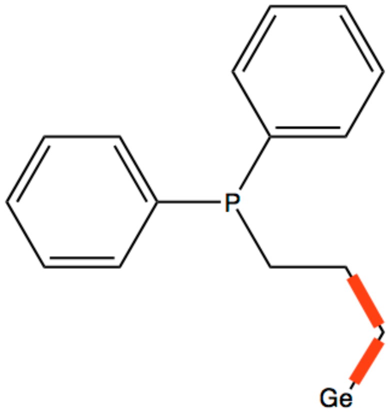


ADPP







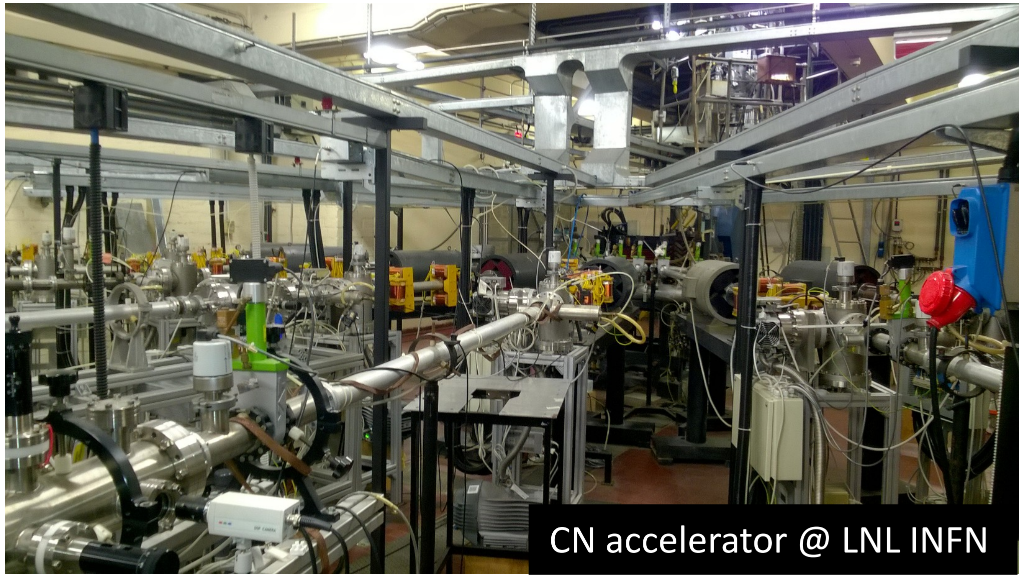
Buriak, J. M., *Chemical Reviews (2002), 102,* 5

Surface Characterization techniques

Nuclear Reaction Analysis (NRA)

- Absolute quantification
- Selective to one specific isotope
- Sensitive to deep layers

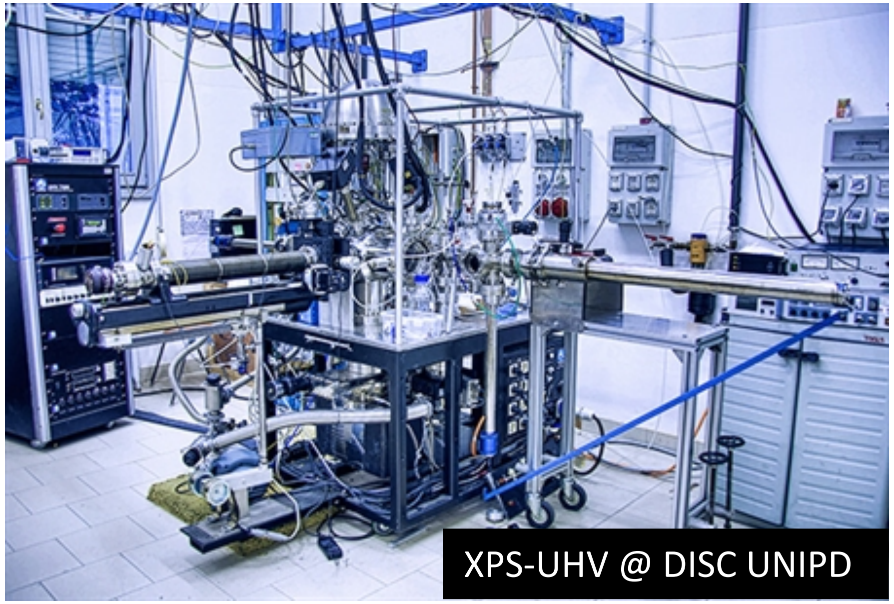
$$^{31}_{15}P(\alpha,p)^{34}_{16}S$$



CN accelerator @ LNL INFN

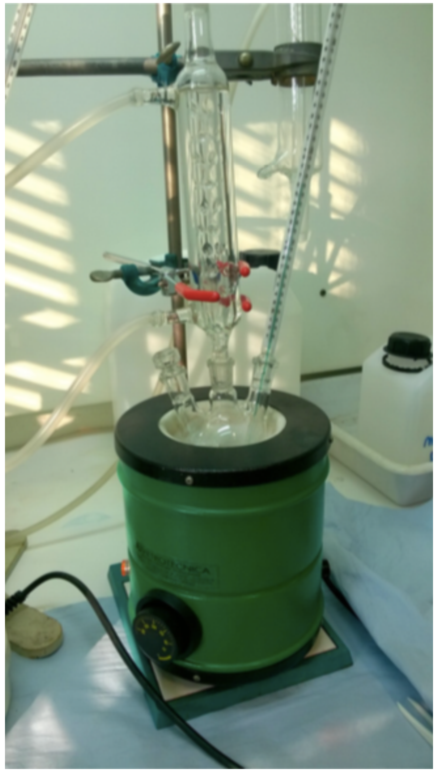
X-Ray Photoelectron Spectroscopy (AR-XPS)

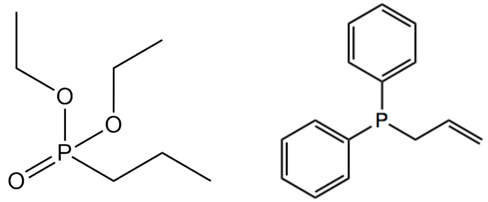
- Sensitive to oxidation states
- Detection of all atomic species
- Layer model available with Angle Resolved XPS



XPS-UHV @ DISC UNIPD

Deposition of DPP and ADPP precursors





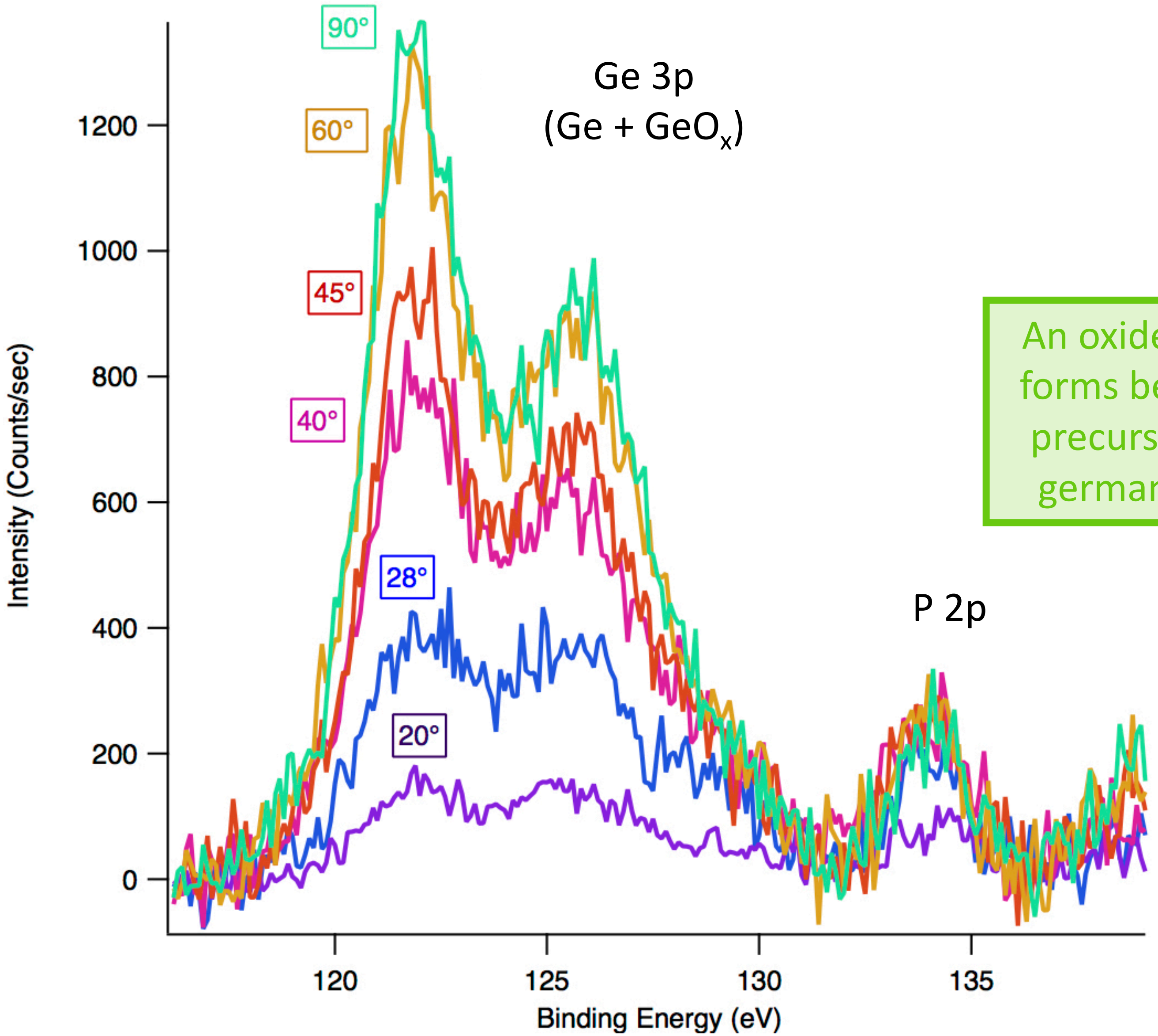
Substrate surface preparation	ML DPP	ML ADPP
Ge native oxide	4,1 $\pm$ 0.3	Compatible with 0
Hydrogenated Ge	4,3 $\pm$ 0.3	0,5 $\pm$ 0.2

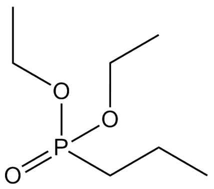
The surface preparation experimentally seems to be pointless in DPP case

Reflux in 1,3,5-Trimetylbenzene (Mesitylene) at 166°C

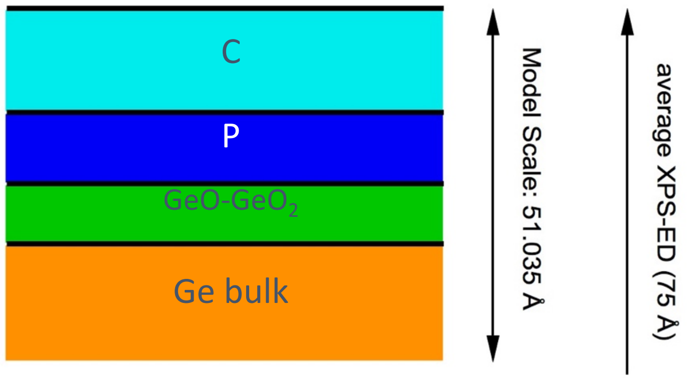
1ML = 1 Ge (100) ML = 6,25 10^{14} cm^{-2}

Angle Resolved XPS: DPP molecule from Ge-H surface



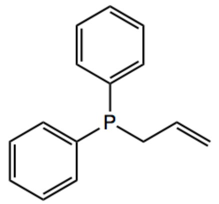


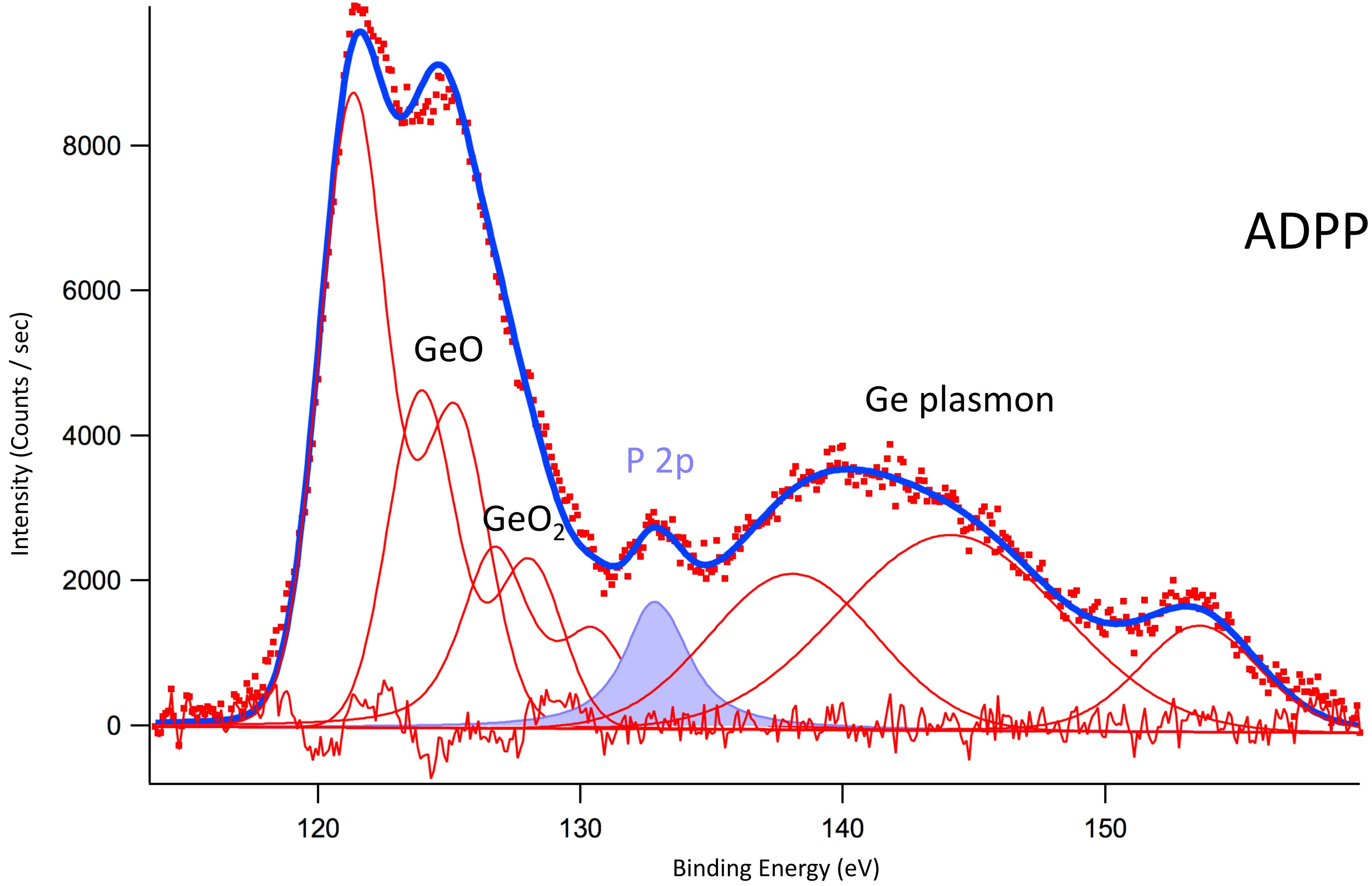
An oxide interlayer forms between the precursor and the germanium bulk.



GeO$_x$ layer: 3,2 $\pm$ 0,4 ML

XPS: ADPP molecule





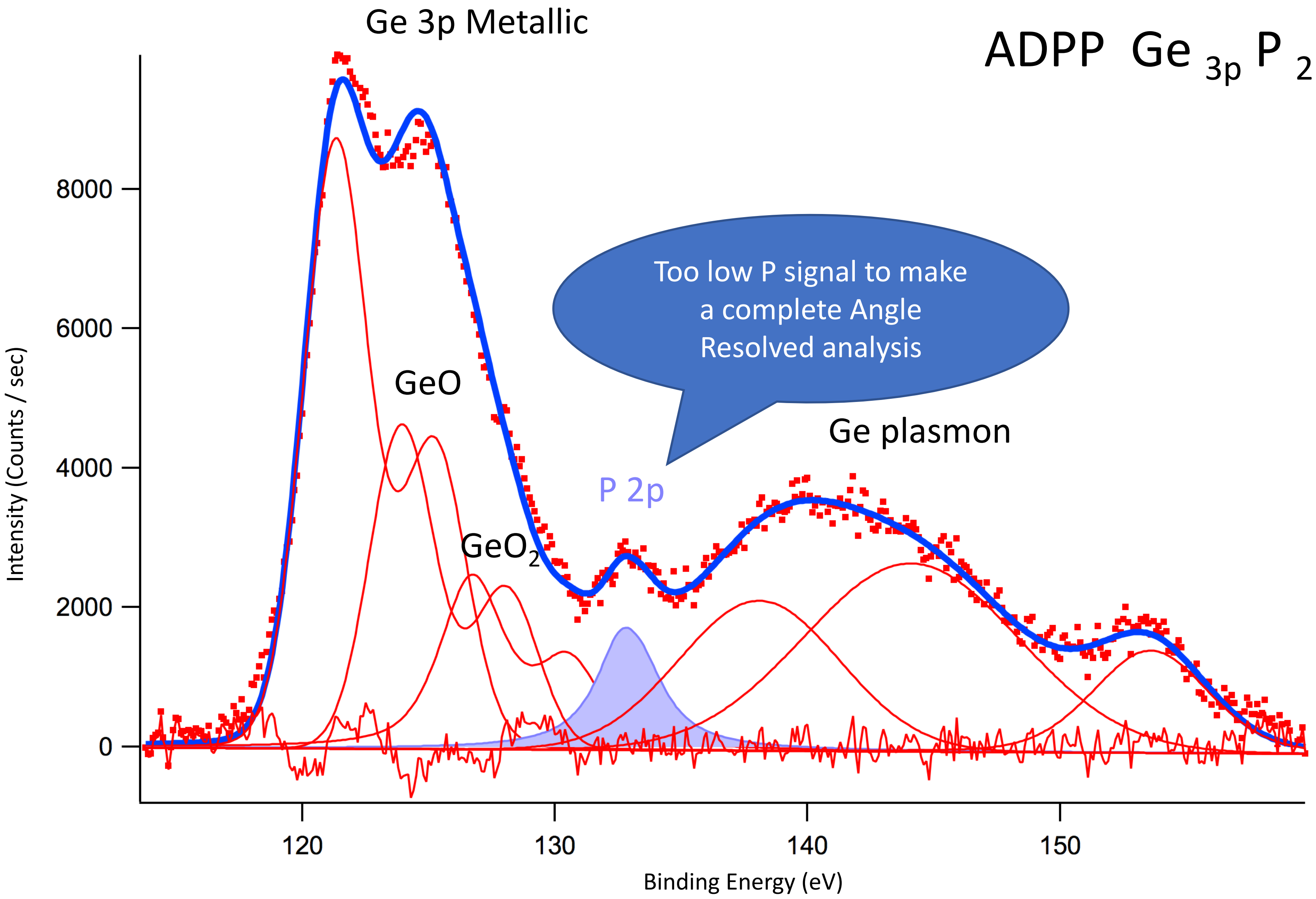
ADPP Ge $_{3p}$ P $_{2p}$ Analysis @ 20°

P layer: 0,5 ML

(NRA cross check)

GeO_x layer: 4 ML ± 1

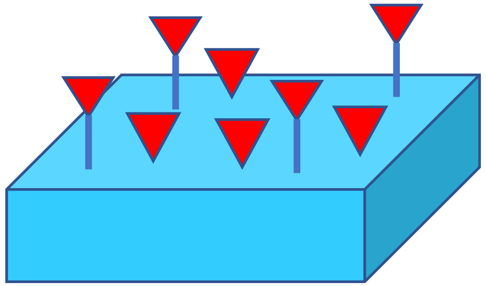
XPS: ADPP molecule

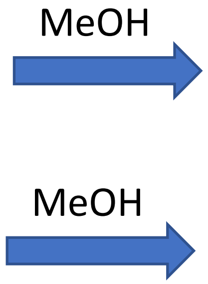


ADPP Ge $_{3p}$ P $_{2p}$ Analysis @ 20°

Surface Characterizations starting from Ge-H surface

Precursor	ML
DPP	4,3 $\pm$ 0.3
ODPA	1,9 $\pm$ 0.3
ADPP	0,5 $\pm$ 0.3

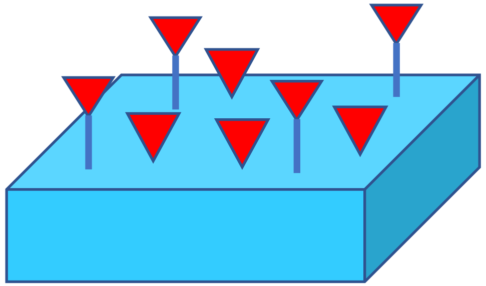




Rinsing procedure to remove physisorbed fraction

Surface Characterizations starting from Ge-H surface

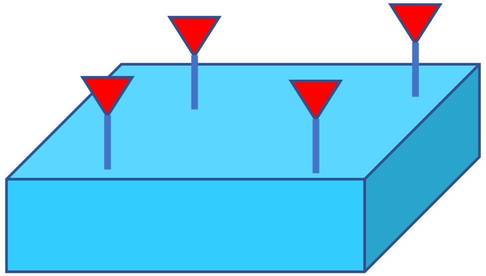
Precursor	ML
DPP	4,3 $\pm$ 0.3
ODPA	1,9 $\pm$ 0.3



MeOH →

MeOH →

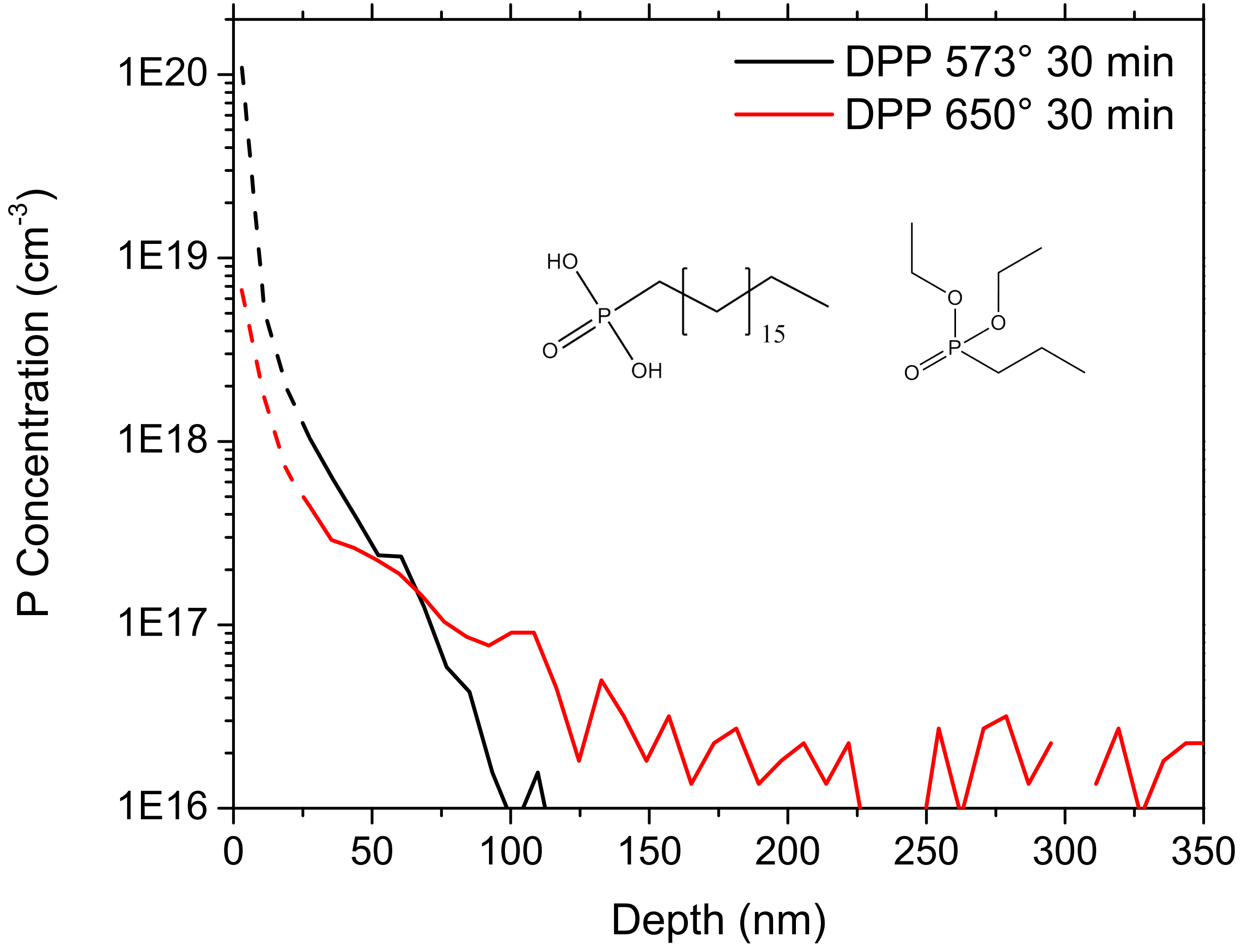
ML
1,9 $\pm$ 0.3
1,2 $\pm$ 0.2

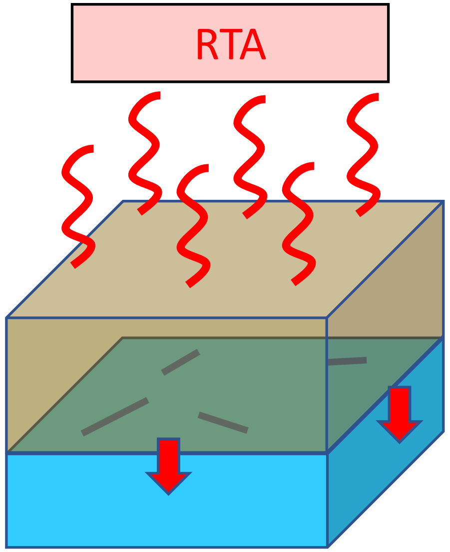


Strong Physisorbed fraction still remain

Rinsing procedure to remove physisorbed fraction

Thermal Annealing Results: SIMS analysis

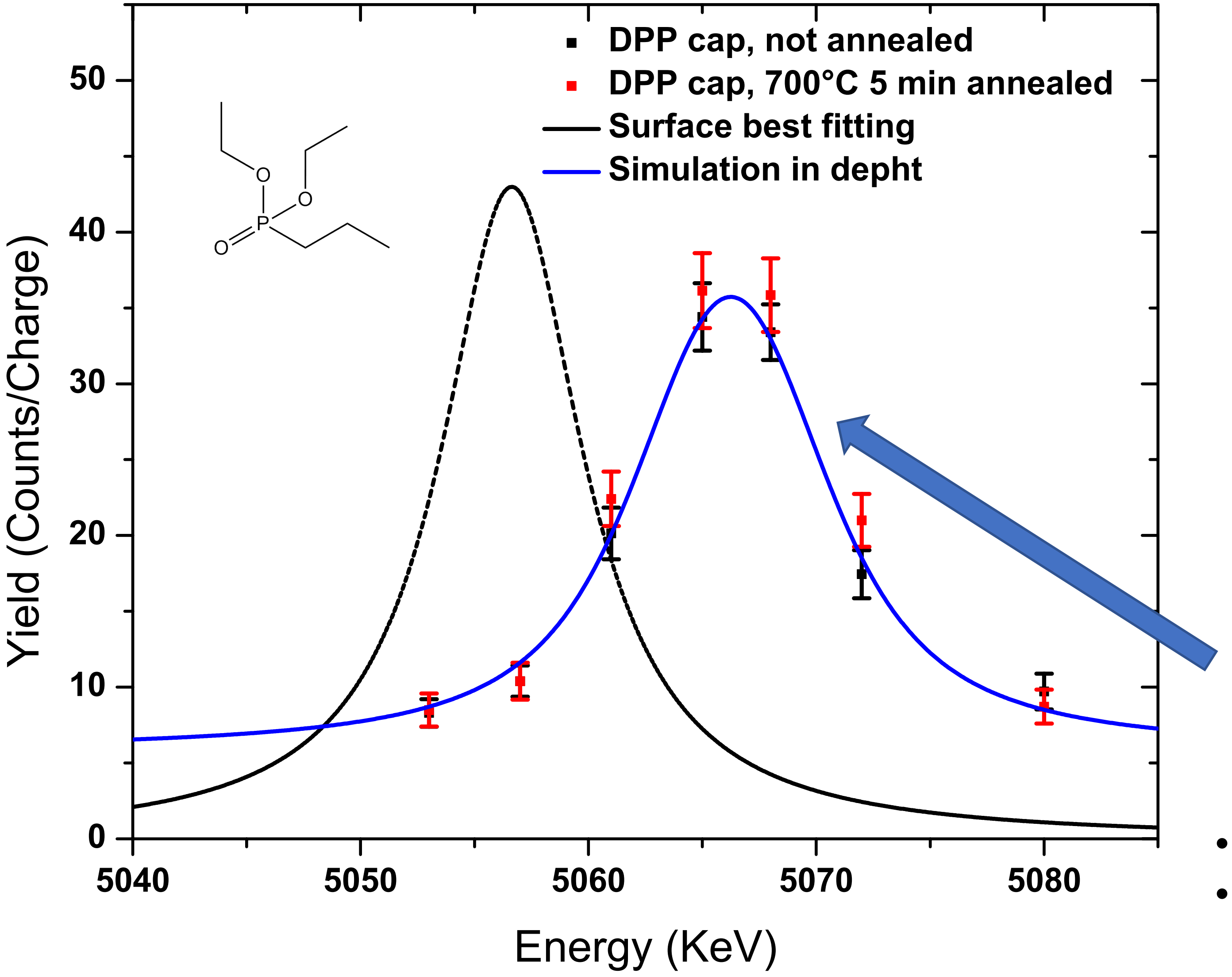




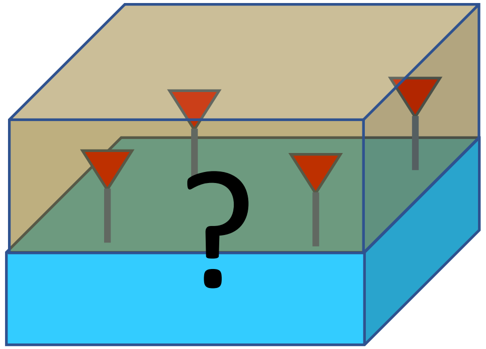
- Very low signals: dose << 1%
- Not reproducible profiles
- Profiles comes from localized signals

NO clear evidence of diffusion

NRA in depth: DPP



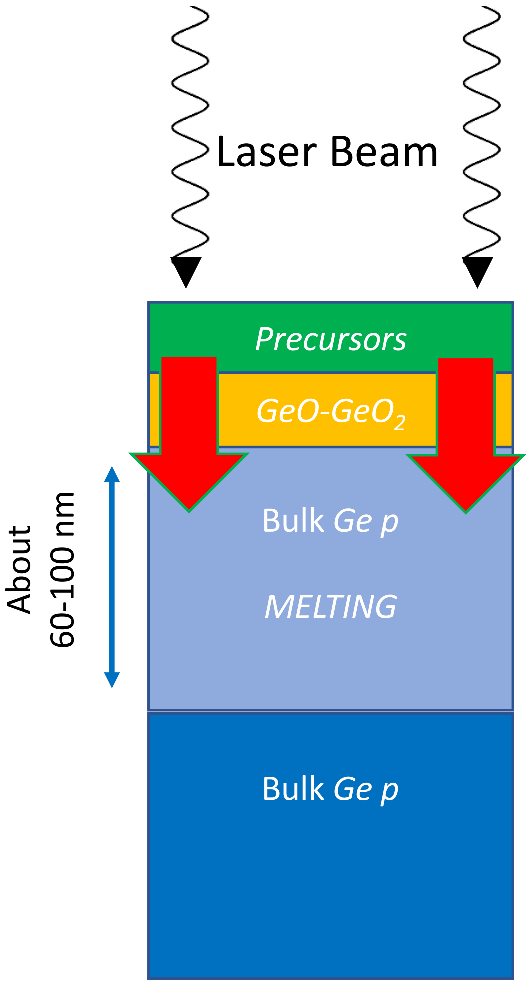
Where is Phosphorus after Thermal Annealing?

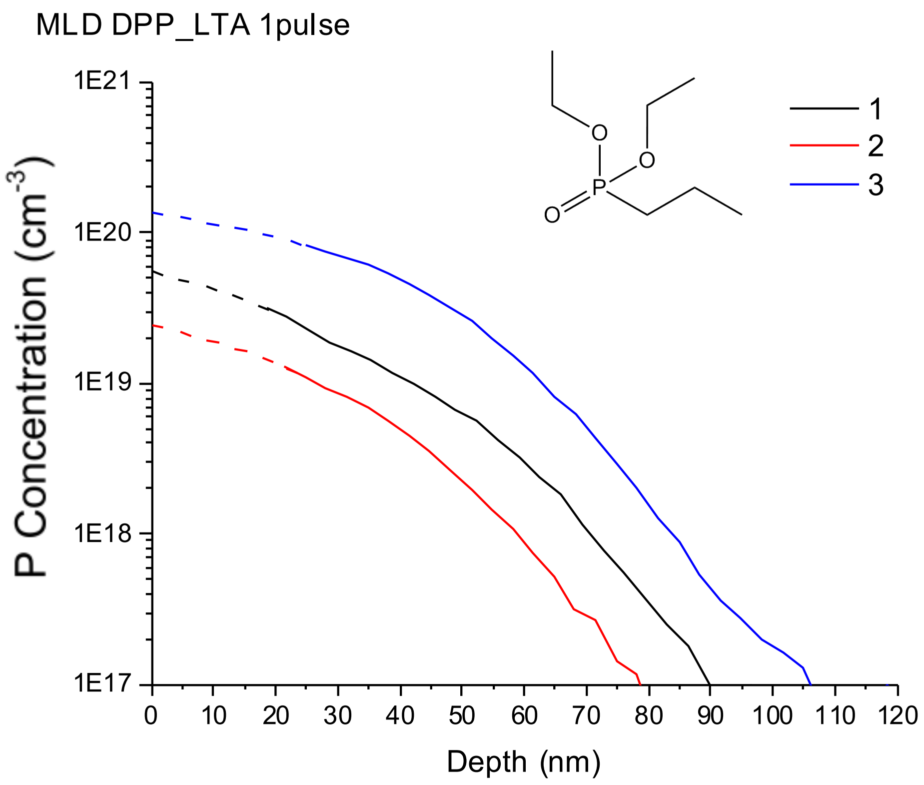


The Phosphorus remain at the SiO_2 – Ge interface

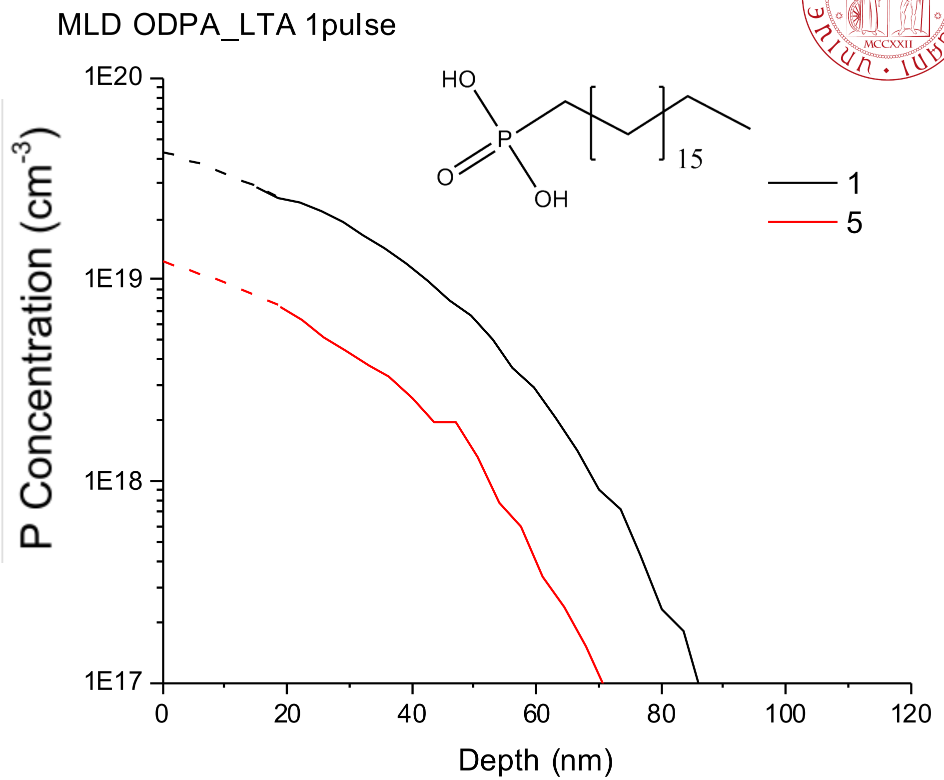
- Is 3 ML of GeO_x a diffusion barrier?
- Can we degradate the molecules with a thermal annealing smaller that the Ge start to melt?

Laser Thermal Annealing





8% of diffused dose



6% of diffused dose

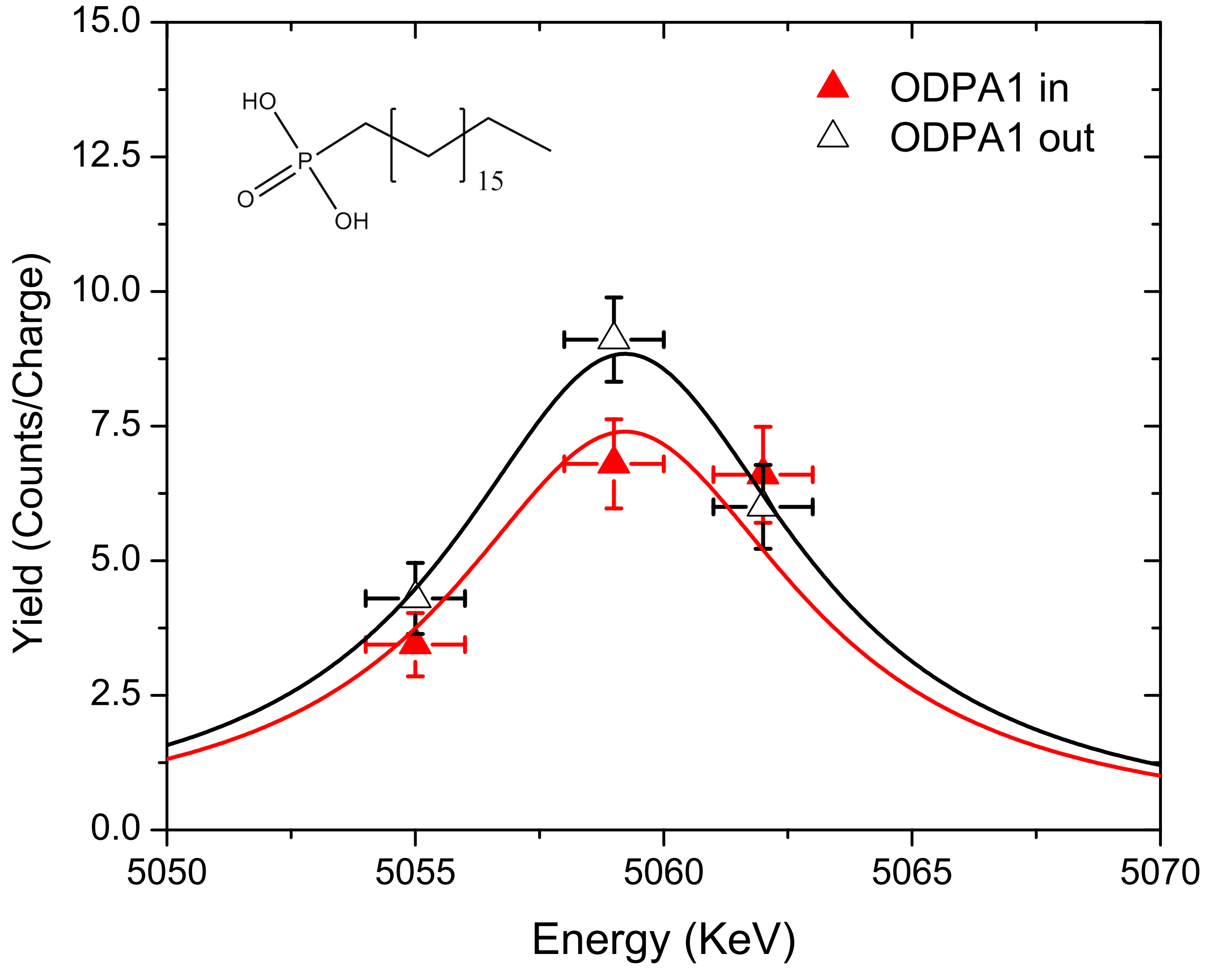
- The P diffuse inside Ge in both cases
- There are fluctuations of the P surface concentration
- Maybe molecules are not well laterally distributed on the surface.

NRA after LTA: residual surface P

We check the residual P on surface.

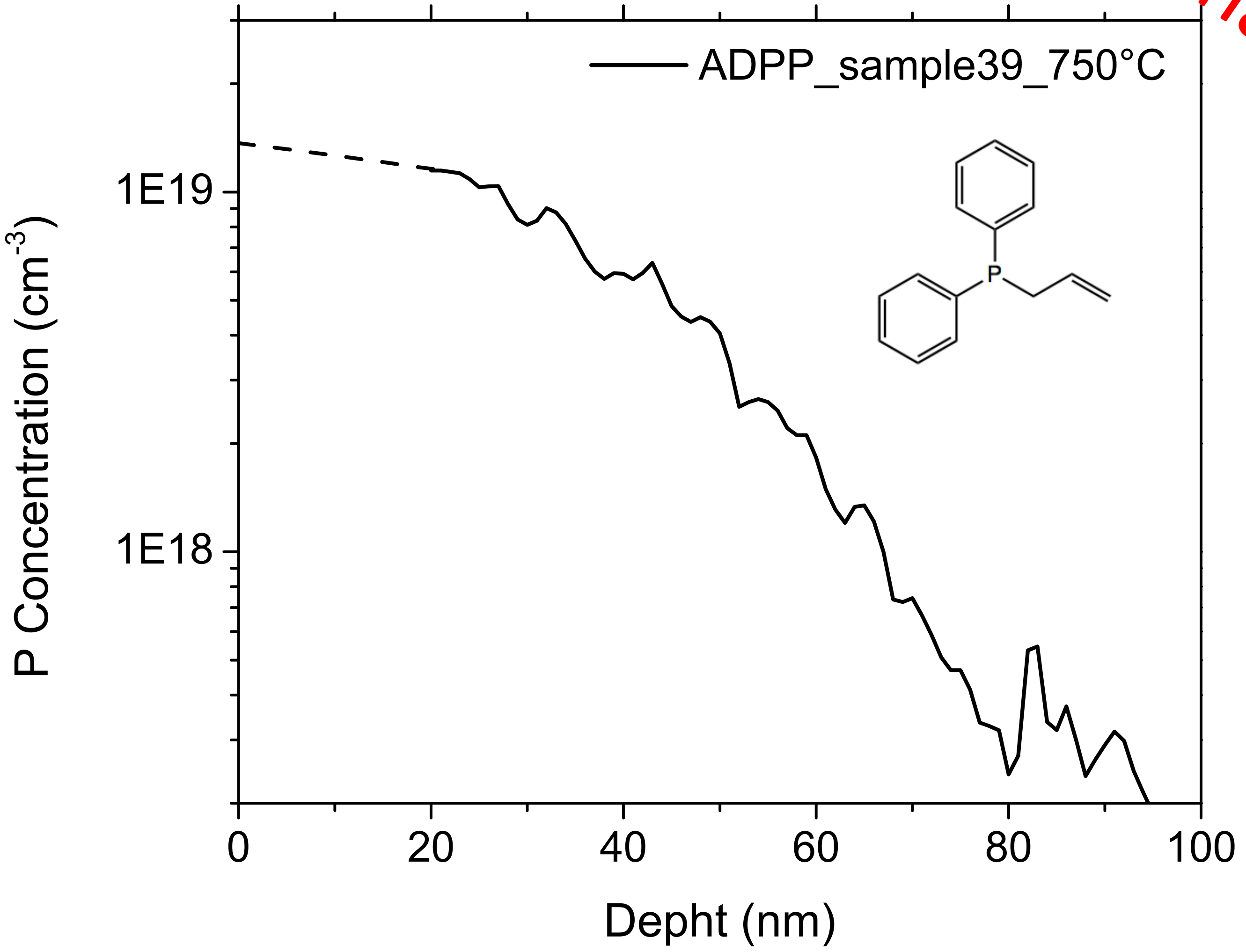
The residual P remains on surface

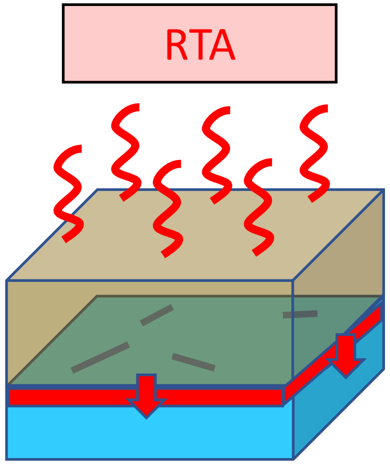
ODPA Surface NRA quantification example



Thermal Annealing Results: ADPP

Preliminary results





NRA in depth reveal that most of P remains at SiO_2 - Ge interface

Conclusion

- MLD processes cause Ge oxidation

- The P quantification and the surface oxidation characterization confirm the literature's reaction:

  - DPP physisorbed after Ge oxidation **>** 2 ML
  - ODPA chemisorbed ~ 1 ML
  - ADPP chemisorbed only on the Ge-H surface ~ 0.5 ML

- ADPP is the most promising candidate for P thermal in-diffusion

- DPP and ODPA act as a source for Laser Annealing doping

In the near future

- Optimize the deposition and the thermal treatment for ADPP precursor
- Deepen the chemical analysis of the ADPP functionalized Ge surface
- Probe the activation of the diffused dopant
- LTA on ADPP precursor

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