COST Action TUMIEE (CA17126) - 18th July 2022, Crete.

Ultrafast Transient Absorption Spectroscopy of Some Potential EUV Resist Molecules

R McGarry[1], S Durkan[2], L Varvarezos[2], M Pryce[1], M Shaw[3] and J T Costello[2]

1. School of Chemical Sciences and NCSR, Dublin City University, Dublin 9, Ireland
2. School of Physical Sciences and NCPST, Dublin City University, Dublin 9, Ireland
3. Intel Ireland Ltd., Leixlip, Ireland

Science Foundation Ireland sfi For what's next

DCU

https://dcu-seai-laserab.com http://uf-dynamics.org https://www.dcu.ie/physics/people/john-costello

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Ultrafast Transient Absorption Spectroscopy of an EUV Candidate Resist Molecule

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Firstly

DCU
Ollscoil Chathair
Bhaile Átha Cliath
Dublin City University

- We are an Intense Laser Matter Interactions Group
- Laser Plasma Diagnostics (Optical & Particle)
- Laser Plasma Spectroscopy (UV, VUV and EUV)
- Dual Laser Plasma Photoabsorption (VUV & EUV)
- Photoionization in Ultrafast FEL (or FEL + IR) Fields
- UTAS is a completely new option & technique for us
- So, I'm talking about something I know little about
- For a reason….

Motivation

Huge number of synthesis + steady state analysis resist papers published over more than two decades now

Analysis mainly using NMR and FTIR but also UV-Vis and MS

Little done/known about dynamics on a femtosecond timescale

Industry has many questions about dynamics

Very large nvestments (being) made in IMEC[1] and ARCNL[2]

EUVL (being) rolled out e.g., in TSMC and INTEL (FAB 34 - Ireland)[3]

So, collaboration established with synthetic chemistry colleagues (funded by SFI exploratory grant)

1. https://www.kmlabs.com/news-and-events/icaleo-2020
2. https://arcnl.nl/research-groups/high-harmonic-generation-and-euv-science
3. https://www.eenewseurope.com/en/asml-ships-euv-scanner-to-irish-fab

Sample Industry Questions

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- Are there good and bad ways to increase photon absorption?
- How many electrons can the resist use for good chemistry?
- Are all electrons created equal (e.g., Photo vs Auger)?
- What are the e-driven reactions occurring in the resist?
- Are they competing reactions?
- Can reactions be controlled (even suppressed)?

- One also needs to understand chemical noise (stochastic effects) and its effect on e.g., LER/LWR

In summary

Ollscoil Chathair Bhaile Átha Cliath
Dublin City University

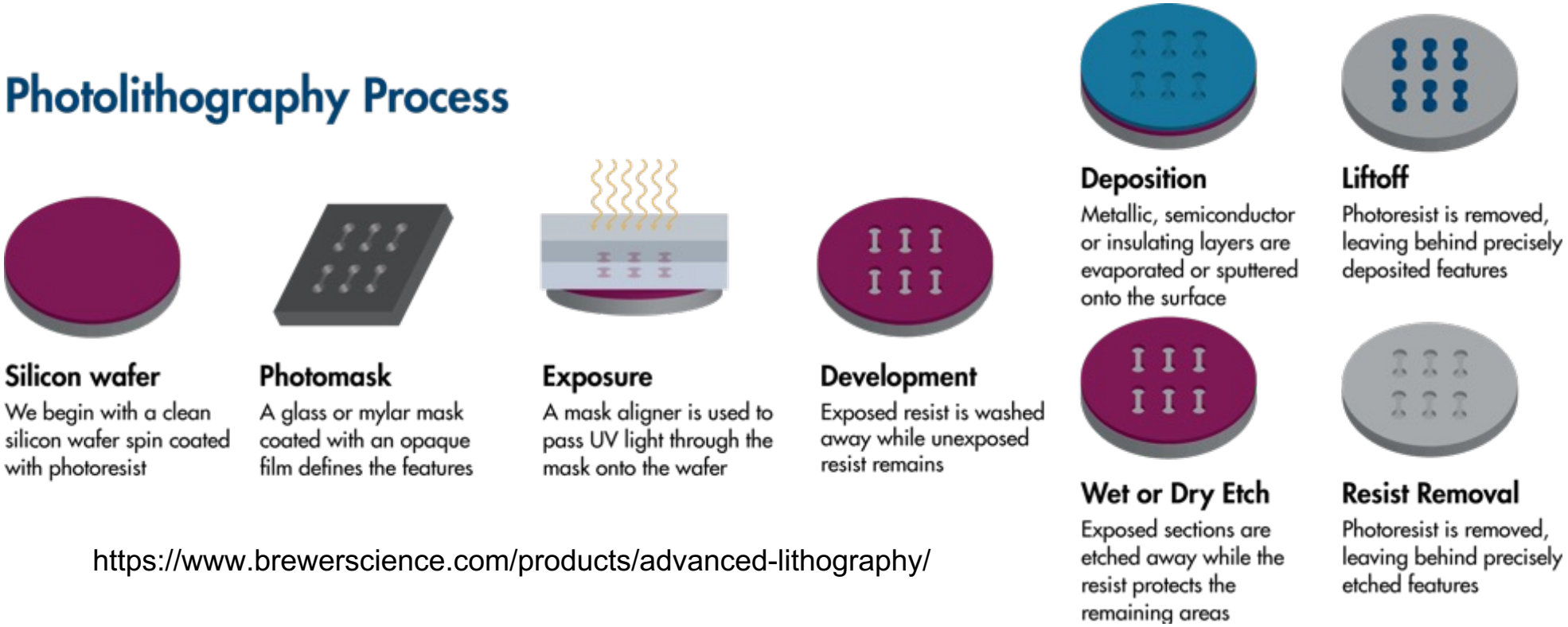
Radiation chemistry fundamentals (experiment and modeling) are believed to be the way forward to enhance photoresist design - ‘wafer-based learning is no longer sufficient’

Talk Outline

Ollscoil Chathair
Bhaile Átha Cliath
Dublin City University

- EUVL – Some Fundamentals
- EUVL – Current Candidate Resist Types
- UTAS Experimental Setup
- (Very) Preliminary Measurements
- Perspective

Some Fundamentals



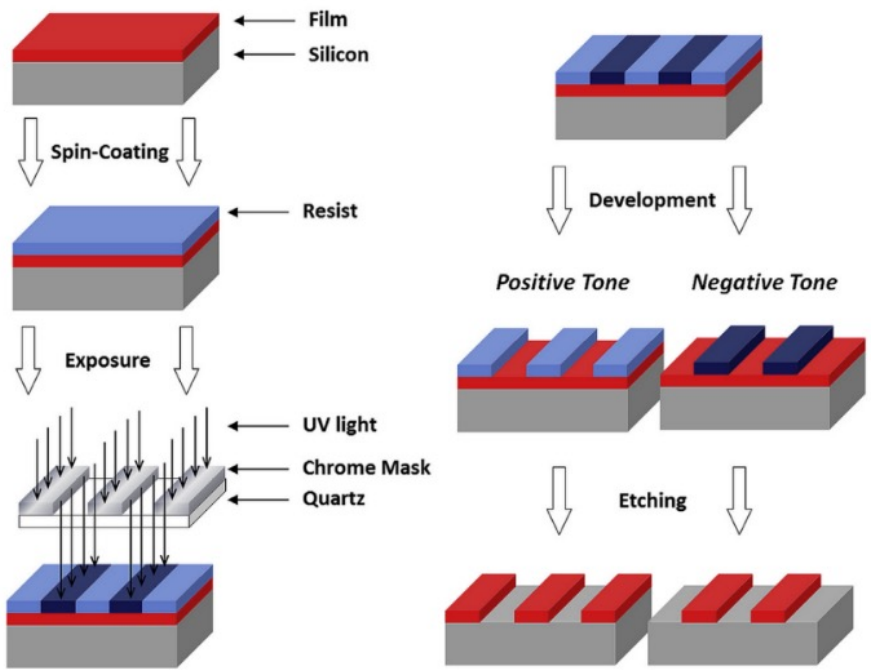
https://www.brewerscience.com/products/advanced-lithography/

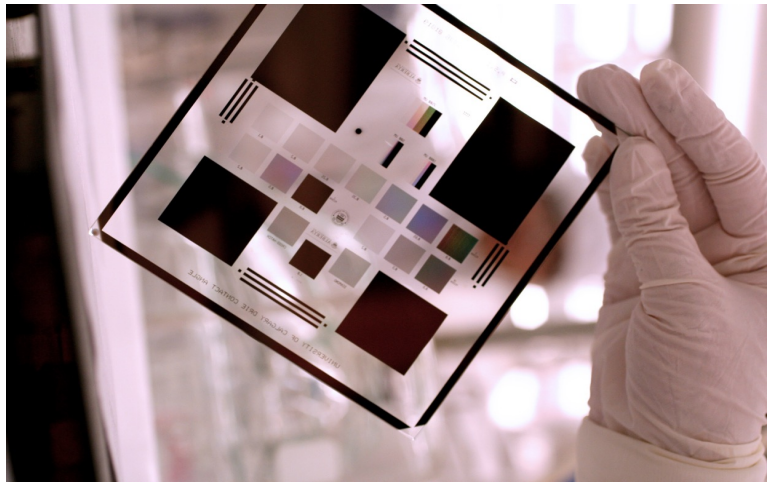
$$Resolution = k.\frac{\lambda}{NA}$$

$K_{typ.} \sim 0.25$

Some Fundamentals

- Photolithography is a key step in the manufacture of ICs
- Uses light to imprint patterns (think of it as old style photographic recording)
- A photoresist is a light sensitive material, applied to the surface (the emulsion)
- When exposed to light, it undergoes a solubility change - (de)protection
- The resist can become more soluble (positive tone) via fragmentation or less soluble (negative tone) through cross-linking or polymerization.





Global Extreme Ultraviolet Lithography EUVL Systems Market Research Report 2022 - https://www.researchandmarkets.com

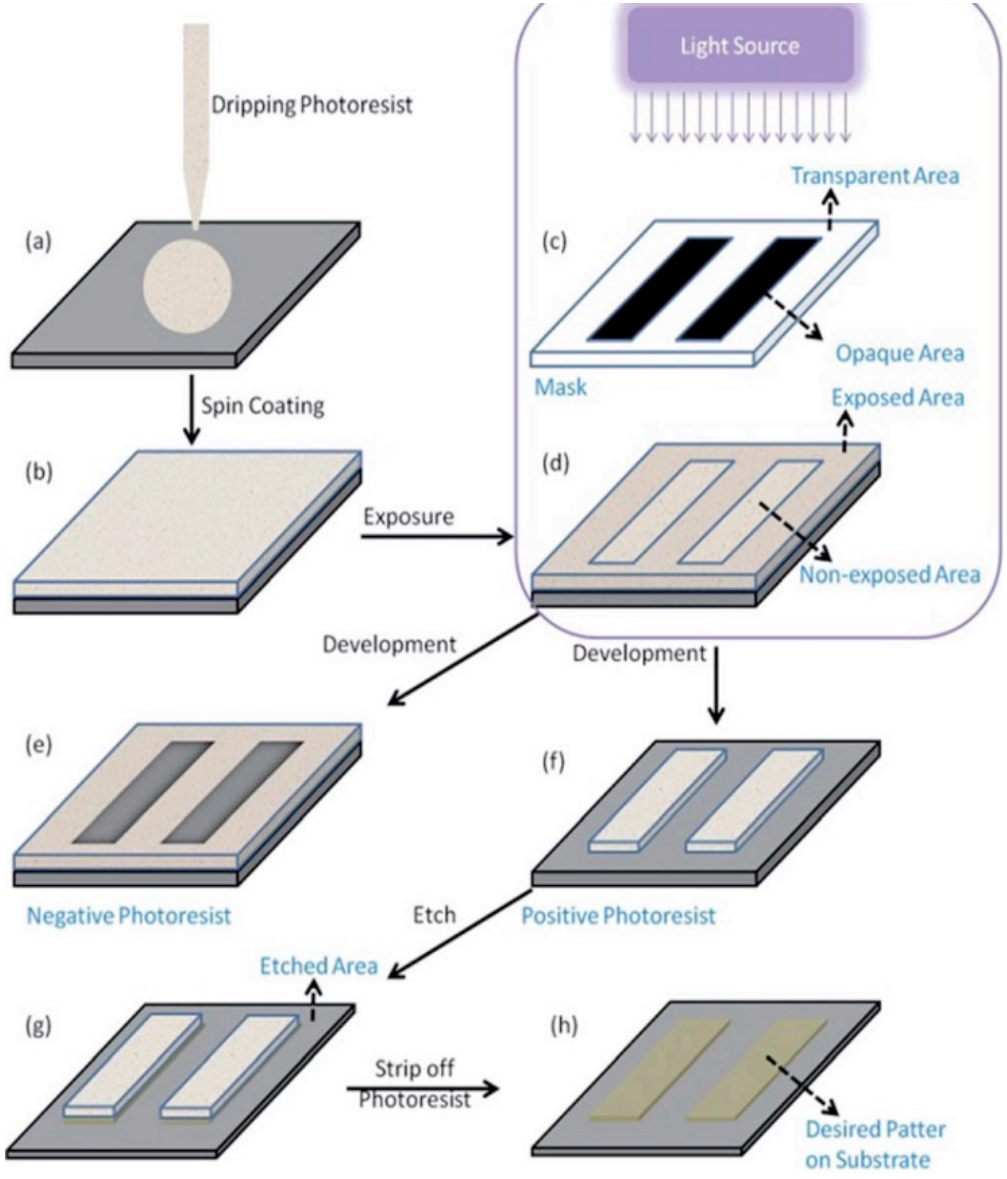
Some Fundamentals

Current Standard: UV Immersion Lithography

Theoretical limit for 193 nm lithography, i.e., 36 nm half-pitch patterning, has been reached

Usage of double and triple patterning techniques has extended UV(I)L shelf-life, but has also resulted in an increase in manufacturing steps and costs

RSC Adv., 2020, 10, 8385-8395 - DOI: 10.1039/C9RA08977B



Some Fundamentals

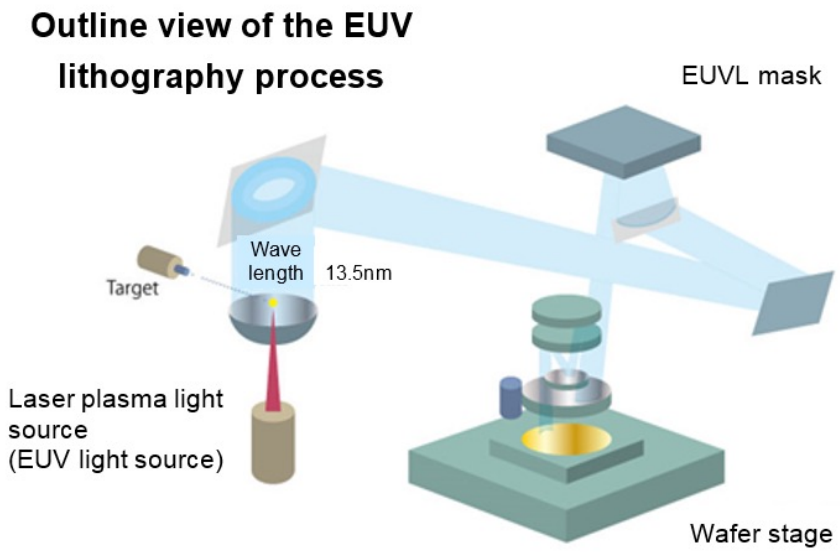
EUV (13.5 nm) vs UV (193 nm)

Absorption at the (Sn) 13.5 nm wavelength

Carried out in vacuum

Allows for printing of patterns X14 smaller than with 193 nm (Rayleigh criterion)

EUV Lithography (EUVL) will allow for sub-7 nm patterned circuits

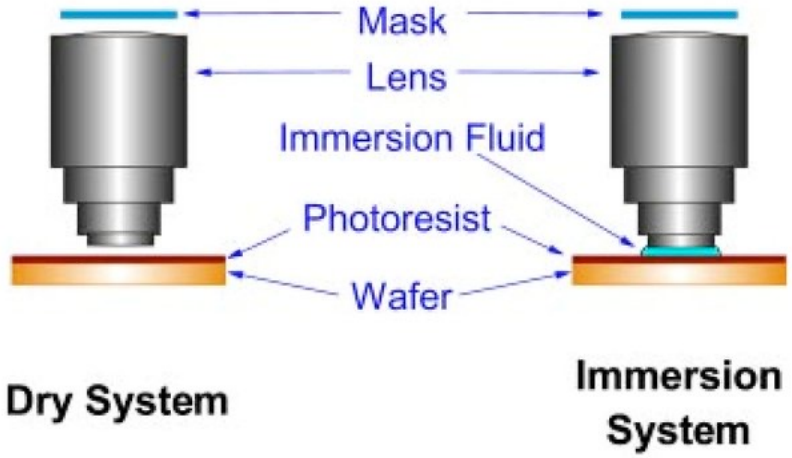


Absorption at the (ArF) 193 nm wavelength

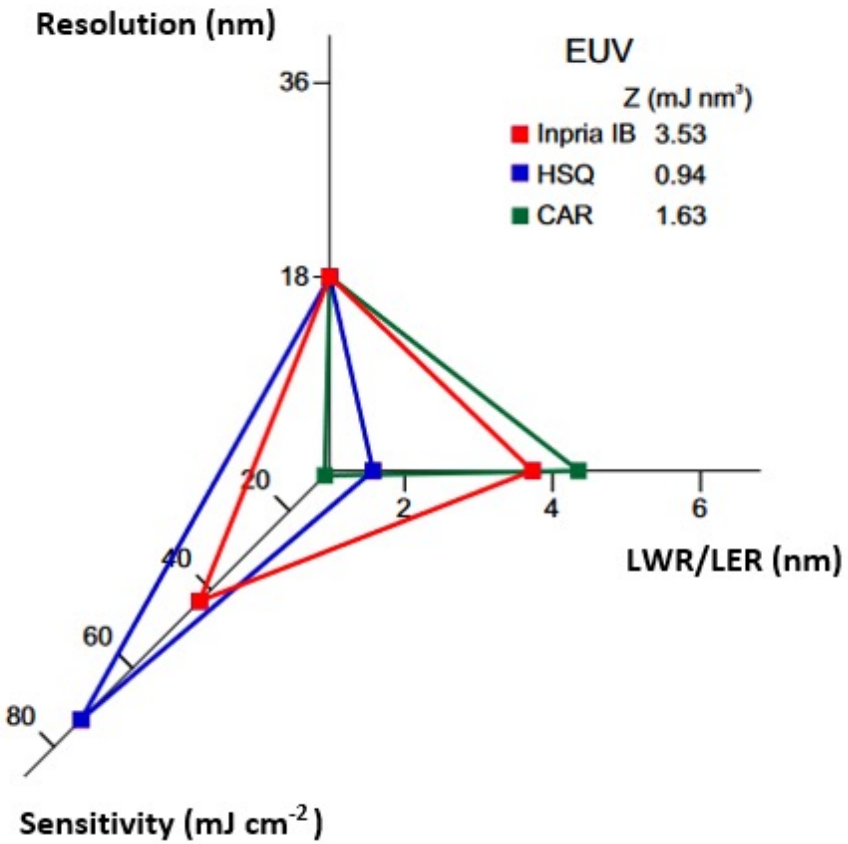
Wafers immersed in water during manufacture

Improves resolution by ~refractive index of the liquid component

Allows for double or triple patterning



Some Fundamentals



RLS targets:

- Resolution: <20nm
- Line Edge Roughness (LER): <20% (nm)
- Sensitivity (D_0): <20 mJ cm^{-2}
- RLS Displayed as Triangles

Figure of Merit:

$Z = D_0 \times (LER)^2 \times (HP)^3$ (mJ/nm^3)

NP (MOx): Nanoparticle Resists (https://www.inpria.com)
HSQ: Hydrogen Silsesquioxane Resists (non-CAR, https://www.aqmaterials.com)
CAR: Chemically Amplified Resist (https://www.jsrmicro.be)

Proc. SPIE **7972**, 797202 (2011) / https://doi.org/10.1117/12.882955

Current Candidate Resist Types

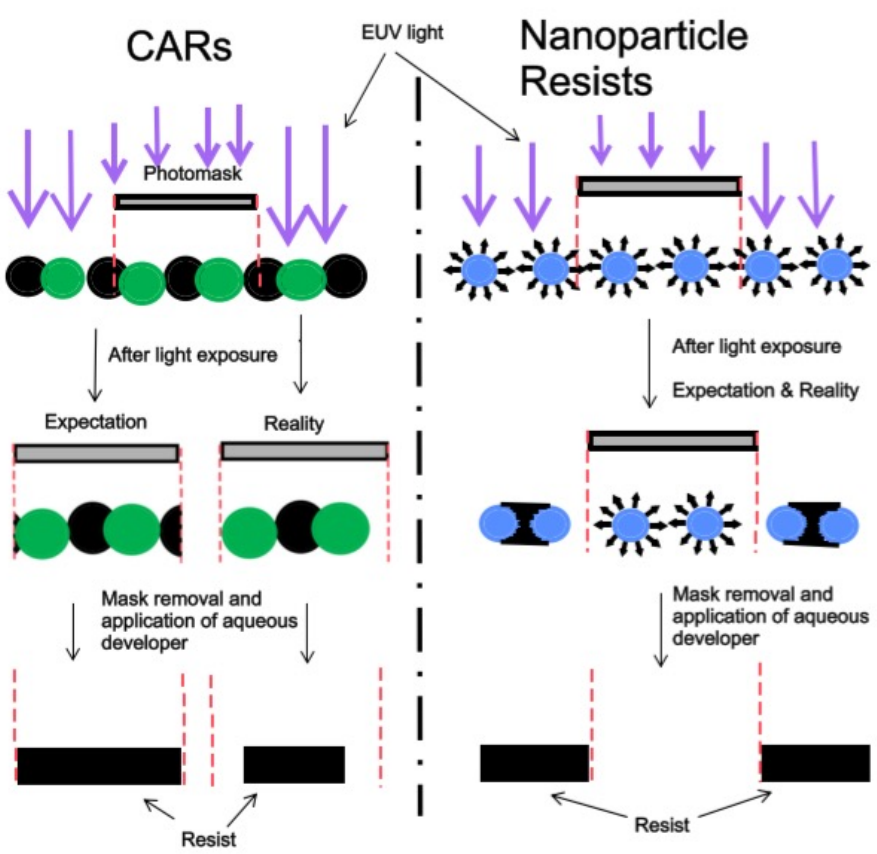
Currently – four resist types under investigation for EUVL

1. Chemically Amplified (CAR)
2. Nanoparticle (NPR)
3. Multi-Trigger (MTR)
4. Organo-Metallic (OMR)

Current Candidate Resist Types

Chemically Amplified Resists (https://www.jsrmicro.be)

Invented by IBM research to increase the resist sensitivity of Diazonaphthoquinone (DNQ) or Novolac*



- An acid amplifier is a compound added to improve RL**S** performance of photoresists. It works in conjunction with a photoacid generator
- The photoacid generator (PAG) is a molecular group that generates acids can then defuse into the polymer chain and catalyses the deprotection of the side groups, which in turn leads to a reduction in the energy requirement of the photoinduced reaction. This lowers the dose of 13.5 nm required improving the sensitivity of the polymer
- Acid seepage, leading to poor LER/LWR values is the main weakness

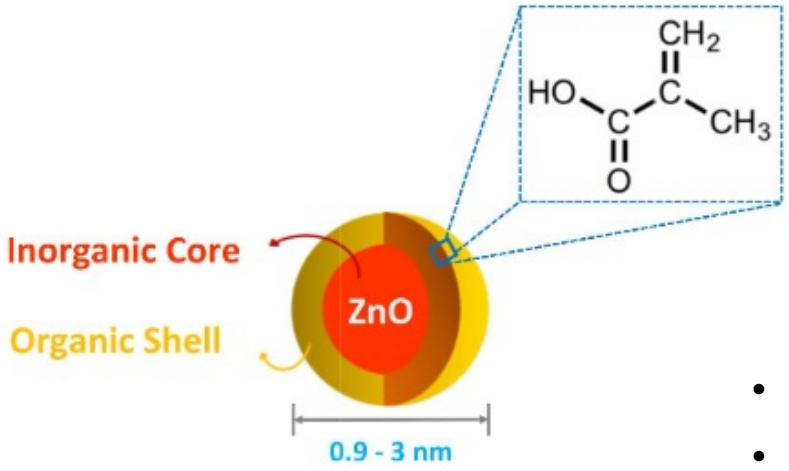
* VLSI Technology, 1982. Digest of Technical Papers. Symposium on, pp. 86-87, Sept 1982.

Muyoung Kim et al., Macromolecules **51**, pp6922−6935 (2018)

Current Candidate Resist Types

Nanoparticle (MOx) Resists (https://www.inpria.com)

Methacrylic acid (MAA) modified zirconium (or hafnium) oxide nanoparticles (ZrO_2 -MAA-NP or HfO_2 -MAA-NP) tend to produce the best over-all RLS performance



- CARs are slowly being phased out and replaced with nanoparticle resists (NPRs). Commercial NPRs are (currently) based on a tin or hafnium- oxide NPs
- Zinc-oxide based nanoparticles possess small size, good solubility in spin-coating solvents, good film-forming ability, but moderate pattering performance under deep-UV irradiation

- EUV light hits exposed resist area
- EUV light is absorbed by the ligands (photoacid spikes)
- The ligands join with the neighbouring nanoparticle if the neighbour nanoparticle has also absorbed a photon.
- The exposed resist area hardens, and the unexposed area is washed away by aqueous developer
- The final resist pattern has sharp edges and very sturdy features due to the metallic core of tin or hafnium.

N Thakur et al. J Mater Chem C. Vol. 8, pp. 14499-14506 (2020).

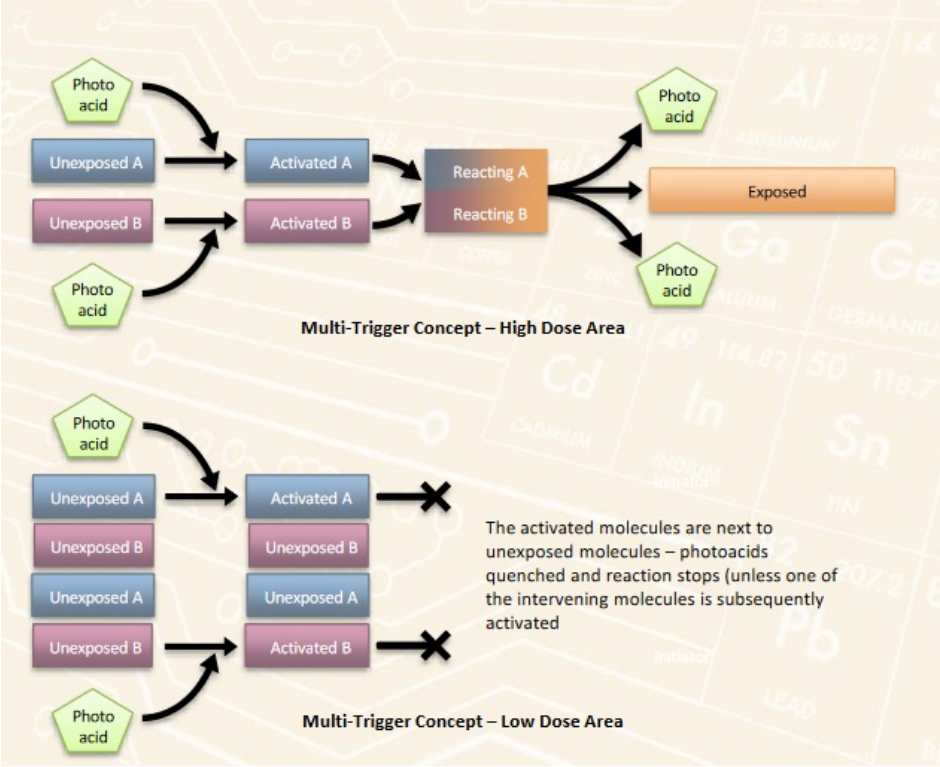
H Xu et al., Proc. SPIE **10583**, 105831P (2018) https://doi.org/10.1117/12.2297266

M Krysak et al. Proc SPIE **9048**, 904805-1 (2014) https://doi.org/10.1117/12.2046677

Current Candidate Resist Types

Multi-Trigger Resists (https://irresistiblematerials.com)

Negative-tone crosslinking resist
Post Exposure Bake (Not required)
High Spatial Resolution (R) and Low Line-Edge Roughness (LER) values



Journal of Photopolymer Science and Technology. Vol 31, pp 227-232 (2018).

- EUV photons produce ‘initiators’ (e.g., acid species) in the PAG
- The initiators activate the resist molecules
- If two activated resist molecules are adjacent, they react and releases the initiators (Figure, Top Panel).
- If two activated resist molecules are not adjacent, then the initiators remain bound and there is no reaction (Figure, Bottom Panel).
- This mechanism prevents acid species moving away from its initial location (this problem happens in CARs and nanoparticle resists), thus helping MTRs achieve higher resolution and lower LER values in comparison to NPRs and CARs.

Current Candidate Resist Types

OMRs - Pd Oxalate: DPPM-Pd-C_2O_4

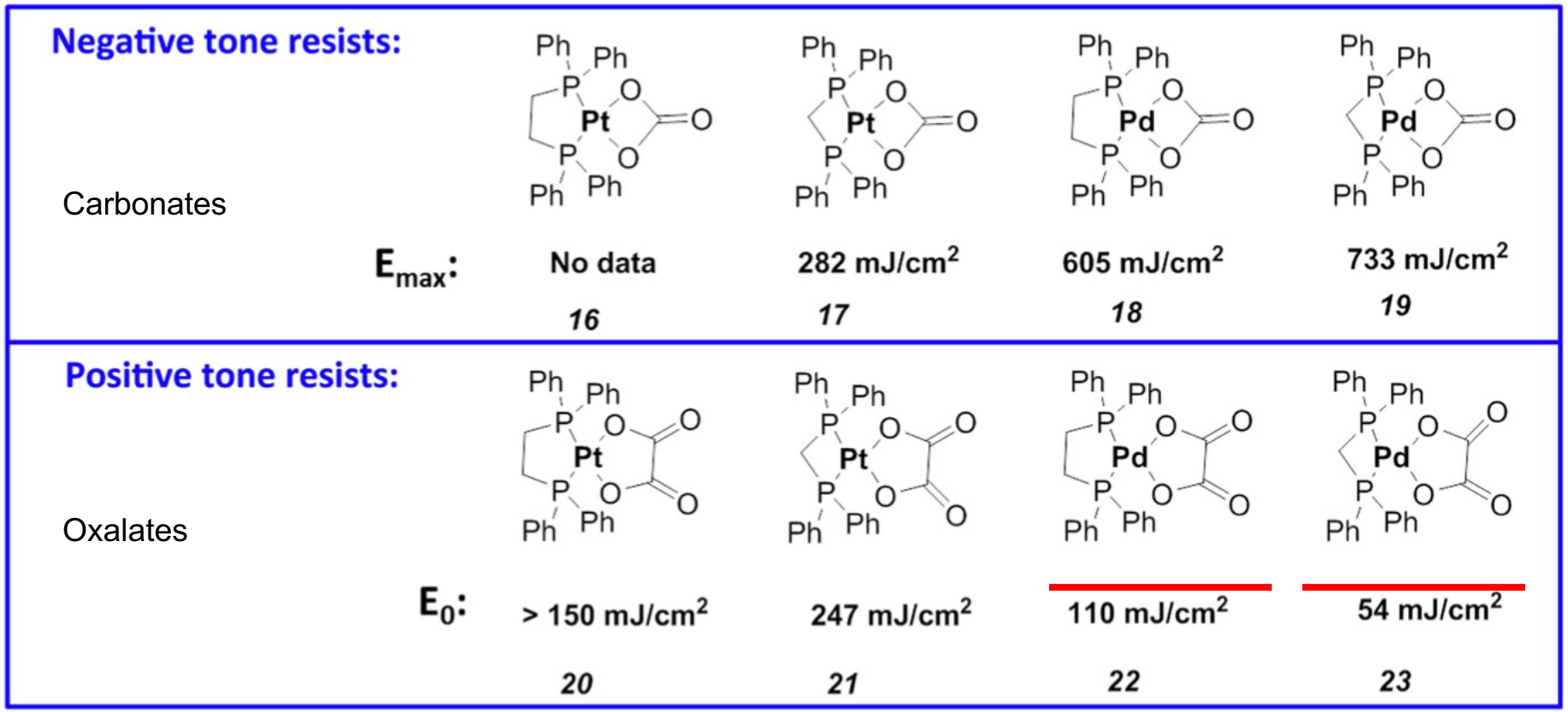


Fig. 4 $L_2M(C_2O_4)$ and $L_2M(CO_3)$ evaluated for EUV sensitivity. (a) Platinum and palladium carbonates showing negative-tone behavior. (b) Platinum and palladium oxalates showing positive-tone.

1,1-Bis(diphenylphosphino)methane (dppm), - $\mathbf{CH_2(PPh_2)_2}$

Miriam Sortland et al., J. Micro/Nanolith. MEMS MOEMS **14**, Art. No. 043511 (2015)

Current Candidate Resist Types

OMRs – Pd/Pt Oxalates (vs Carbonates & Azides)

Findings – Sortland et al.

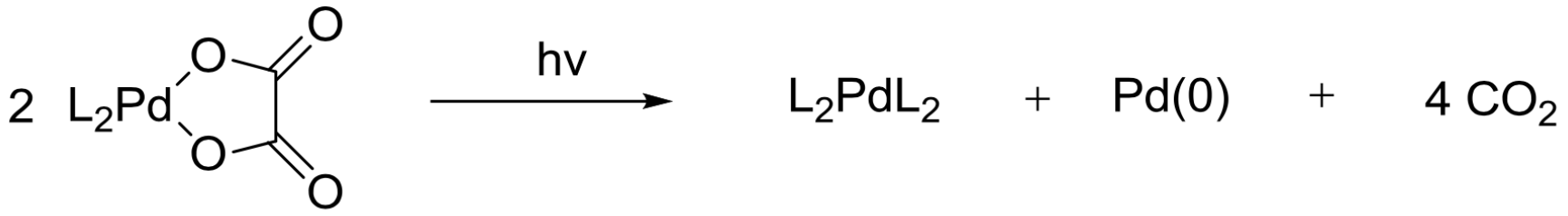
- Many platinum & palladium complexes show little or no EUV sensitivity
- Metal carbonates and metal oxalates ($L_2M(CO_3)$ and $L_2M(C_2O_4)$; M - Pt or Pd) are sensitive to EUV
- Palladium-based resists are more sensitive than platinum-based resists – compare 21 with 23 (Fig 4, previous slide)
- Photo-mechanistic studies to date on L2M(C2O40 in the literature are experimental, at long wavelengths, in solution and usually not in air

Miriam Sortland et al., J. Micro/Nanolith. MEMS MOEMS **14**, Art. No. 043511 (2015)

Current Candidate Resist Types

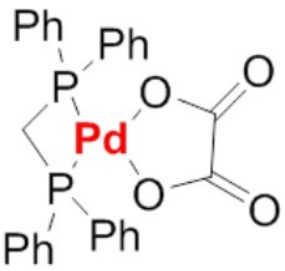
OMRs - Pd Oxalate: Photo-Mechanism (Summary)

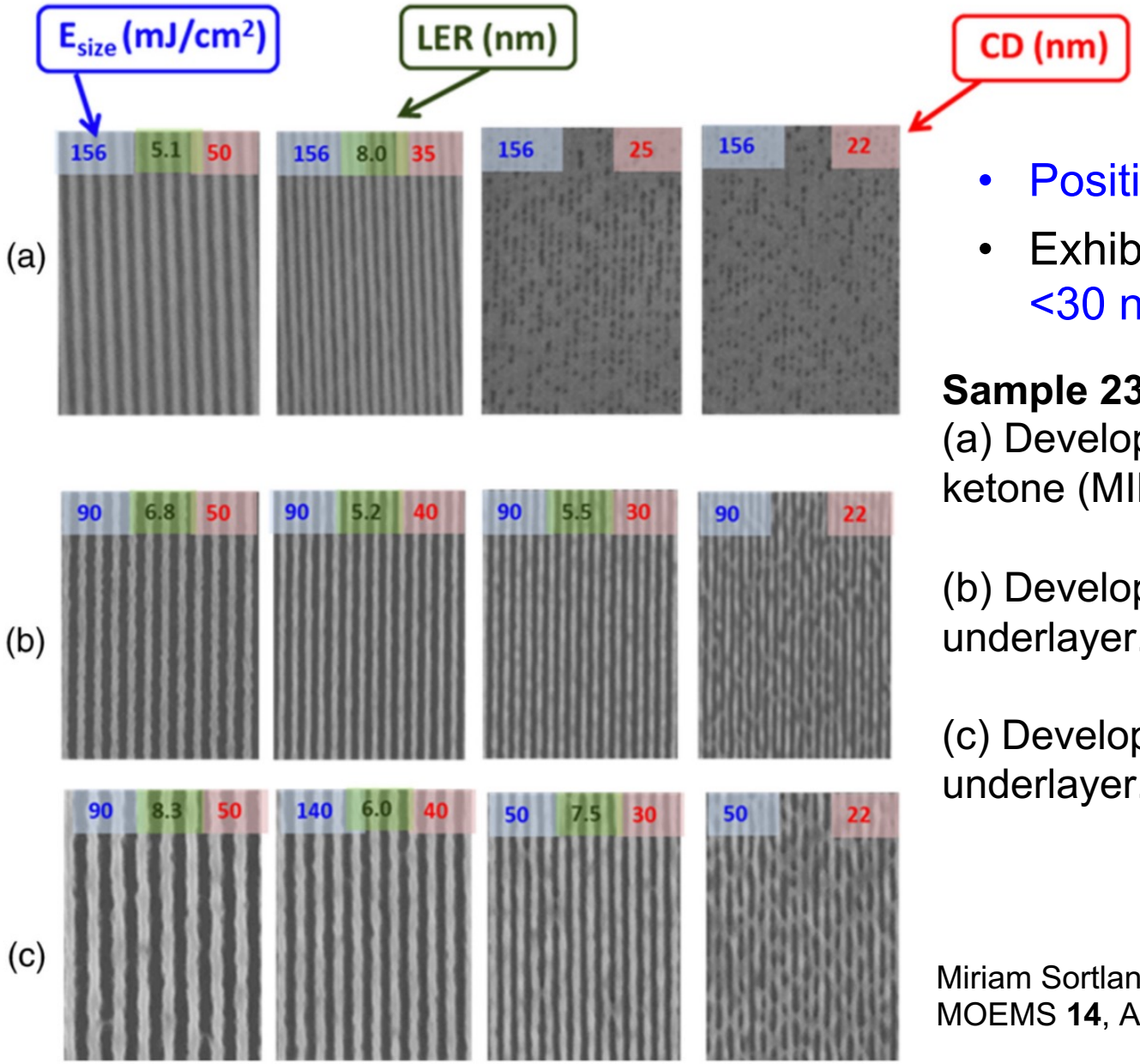
- Exposing $L_2PdC_2O_4$ to an EUV photon results in the reductive elimination of 2 equivalences of CO_2 and the formation of a reactive intemediate L_2Pd
- The L_2Pd reacts with another $L_2PdC_2O_4$ (resist) molecule to form a zerovalent L_2PdL_2 complex, leaving behind a bare Pd metal atom and 2 x CO_2 – i.e., remaining Pd-DPPM complex reforms bond to another complex (Pd-Pd)



Miriam Sortland et al., J. Micro/Nanolith. MEMS MOEMS **14**, Art. No. 043511 (2015)

OMRs - Pd Oxalate: DPPM-Pd-C_2O_4 (Summary Performance)





- Positive tone photoresist
- Exhibits good performance, <30 nm half-pitch

Sample 23:
(a) Developer: 10% methyl isobutyl ketone (MIBK)/ toluene, on underlayer.

(b) Developer: 10% MIBK/toluene, no underlayer.

(c) Developer: 20% MIBK/ toluene, no underlayer.

Miriam Sortland et al., J. Micro/Nanolith. MEMS MOEMS **14**, Art. No. 043511 (2015)

Any (Multi-Scale) Modelling Available?

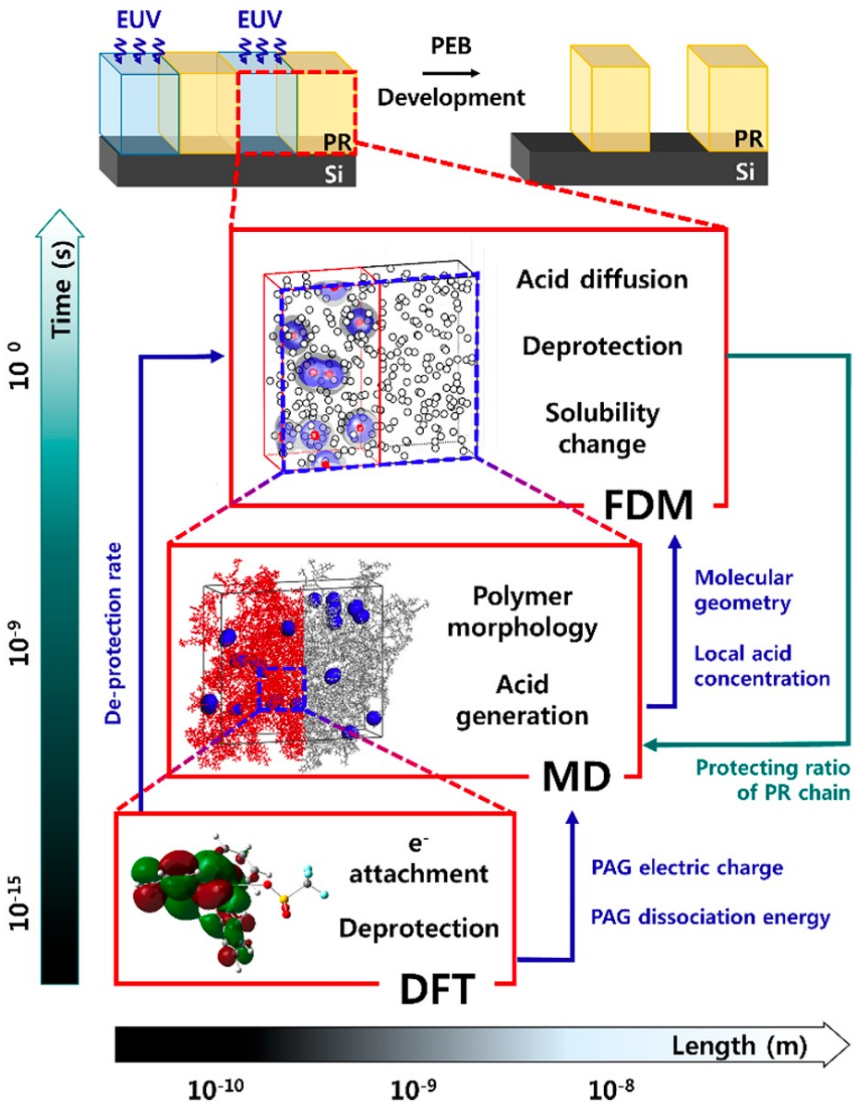


Figure 1. Sequential framework of the multiscale model: integration of density functional theory (DFT), molecular dynamics (MD), and the finite difference method (FDM).

Muyoung Kim et al., Macromolecules **51**, pp6922−6935 (2018)

Positive tone-chemically amplified resist (CAR), poly(hydroxystyrene-co-[tert-butoxy-carbonyl]oxystyrene), or P(HOSt-co-tBOCSt)

PAG, triphenylsulfonium triflate (TPS-tf), loaded by 5.68−30.12 wt% of the resist

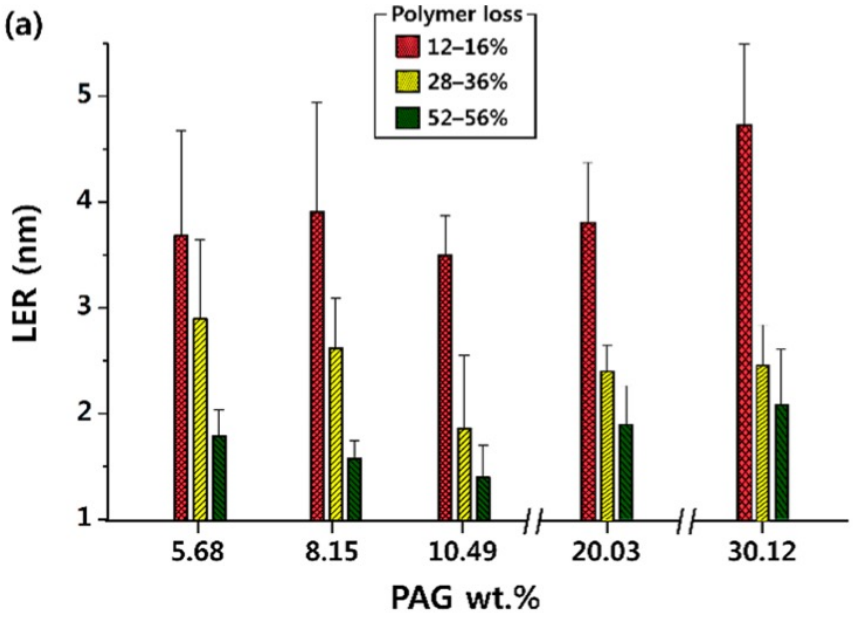


Fig. 10 LER variation with PAG concentration 5.68−30.12 wt%

UTAS Experimental Setup

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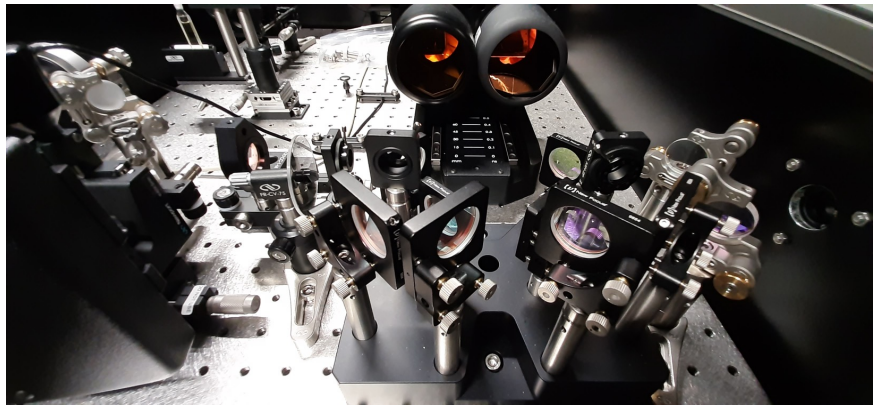
UF Spectroscopy Laboratory

Astrella 30 fs /7 mJ / KHz
Regen Amplifier
(800/ 400/ 267 nm)

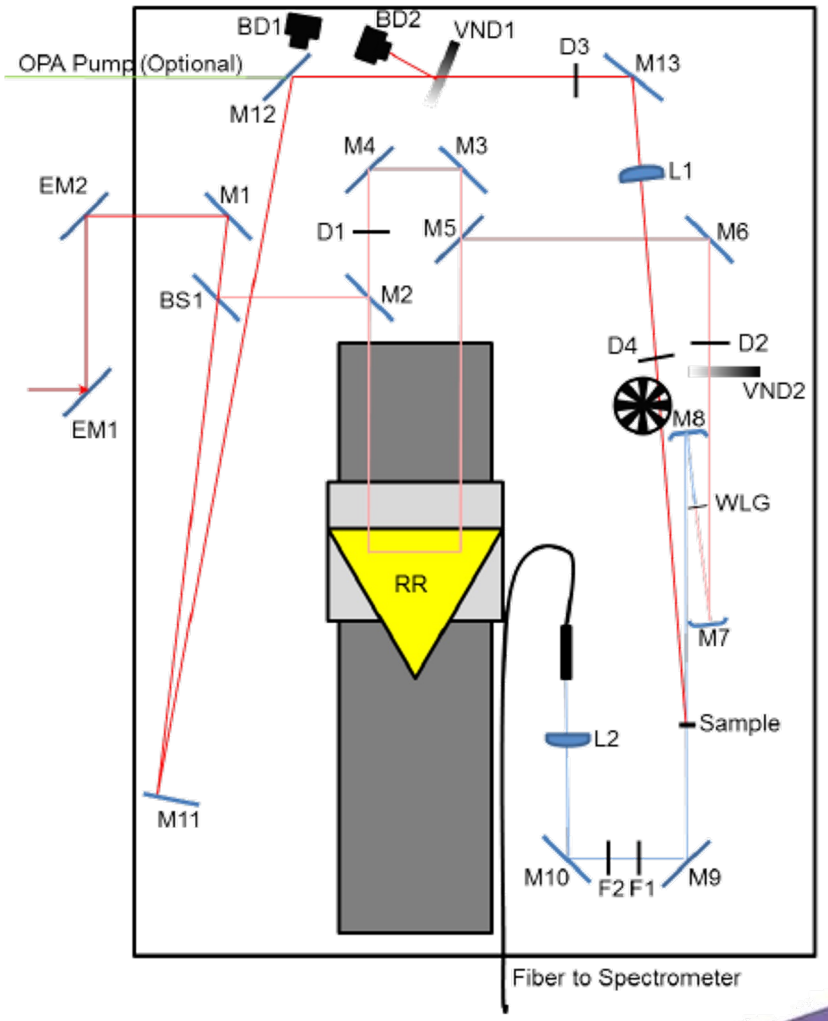
OPAs:
0.2- 2 μm & 2 – 12 μm

Transient 2D-IR (Phasetech) & Newport TAS (350 – 900 nm)

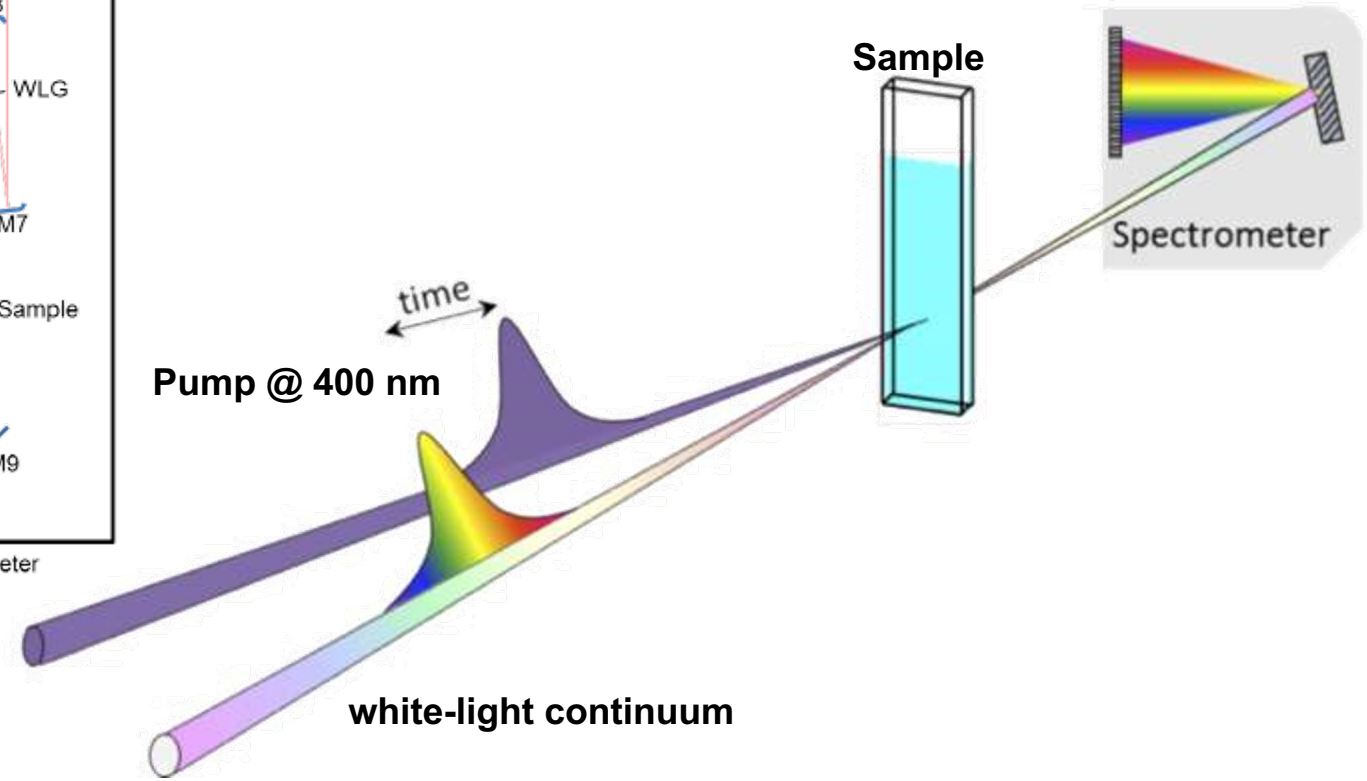


Newport TAS

UTAS Experimental Setup

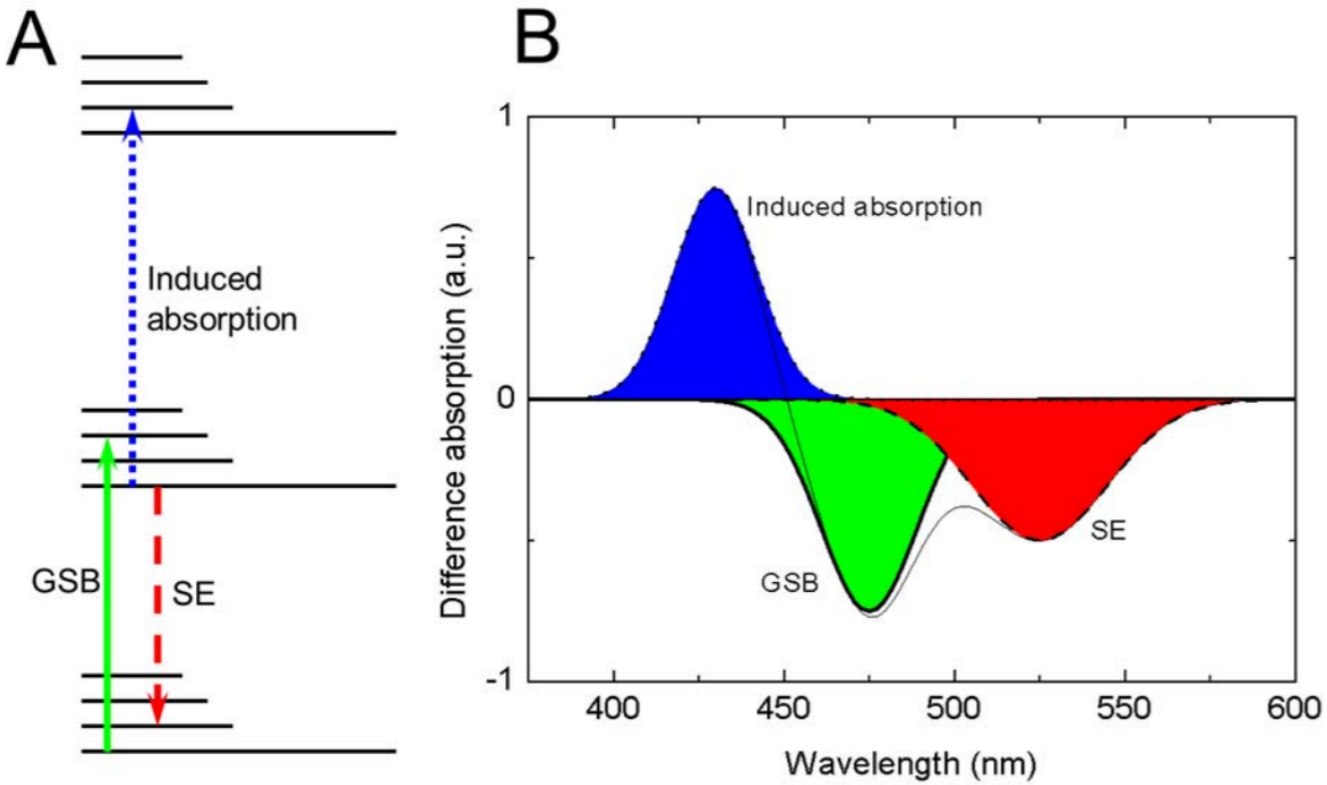


- A monochromatic energetic **pump** pulse triggers a photoreaction
- A time delayed spectrally broad **probe** pulse generates the TA signal.



UTAS Experimental Setup

Phenomena occurring during TA



Ground State Bleaching (GSB)

Simulated Emission (SE)

Induced Absorption (IA)

Very Preliminary Measurements

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Dublin City University

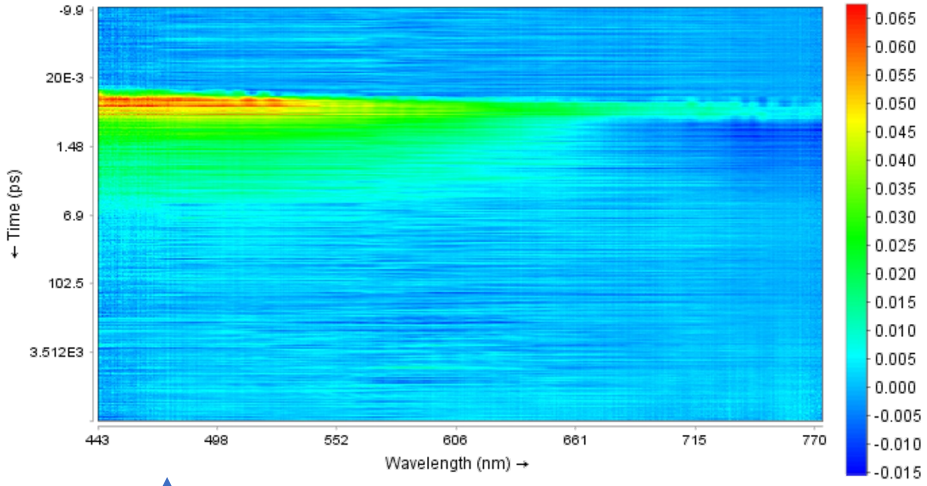
Commercial Resists: Solvent: Acetone, OD_{400nm}: 1
nLOF 2020M - CAR - Negative Tone - h & i line sensitive

AZ ECI 3007 - CAR - Positive Tone - g, h & i line sensitive

AZ 1505 - CAR - Positive Tone - g, h & i line sensitive

Synthesized: Solvent: Dimethylformamide (DMF), OD_{400nm}: 1
Palladium Oxalate DPPM - Positive Tone – EUV line sensitive

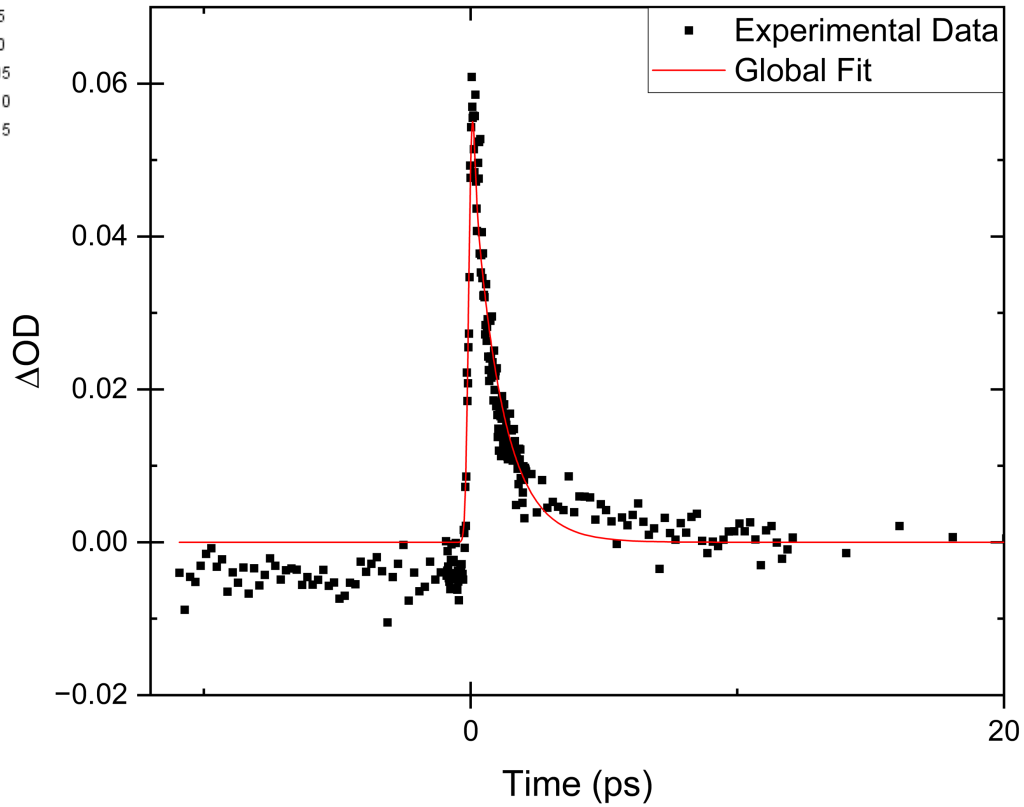
Very Preliminary Measurements (nLOF 2020)



Commercial CAR

Lineout taken at 450 nm

Range 440-770nm

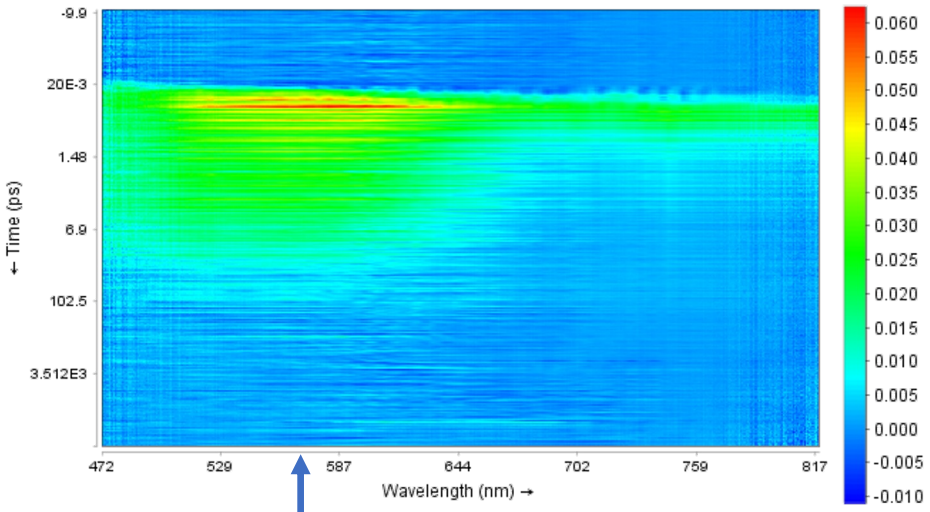


Pump Wavelength: 400 nm/60 fs

Pump (400nm) Power: 4 mW

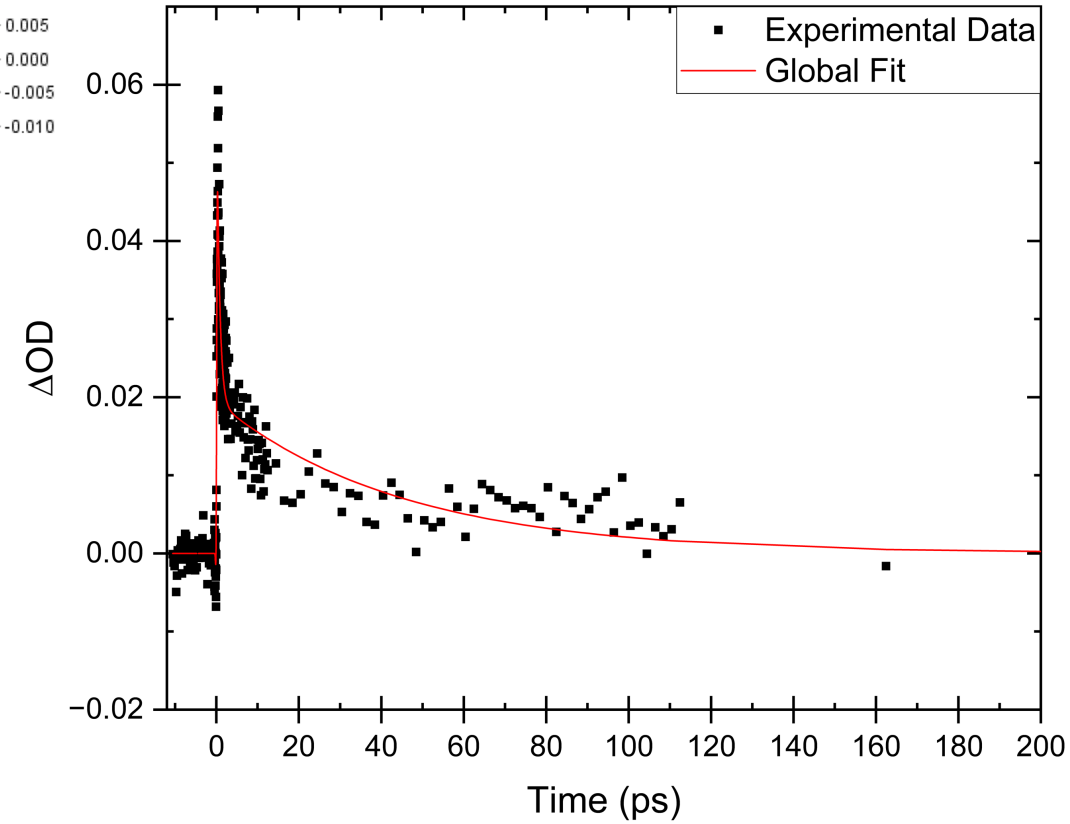
1 Lifetime: 1 ps

Very Preliminary Measurements (AZ ECI 3007)



Commercial CAR

Lineout taken at 560 nm
Range 470-820nm

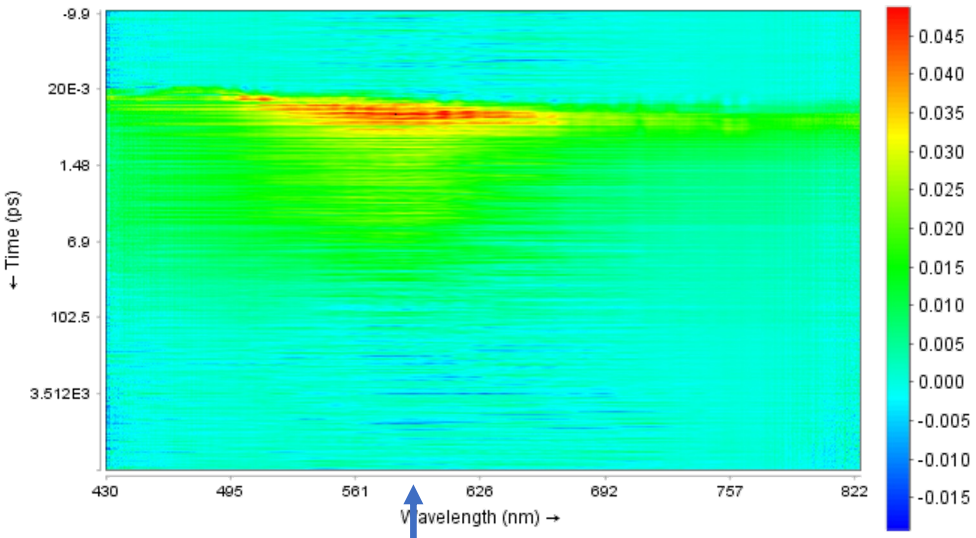


Pump Wavelength: 400 nm/60 fs

Pump (400nm) Power: 3 mW

2 Lifetimes: 700fs, 45ps

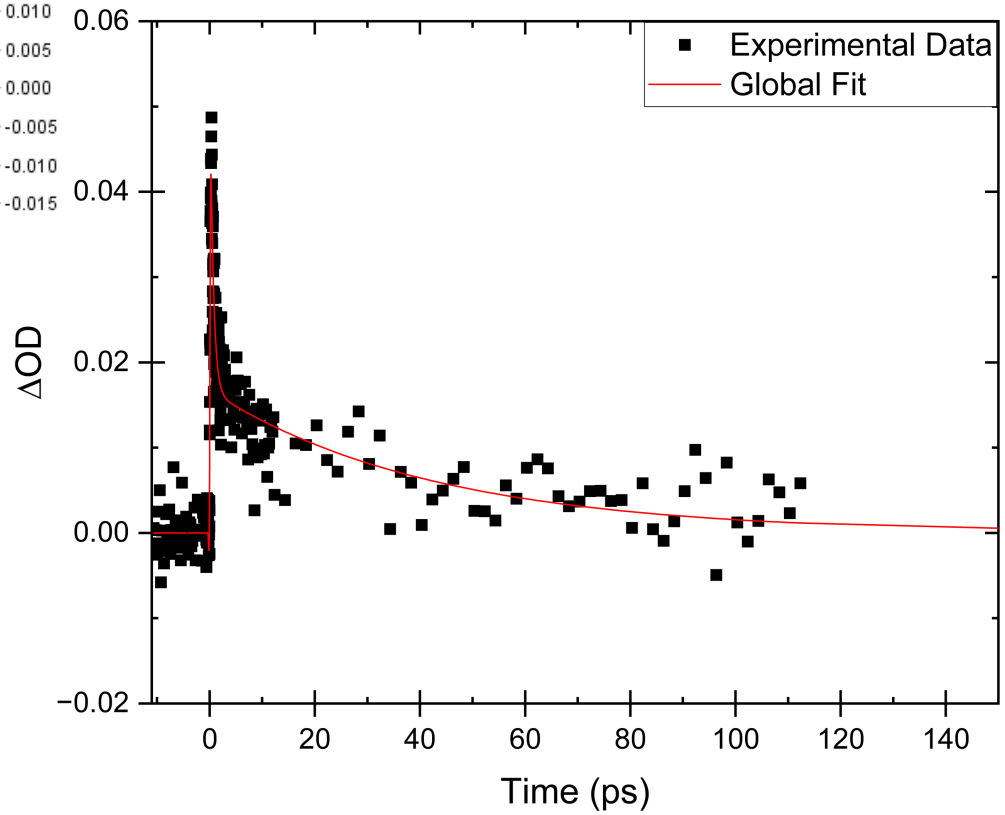
Very Preliminary Measurements (AZ 1505)



Commercial CAR

Lineout taken at 580 nm

Range 430-820 nm



Pump Wavelength: 400 nm/60 fs

Pump (400nm) Power: 2 mW

2 Lifetimes: 600fs, 42ps

Very Preliminary Measurements (DPPM Pd C_2O_4)

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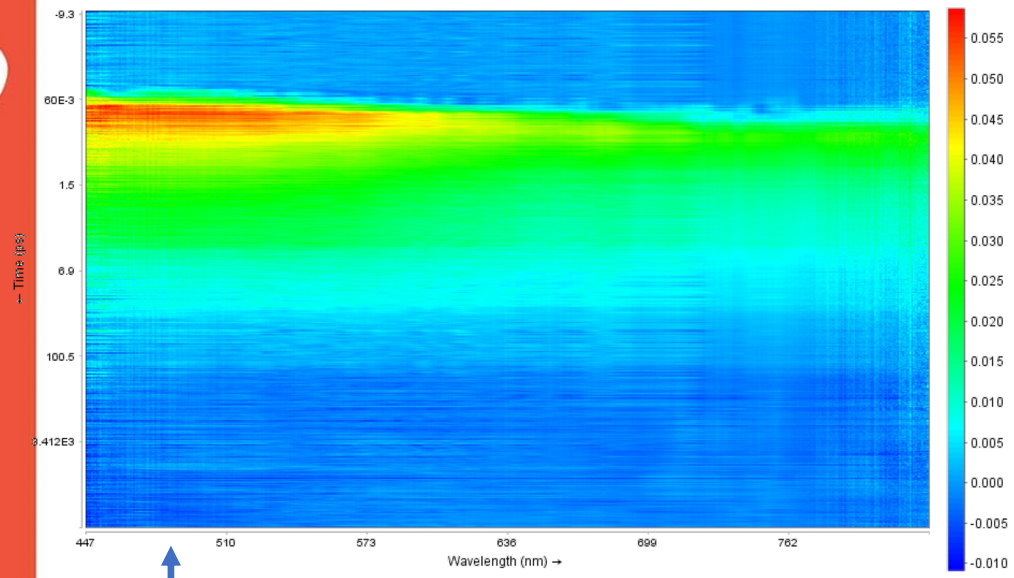
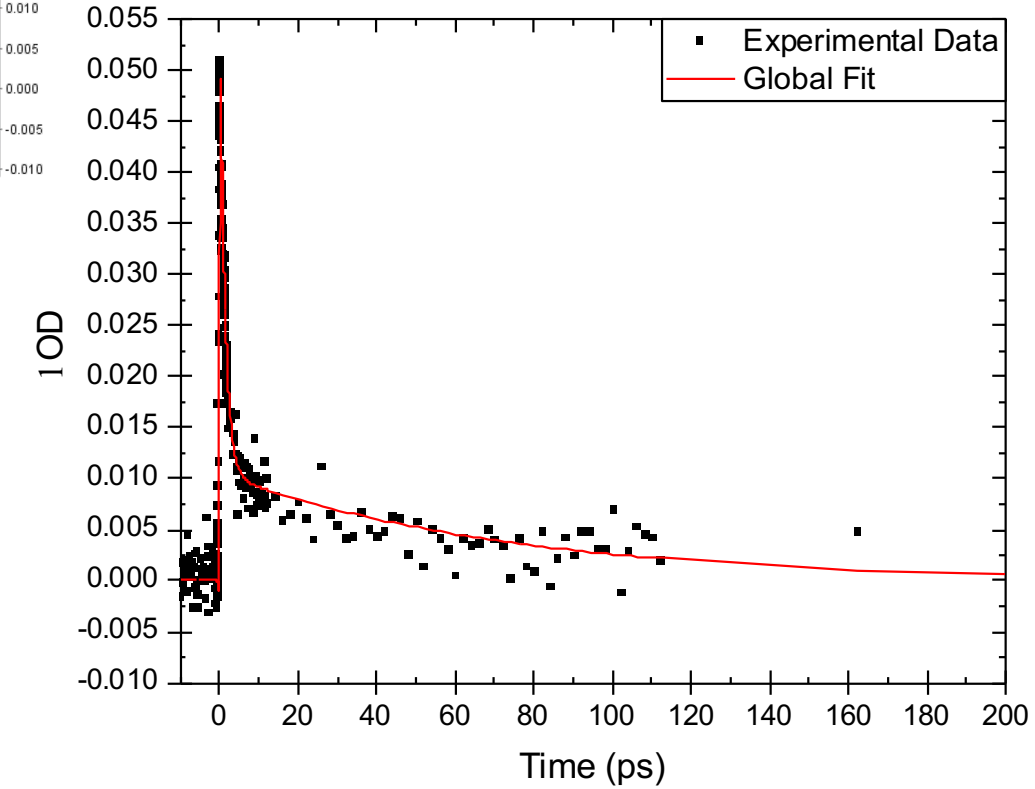
Dublin City University



Synthesised non-CAR



Lineout taken at 475 nm
Range 440-820nmm

Pump Wavelength: 400 nm/60 fs

Pump (400nm) Power: 4 mW

2 Lifetimes: 1.3 ps and 71 ps

Very Preliminary Results – Time Resolved Spectroscopy

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Dublin City University

- Fell into this line of research but looks promising scientifically
- Many candidate resists but the industry is trying to extend CAR use
- Strong (ΔD) signals for 400 nm pump in all samples to date
- Puzzle – no response for 267 nm pump?
- Calculations on the electronic structure of Pd-Oxalate are needed now to help with UTAS pump selection(searching literature)
- We have some access to ICHEC (Gaussian 16) & ORCA
- But TDDFT level at best
- Into the (near/midterm) future we will explore laser ablation nanoparticle formation in e.g., MMA based resists for NPRs

People

Stephen Durkan

Lazaros Varvarezos

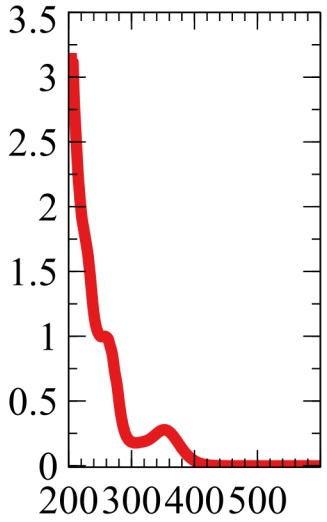
Ross McGarry

Mary Pryce

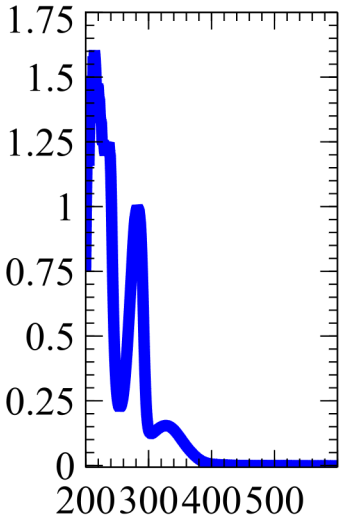
Matt Shaw

Extra Slides

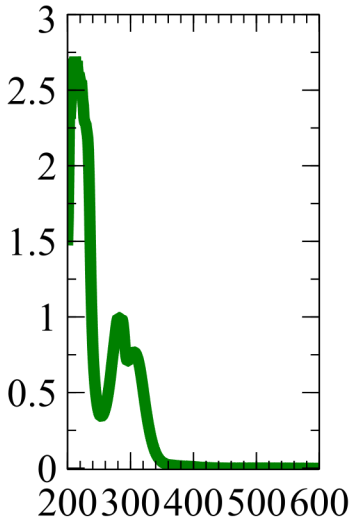
Very Preliminary Measurements (UV-Vis)



DPPM Pd Oxalate EUV resist



Microchem AZ nLOF 2020



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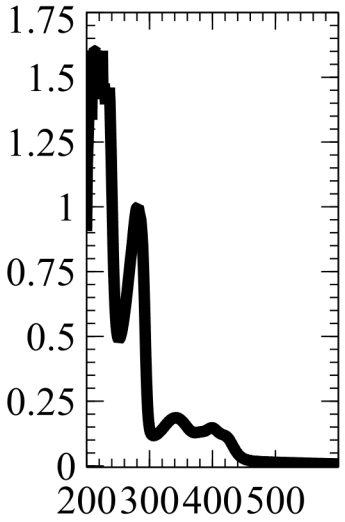

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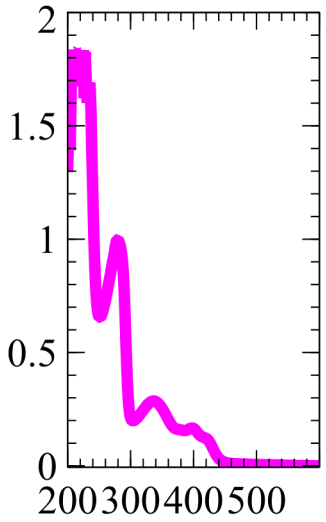

Microchem AZ 1505

Weak absorption at 400 nm

Strong UTAS signals for all samples

Possibly a multiphoton excitation

Standoff LIBS Prototype – Under Construction

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Dublin City University

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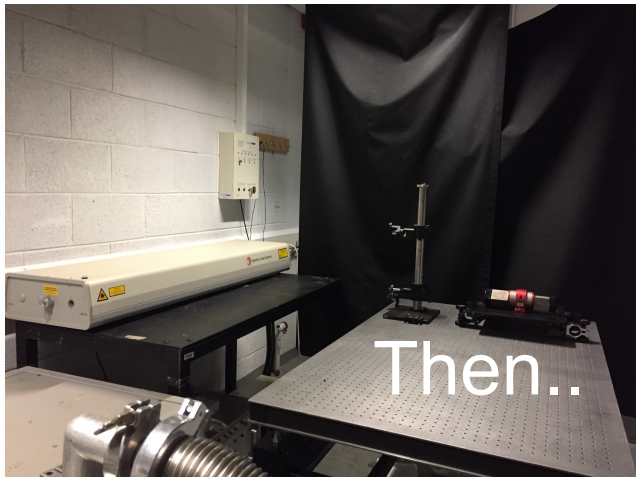
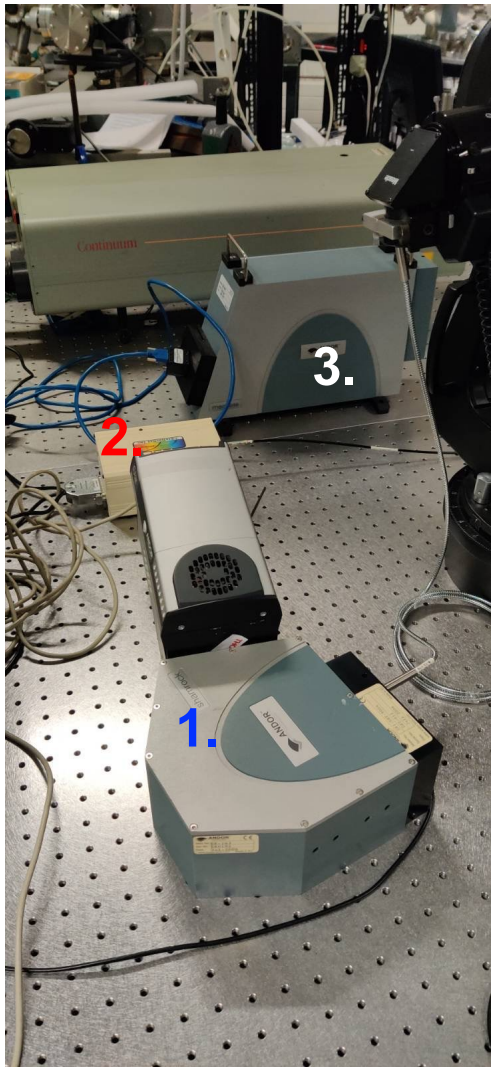
ESB Energy for generations

UCD DUBLIN

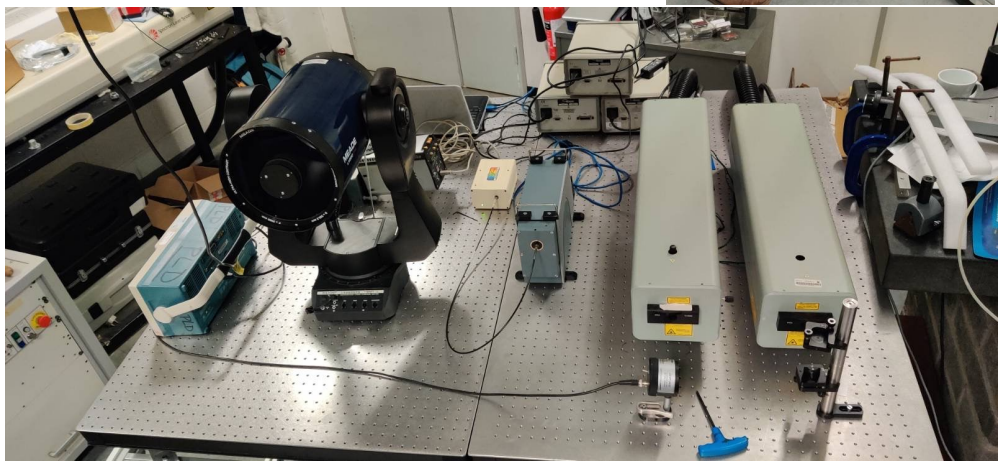
First in pictures….



Split tables with laser PSUs

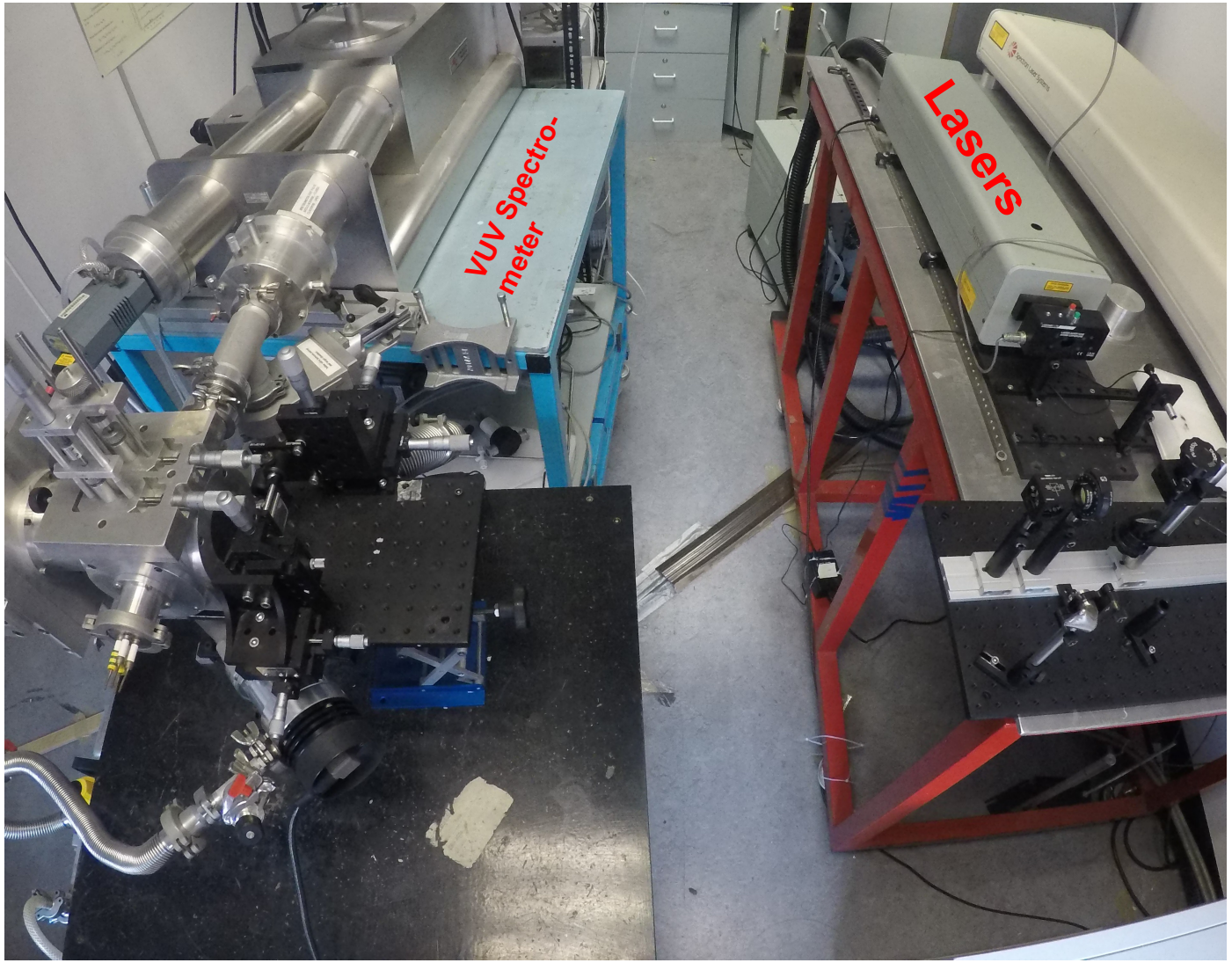


Spectrometers for WP1
1. Time-Gated
2. Continuous-Readout
3. Wide-Spectral Range



Top view showing double pulse laser setup with telescope.

VUV LIBS (and Photoabsorption)



Dual Pulse Vacuum-UV (VUV) LIBS Lab.

Laser Plasma (Optical) Diagnostics Lab

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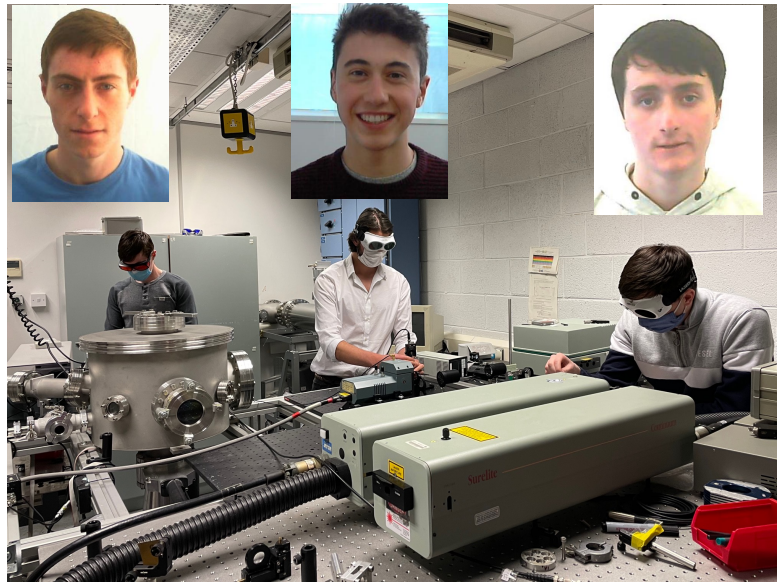
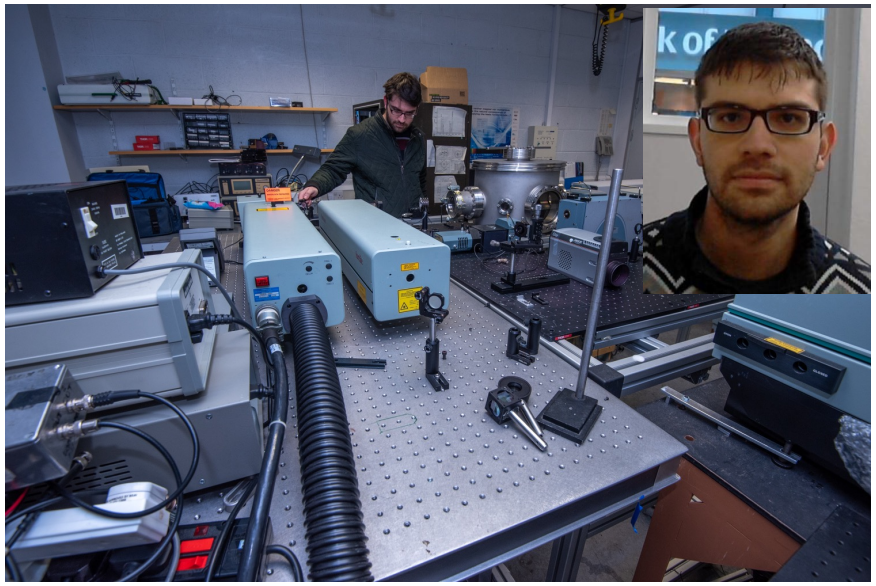


Stephen Durkan / Séamus Cummins/
James Campbell - all PhD students



Lazaros Varvarezos (PD)

Ross Murray (UCD)

Ultrafast (UF) Laser Spectroscopy Lab

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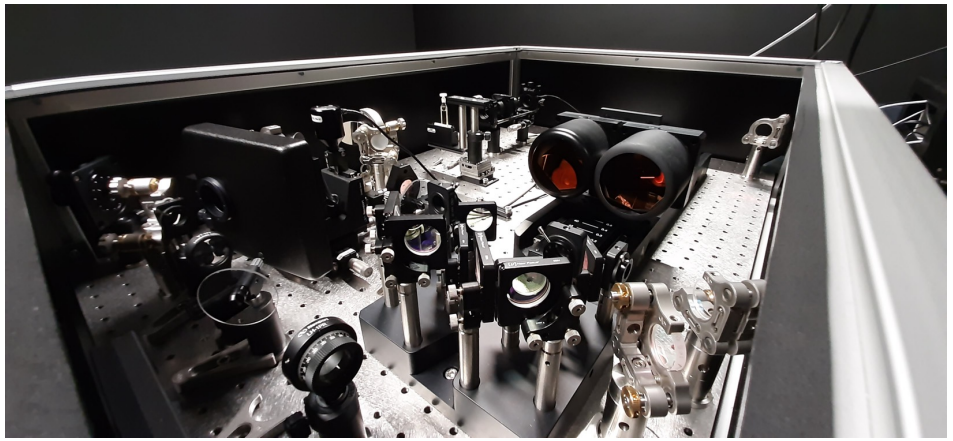
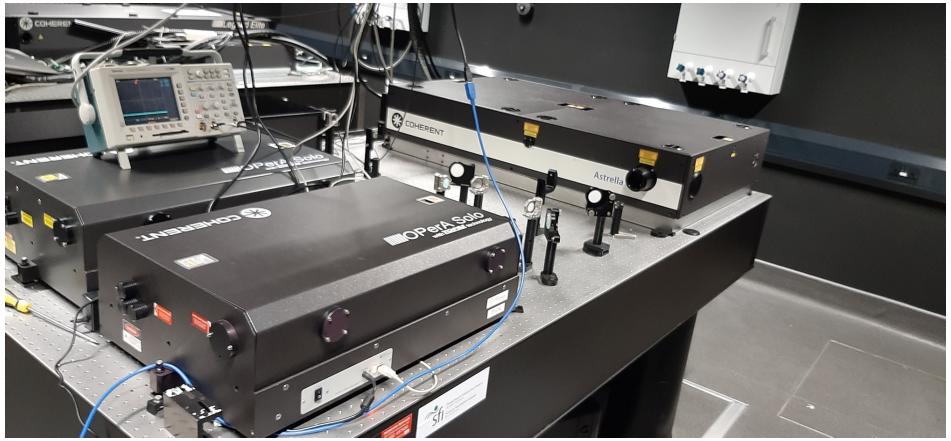
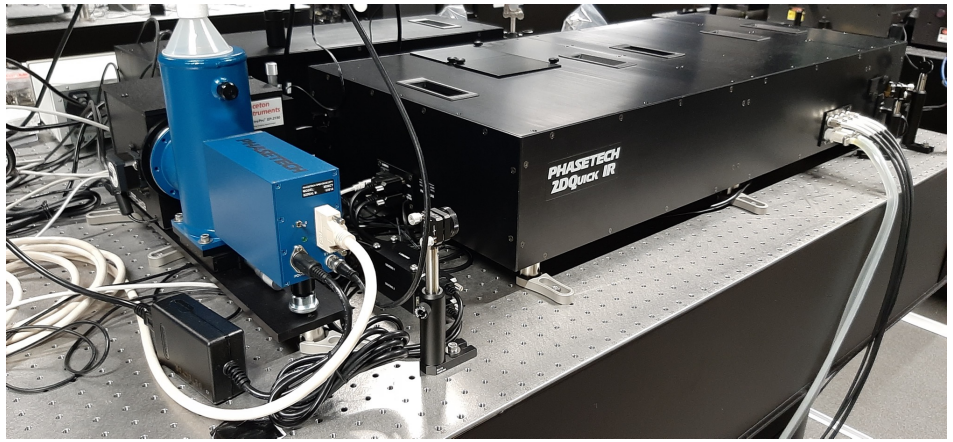
WP4. UF Laser Spectroscopy Laboratory @ DCU



WP4. Inside the UF Transient Spectrometer



WP4. UF Laser Table with Astrella Amplifier & OPAs



WP4. UF Time Resolved IR Spectrometer