CORRELATIVE CHARACTERIZATION OF PLASMA ETCHING RESISTANCE OF VARIOUS ALUMINUM GARNETS

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MOTIVATION – PLASMA/ DRY ETCHING

Semiconductor manufacturing process

Patterning → **Etching** → Doping

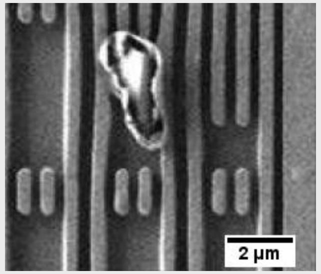
- **YAG** ($Y_3Al_5O_{12}$) is an advanced ceramic used as **inner wall** material in **plasma etching chambers**
- Continuous refinement of the manufacturing process increases requirements for process conditions
  - Higher cleanliness
  - Wafer to wafer reproducibility
- Need for materials with **higher plasma resistance**
- **Hypothesis**: Plasma resistance of YAG can be improved by **replacement of Y by rare earth ions** (e.g. Er, Lu)

Etching chamber

[1]

Producer® Selectra® Etch

"Killer defect" on wafer



[2]

1. https://www.appliedmaterials.com/us/en/product-library/producer-selectra-etch.html#carousel-94c4c76187-item-f3e253bb6e-tabpanel
2. Hong Shih. *"A Systematic Study and Characterization of Advanced Corrosion Resistance […]."* Corrosion Resistance. DOI: 10.5772/31992

OBJECTIVES

- Substitution of Y in YAG with rare earth elements (Er, Lu)
- Synthesis of ceramics with garnet type structure by reactive SPS
- Systematic etching study in fluorine based etching plasma
- Investigation of plasma erosion by AFM, SIMS and TEM

Produced samples:

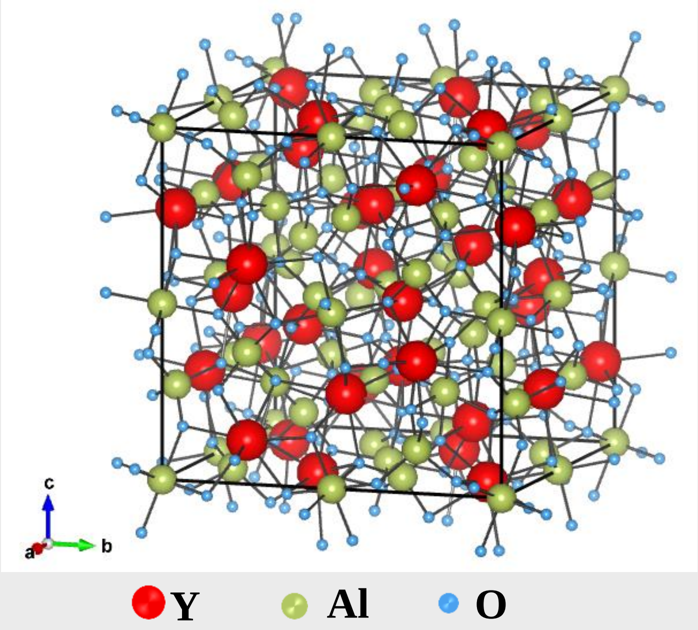
Sample	Composition
YAG	$Y_3Al_5O_{12}$
ErAG	$Er_3Al_5O_{12}$
LuAG	$Lu_3Al_5O_{12}$

Relevant ions:

Ion	Atomic mass (u)	Effective ionic radius (Å)
Y^{3+}	88.906	1.019
Er^{3+}	167.26	1.004
Lu^{3+}	174.97	0.977

[3]

YAG: crystal structure



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3. Shannon, R.D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Crystallographica Section A, 1976. 32(5): p. 751-767.

SPS: Spark plasma sintering. **AFM**: Atomic force microscopy.
SIMS: Secondary ion mass spectrometry. **TEM**: Transmission electron microscopy

SYNTHESIS

Reactive Spark Plasma Sintering (RSPS)

Overall chemical reaction:

$$3\,Y_2O_3 + 5\,Al_2O_3 \rightarrow 2\,Y_3Al_5O_{12}$$ (YAG)

$$2\,Y_2O_3 + Al_2O_3 \rightarrow Y_4Al_2O_9 \text{ (YAM)}$$

$$Y_4Al_2O_9 + Al_2O_3 \rightarrow 4\,YAlO_3 \text{ (YAP)}$$

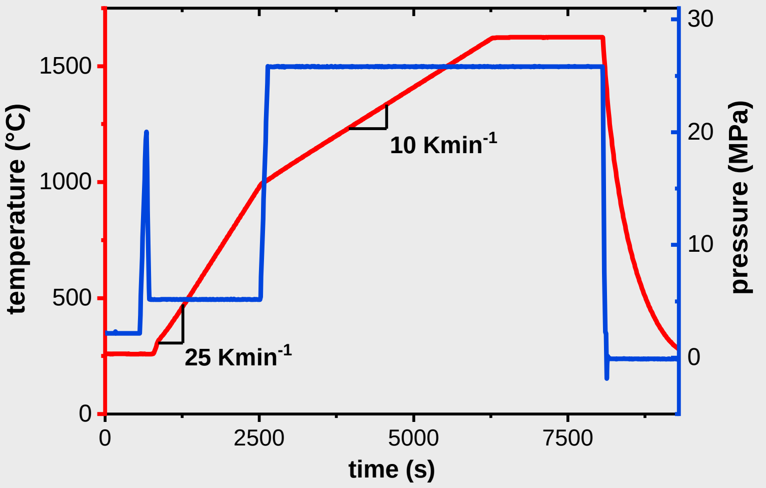
$$3\,YAlO_3 + Al_2O_3 \rightarrow Y_3Al_5O_{12} \text{ (YAG)}$$

(T = 1000 – 1600 °C)

SPS Parameters:

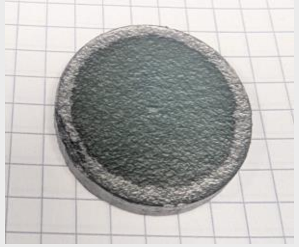
Heating:	25 $Kmin^{-1}$, 5 MPa, RT-1000°C
	10 $Kmin^{-1}$, 25 MPa, to 1600°C
Dwell:	30 min, 25 MPa, 1600°C
Cooling:	switch off power source
Die:	30 mm disk

SPS data



FCT HP-D 5

Sintered sample:

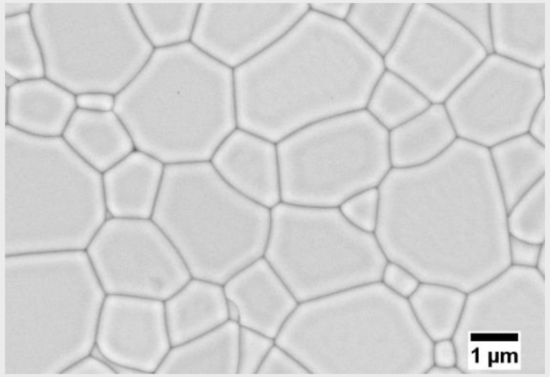


CHARACTERIZATION OF AS-SINTERED SAMPLES

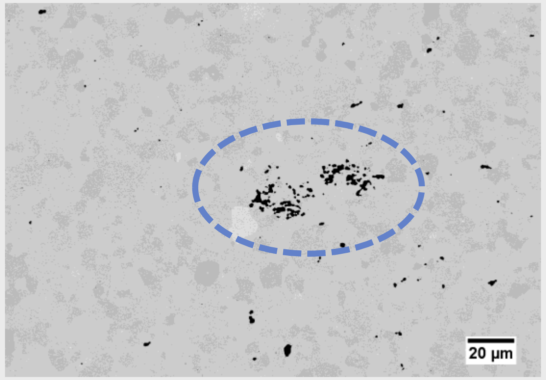
Scanning electron microscopy (SEM) and X-ray diffraction (XRD)

Microstructure

- homogenous, dense (ρ~99.9%)
- Grain size: d_{50} = 2-3 µm
- Small amounts of residual alumina (~1 %)



YAG (thermally etched)

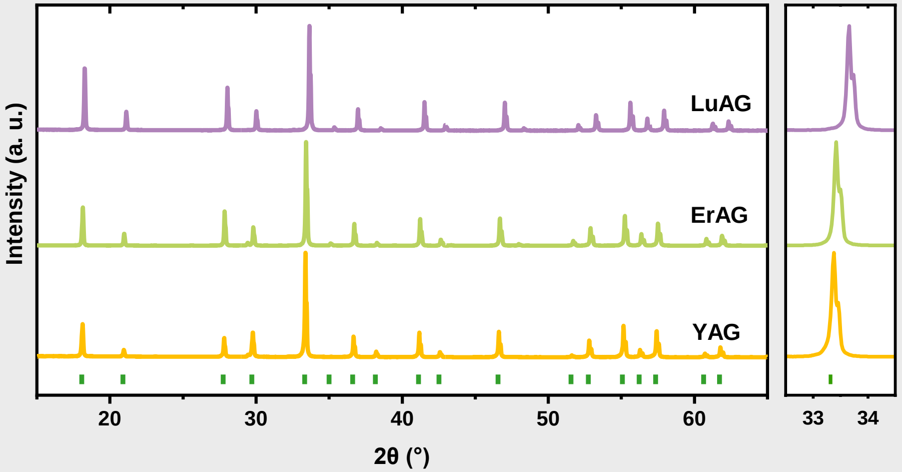


LuAG with residual alumina

Microscope: Ultra 55 (Carl Zeiss AG, Oberkochen, Germany)

X-ray diffraction

- Residual alumina (Al_2O_3) phase falls below detection limit
- Same crystal structure for all garnets
- Slight deviations in lattice parameters



Device: D4 ENDEAVOR (Bruker, Billerica, MA, USA)
increment 0.02°, 0.75 s/step

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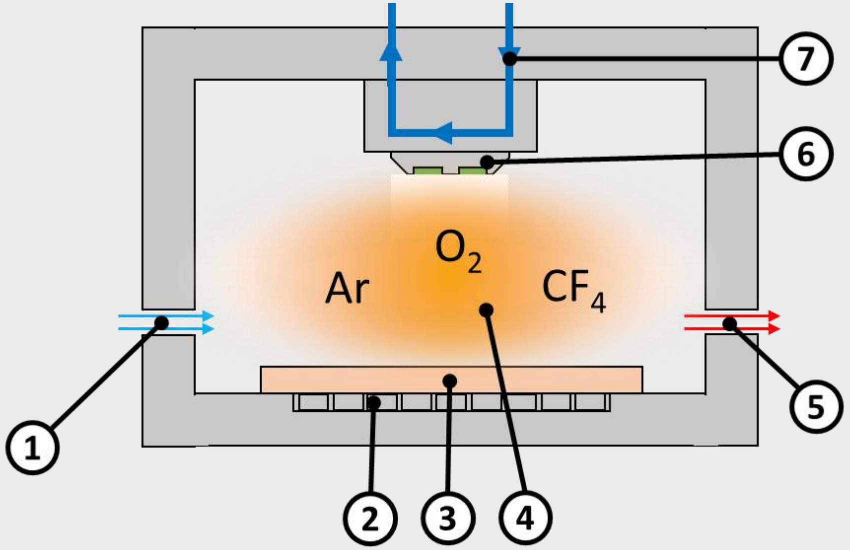
PLASMA ETCHING

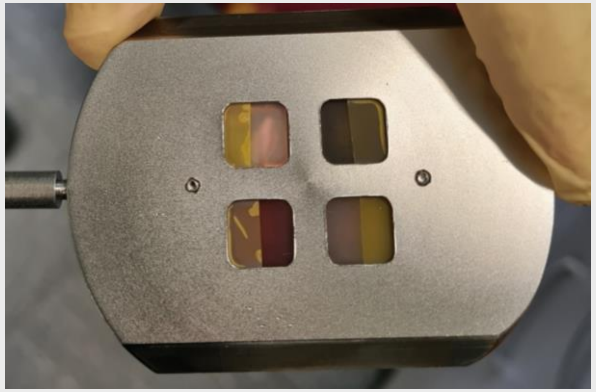
Experimental setup and plasma parameters

ICP-etching chamber



(1) Gas inlet (2) ICP generator (3) Protective window (4) Plasma (5) Vacuum pump (6) Sample holder (7) Water cooling system

Samples masked with Kapton® tape



Plasma parameter sets

	P_{ICP} (W)	t_{etch} (min)	p (mbar)	U_B (V)	CF_4 (sccm)	Ar (sccm)	O_2 (sccm)
Weak:	600	120	0.02	-150	1.0	5.0	0.3
Aggressive:	600	120	0.0083	-250	1.0	5.0	0.5

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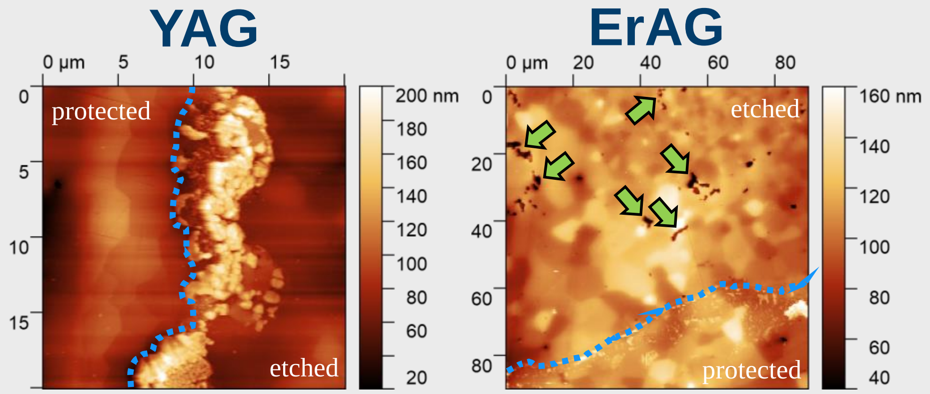
CHARACTERIZATION: WEAK PLASMA PARAMETERS

CHARACTERIZATION

Surface topography: AFM + SEM/EDS

Atomic force microscopy (AFM)
(Dimension Icon, Bruker; Tapping mode)

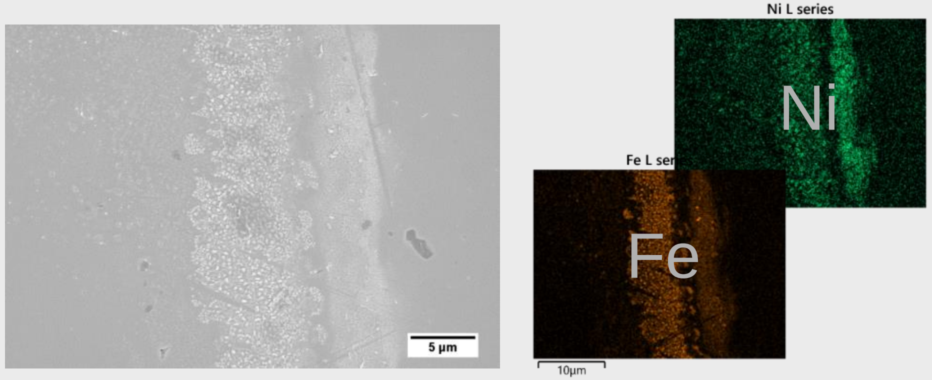
- **No physical erosion** of matrix phase detected
- Physical erosion of alumina
- **Contamination** covering the etch step



Scanning electron microscopy (SEM/EDS)
(Ultra 55, Carl Zeiss AG)

- **Contamination** consists of **metal ions**
- Source: Erosion of sample holder or chamber wall

SEM/EDS of contaminated etch step in YAG



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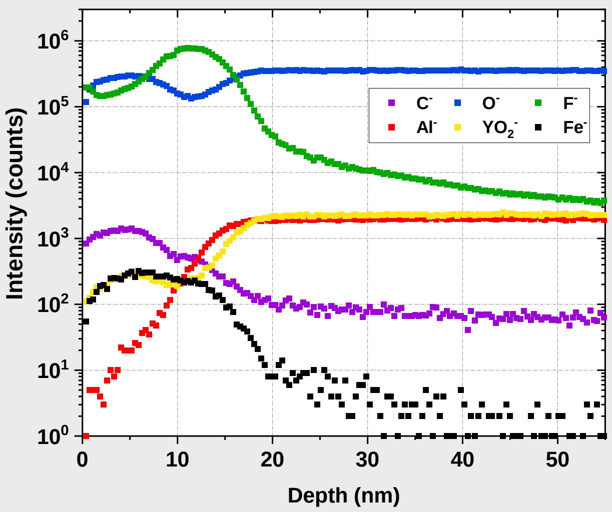
CHARACTERIZATION: CORRELATIVE APPROACH

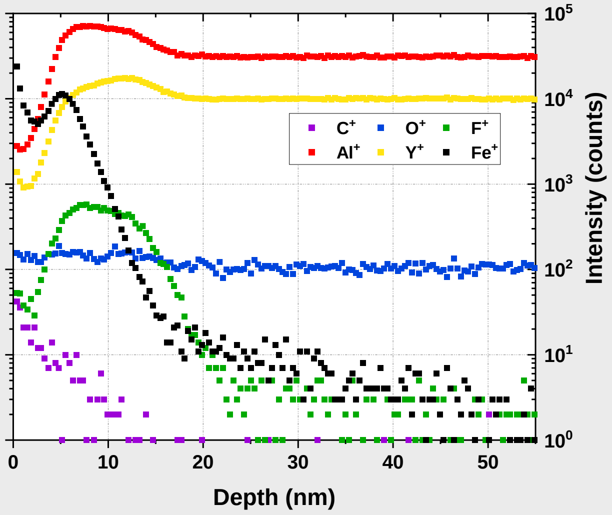
Induced chemical gradient on the example of YAG

ToF-SIMS*

Negative polarity



Positive polarity



- Device: ToF-SIMS 5, IONTOF
- Reaction layer:
  - ~ 20 nm thick
  - high F, Fe* and C intensities
- Fluorination reaches deeper into bulk

⇨ Different yield depending on measurement polarity

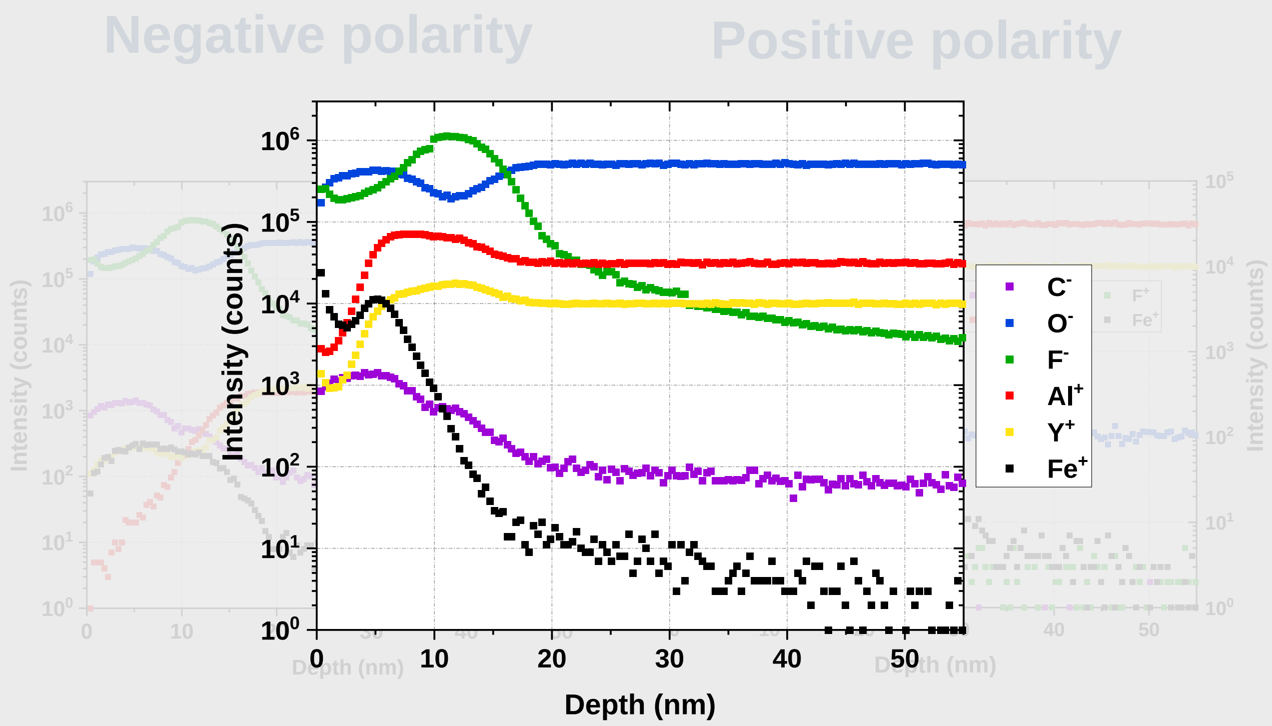
ToF-SIMS by Dr. Christian Schwab @IMD-2

*Cr and Ni have been found in comparable amounts as Fe

CHARACTERIZATION: CORRELATIVE APPROACH

Induced chemical gradient on the example of YAG

ToF-SIMS*



- Combined SIMS graph showing the measurement with higher yield:
  - Negative polarity: C, O, F
  - Positive polarity: Al, Y, Fe

ToF-SIMS by Dr. Christian Schwab @IMD-2

*Cr and Ni have been found in comparable amounts as Fe

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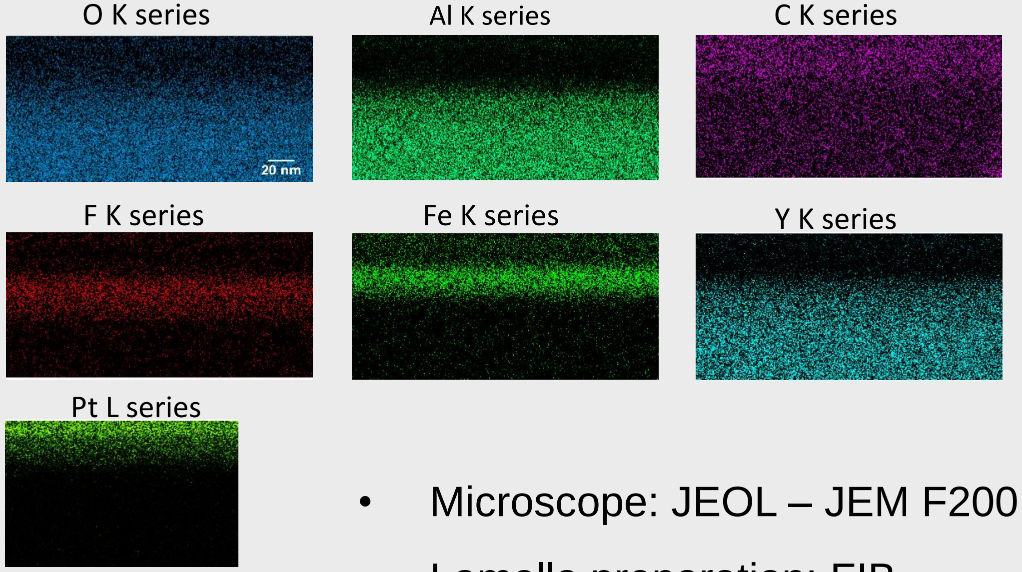
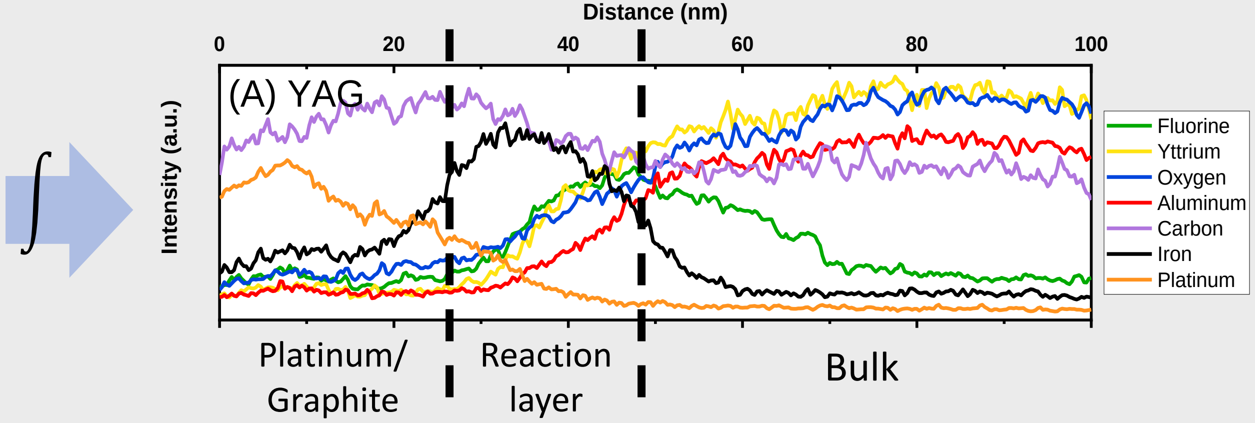
CHARACTERIZATION: CORRELATIVE APPROACH

Induced chemical gradient on the example of YAG

(S)TEM-EDS





- Microscope: JEOL – JEM F200
- Lamella preparation: FIB
- Collaboration with RWTH Aachen

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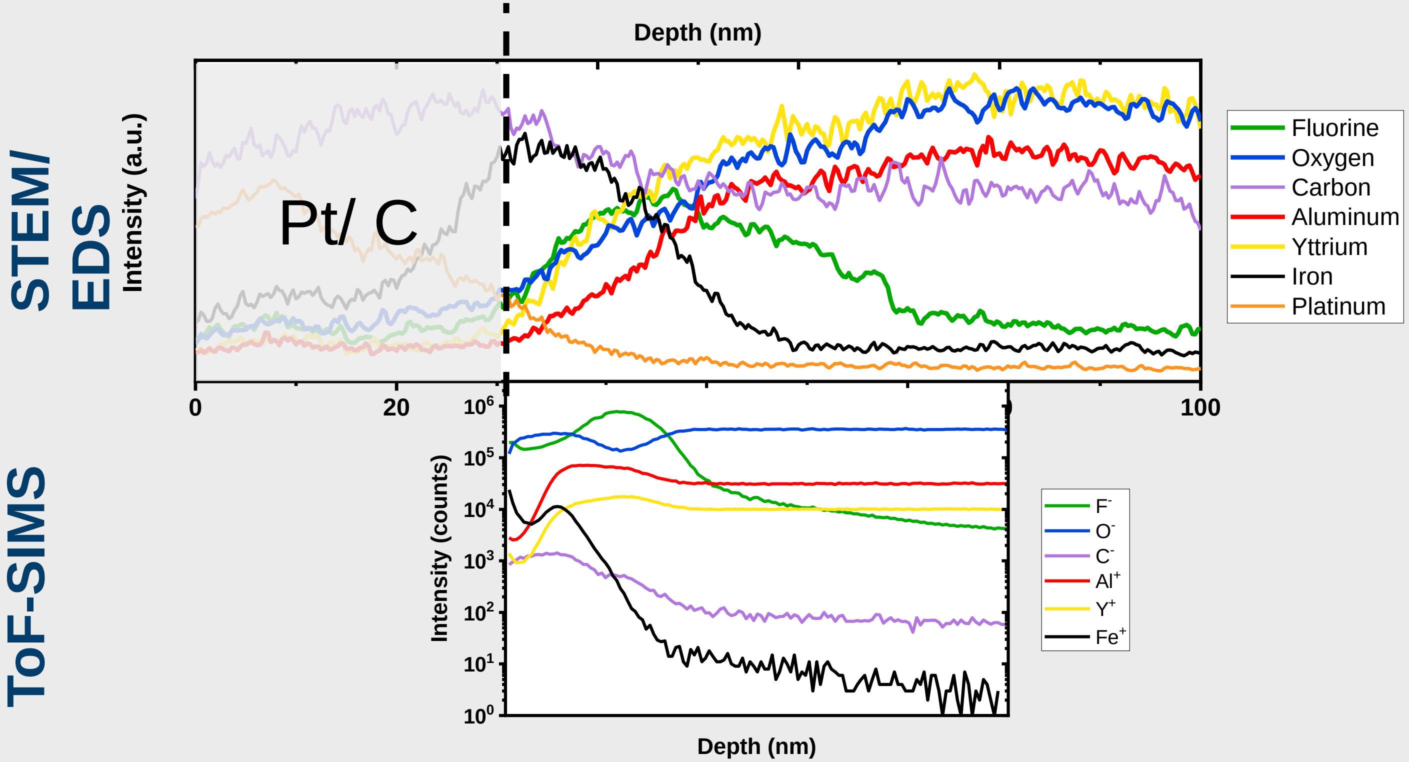
CHARACTERIZATION: CORRELATIVE APPROACH

Correlative Characterization of induced chemical gradient on the example of YAG



- **Good accordance** and same trends
- Better visibility of F, O in ToF-SIMS
- **Scaling: ToF-SIMS compressed** compared to STEM

⇨ Local differences in reaction layer

⇨ ToF-SIMS averaged over larger area (50 µm x 50 µm)

⇨ Surface roughness

CHARACTERIZATION

Reaction layer characteristics

Critical parameters

Thickness: $$\frac{dy}{dx} I_{bulk\ ions}(x) \approx 0$$

Fluorination depth: $$\frac{d^2y}{dx^2} I_{fluorine}(x) = 0$$

Material	Thickness	Fluorination depth
YAG	18	17.5
ErAG	10	9.4
LuAG	6	5.3

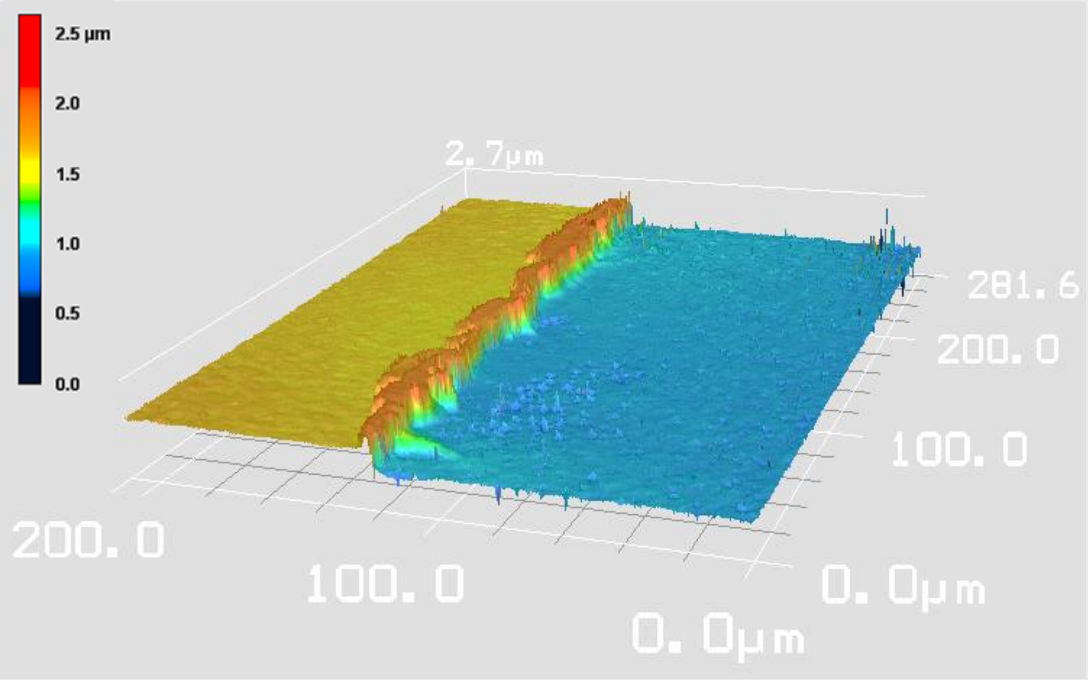
⇨ Replacing Y^{3+} with heavier lanthanoids reduces the extent of chemical interaction

CHARACTERIZATION: AGGRESSIVE PLASMA PARAMETERS

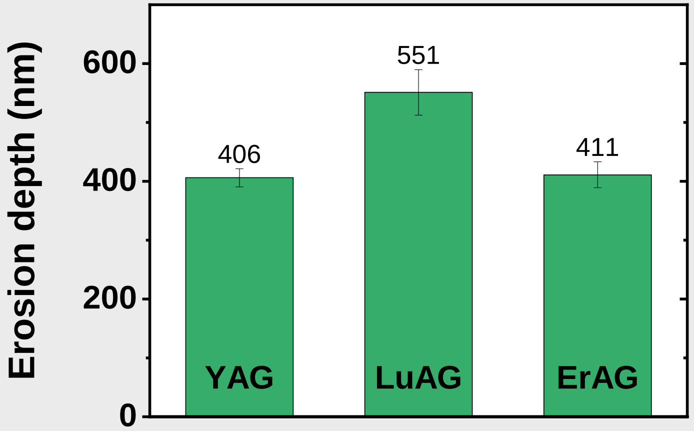
CHARACTERIZATION:

Physical erosion

Etch step (YAG)



Results

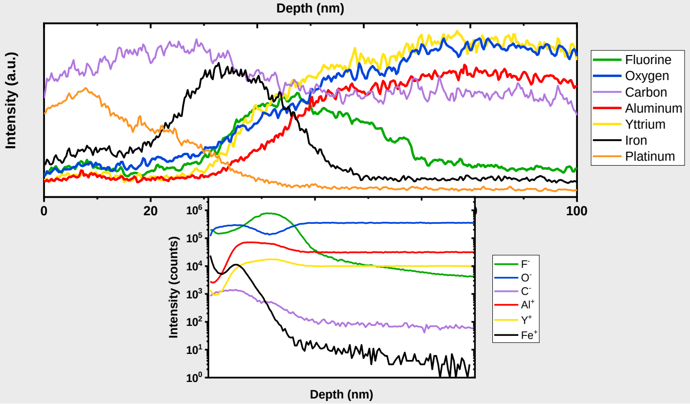


- All samples were **physically eroded**
- **Evaluation:**
  - Laser microscope (Keyence)
  - 4 Profiles were averaged

PERFORMANCE IN WEAK AND AGGRESSIVE PLASMA

Correlation possible?!

	Weak plasma		Aggressive plasma
Material	Thickness (nm)	Fluorination depth (nm)	Physical erosion (nm)
YAG	18	17.5	406
ErAG	10	9.4	411
LuAG	6	5.3	551
SiO_2			8500



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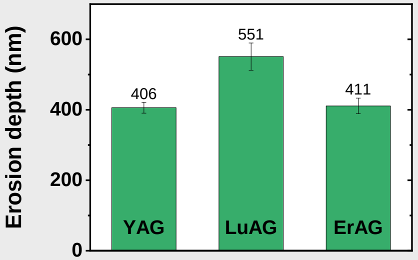

- The performance under weak plasma parameters cannot be used to predict the etch resistance under more severe conditions
- Replacing Y^{3+} with lanthanoid cations does not enhance the etch resistance
- Compared to quartz, all samples perform significantly better

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SUMMARY – PLASMA ETCHING

YAG, ErAG and **LuAG** were exposed to **fluorine based etching plasma (CF_4/Ar/O_2)** of different corrosiveness

Replacing Y^{3+} with heavier lanthanoids **decreases the extent of the reaction layer**

In an **aggressive plasma**, **YAG outperforms** lanthanoid garnets

The **mass** of the A-site **cation** is **not critical** for the plasma etch resistance

The **reaction layer can not predict** the etch resistance in **more aggressive plasma**

All processed samples exhibited **excellent etch resistance compared to SiO_2**


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SPECIAL ISSUE ARTICLE

Correlative characterization of plasma etching resistance of various aluminum garnets

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Abstract
Plasma etching is a crucial step in semiconductor manufacturing. High cleanliness and wafer-to-wafer reproducibility in the etching chamber are essential in order to successfully achieve nanometer-sized integrated functions on the wafer. The trend toward the application of more aggressive plasma compositions leads to higher demands on the plasma resistance of the materials used

Read the paper:

Stay in touch:

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Prof. Olivier Guillon

The Ceramic and Glass Industry Foundation

The American Ceramic Society

Stay in touch

Read the paper

Thank you for your attention! Questions?