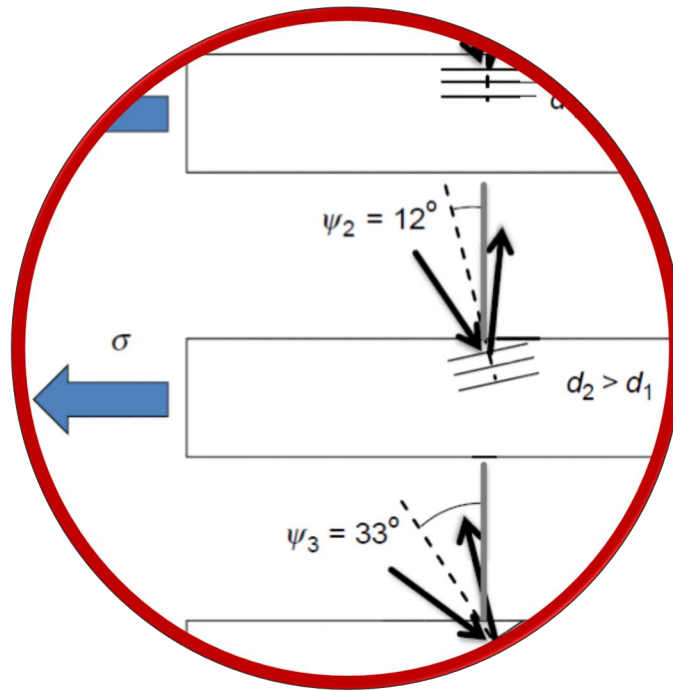
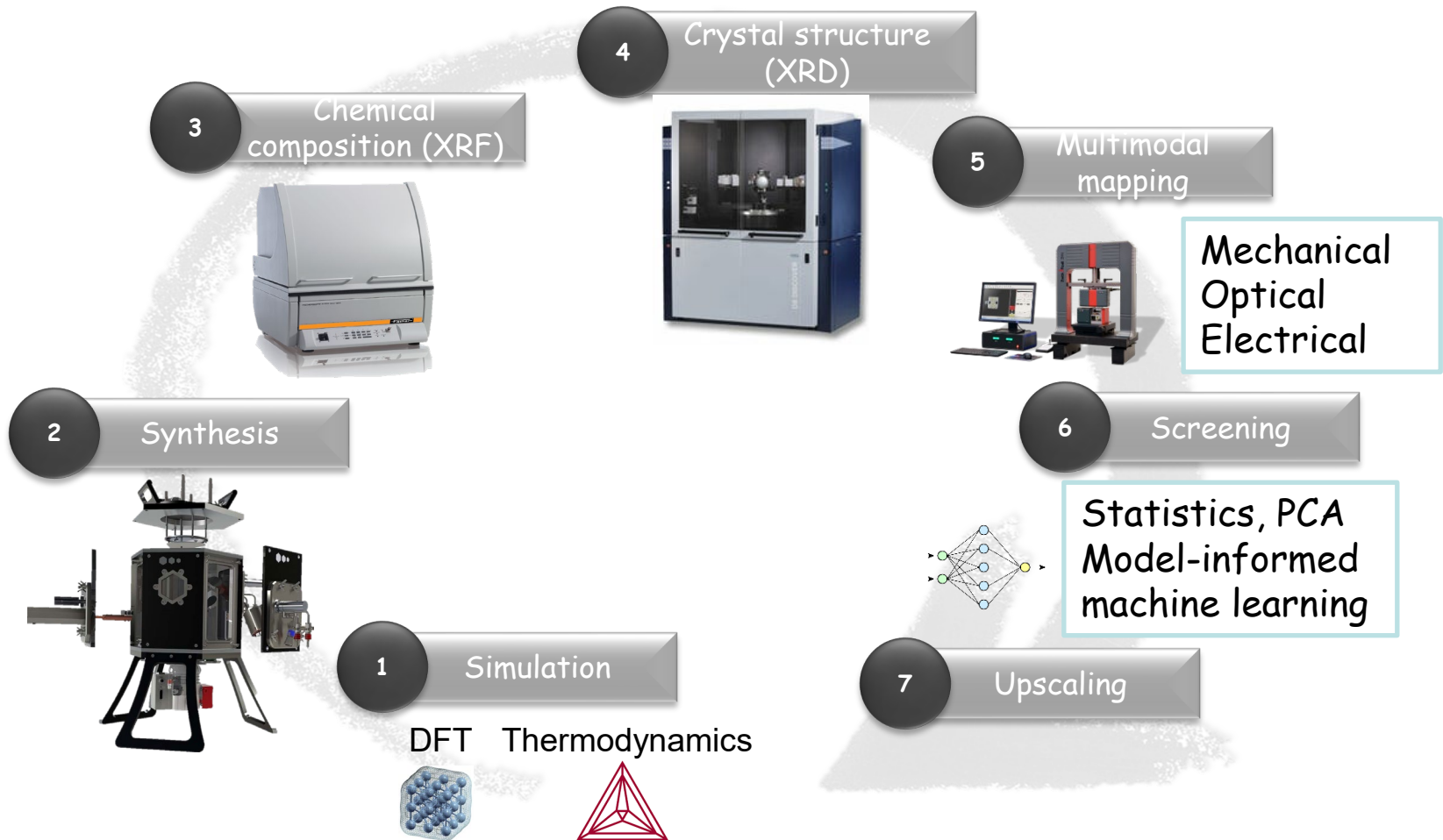


# 7. Outlook

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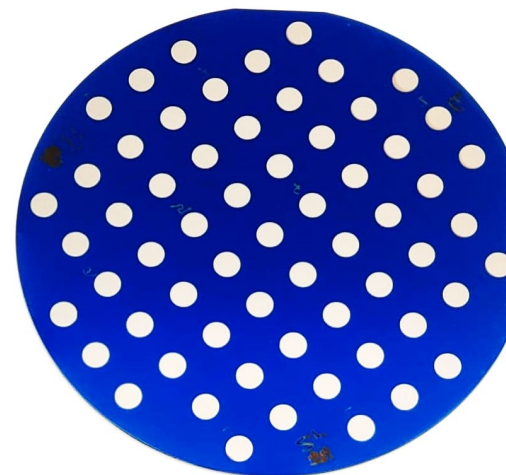
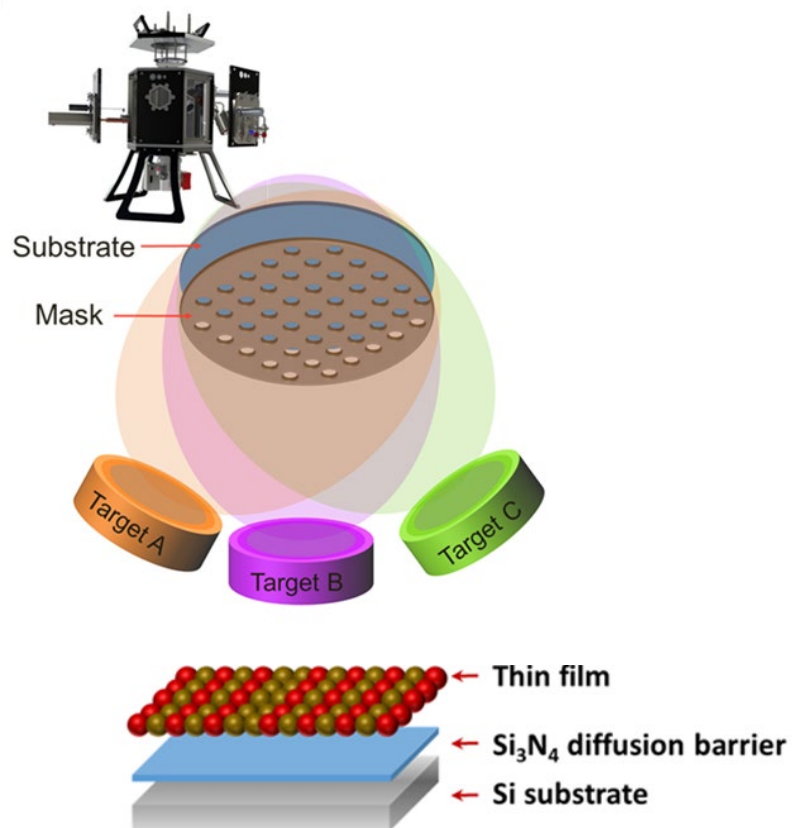


# Outlook: Accelerated materials discovery through combinatorial thin film libraries



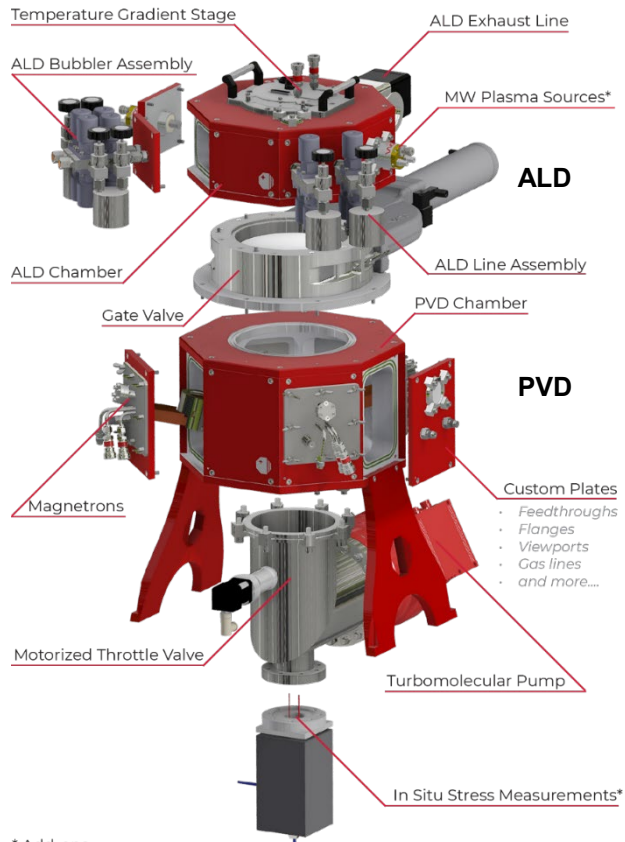


# Deposition - combinatorial thin film libraries

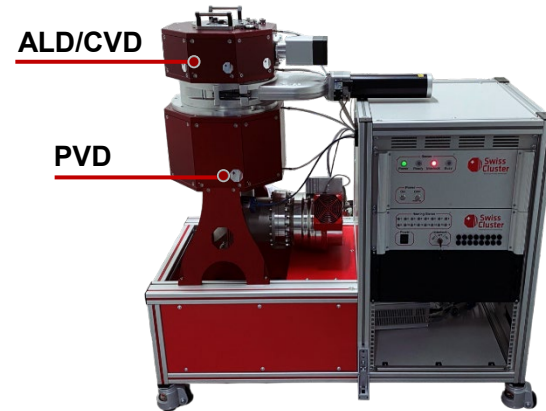


- 4in wafer with 69 patches
- $\text{Si}_3\text{N}_4$  interlayer for diffusion barrier, chemical inertness, electrical isolation
- Composition gradient:  $\pm 20\text{at}\%$

# Deposition - novel equipment



\* Add-ons



- Laboratory cluster system
  - combines PVD and ALD
- Up to 8 magnetrons
- Temperature gradient stage (RT to 400°C)
- HIPIMS compatible
- 4 inch wafer substrates

# PVD possible targets

|                                     |                                  |                                   |                                     |                                       |                                  |                                |                               |                                  |                                    |                                   |                                   |                                |                                 |                                  |                                   |                                   |                                 |
|-------------------------------------|----------------------------------|-----------------------------------|-------------------------------------|---------------------------------------|----------------------------------|--------------------------------|-------------------------------|----------------------------------|------------------------------------|-----------------------------------|-----------------------------------|--------------------------------|---------------------------------|----------------------------------|-----------------------------------|-----------------------------------|---------------------------------|
| 1<br>IA                             |                                  |                                   |                                     |                                       |                                  |                                |                               |                                  |                                    |                                   |                                   |                                |                                 |                                  |                                   |                                   | 18<br>VIIIA                     |
| 1<br>H<br>Hydrogen<br>1.008         |                                  |                                   |                                     |                                       |                                  |                                |                               |                                  |                                    |                                   |                                   |                                |                                 |                                  |                                   |                                   | 2<br>He<br>Helium<br>4.002602   |
| 3<br>Li<br>Lithium<br>6.94          | 4<br>Be<br>Beryllium<br>9.012183 |                                   |                                     |                                       |                                  |                                |                               |                                  |                                    |                                   |                                   | 5<br>B<br>Boron<br>10.81       | 6<br>C<br>Carbon                | 7<br>N<br>Nitrogen<br>14.007     | 8<br>O<br>Oxygen<br>15.999        | 9<br>F<br>Fluorine<br>18.99840323 | 10<br>Ne<br>Neon<br>20.1797     |
| 11<br>Na<br>Sodium<br>22.98976928   | 12<br>Mg<br>Magnesium            | 13<br>Al<br>Aluminum              | 14<br>Si<br>Silicon                 | 15<br>P<br>Phosphorus<br>30.973761998 | 16<br>S<br>Sulfur<br>32.06       | 17<br>Cl<br>Chlorine<br>35.45  | 18<br>Ar<br>Argon<br>39.948   |                                  |                                    |                                   |                                   |                                |                                 |                                  |                                   |                                   |                                 |
| 19<br>K<br>Potassium<br>39.0983     | 20<br>Ca<br>Calcium              | 21<br>Sc<br>Scandium<br>44.955908 | 22<br>Ti<br>Titanium                | 23<br>V<br>Vanadium                   | 24<br>Cr<br>Chromium             | 25<br>Mn<br>Manganese          | 26<br>Fe<br>Iron              | 27<br>Co<br>Cobalt               | 28<br>Ni<br>Nickel                 | 29<br>Cu<br>Copper                | 30<br>Zn<br>Zinc                  | 31<br>Ga<br>Gallium<br>69.723  | 32<br>Ge<br>Germanium<br>72.630 | 33<br>As<br>Arsenic<br>74.921595 | 34<br>Se<br>Selenium<br>78.971    | 35<br>Br<br>Bromine<br>79.904     | 36<br>Kr<br>Krypton<br>83.798   |
| 37<br>Rb<br>Rubidium<br>85.4678     | 38<br>Sr<br>Strontium            | 39<br>Y<br>Yttrium                | 40<br>Zr<br>Zirconium               | 41<br>Nb<br>Niobium                   | 42<br>Mo<br>Molybdenum           | 43<br>Tc<br>Technetium<br>(98) | 44<br>Ru<br>Ruthenium         | 45<br>Rh<br>Rhodium              | 46<br>Pd<br>Palladium              | 47<br>Ag<br>Silver                | 48<br>Cd<br>Cadmium<br>112.414    | 49<br>In<br>Indium             | 50<br>Sn<br>Tin                 | 51<br>Sb<br>Antimony             | 52<br>Te<br>Tellurium             | 53<br>I<br>Iodine<br>126.90447    | 54<br>Xe<br>Xenon<br>131.293    |
| 55<br>Cs<br>Caesium<br>132.90545196 | 56<br>Ba<br>Barium<br>137.327    | 57 - 71<br>Lanthanoids            | 72<br>Hf<br>Hafnium                 | 73<br>Ta<br>Tantalum                  | 74<br>W<br>Tungsten              | 75<br>Re<br>Rhenium            | 76<br>Os<br>Osmium<br>190.23  | 77<br>Ir<br>Iridium              | 78<br>Pt<br>Platinum               | 79<br>Au<br>Gold                  | 80<br>Hg<br>Mercury<br>200.592    | 81<br>Tl<br>Thallium<br>204.38 | 82<br>Pb<br>Lead                | 83<br>Bi<br>Bismuth              | 84<br>Po<br>Polonium<br>(209)     | 85<br>At<br>Astatine<br>(210)     | 86<br>Rn<br>Radon<br>(222)      |
| 87<br>Fr<br>Francium<br>(223)       | 88<br>Ra<br>Radium<br>(226)      | 89 - 103<br>Actinoids             | 104<br>Rf<br>Rutherfordium<br>(261) | 105<br>Db<br>Dubnium<br>(268)         | 106<br>Sg<br>Seaborgium<br>(269) | 107<br>Bh<br>Bohrium<br>(270)  | 108<br>Hs<br>Hassium<br>(269) | 109<br>Mt<br>Meitnerium<br>(278) | 110<br>Ds<br>Darmstadtium<br>(285) | 111<br>Rg<br>Roentgenium<br>(282) | 112<br>Cn<br>Copernicium<br>(285) | 113<br>Nh<br>Nihonium<br>(286) | 114<br>Fl<br>Flerovium<br>(289) | 115<br>Mc<br>Moscovium<br>(289)  | 116<br>Lv<br>Livermorium<br>(293) | 117<br>Ts<br>Tennessine<br>(294)  | 118<br>Og<br>Oganesson<br>(294) |



Can be deposited



Can be deposited, but we prefer to avoid (chamber contamination or health concerns)

|                                    |                                 |                                       |                                  |                                 |                                |                                 |                                  |                                  |                                   |                                  |                               |                                   |                                  |                                  |
|------------------------------------|---------------------------------|---------------------------------------|----------------------------------|---------------------------------|--------------------------------|---------------------------------|----------------------------------|----------------------------------|-----------------------------------|----------------------------------|-------------------------------|-----------------------------------|----------------------------------|----------------------------------|
| 57<br>La<br>Lanthanum<br>138.90547 | 58<br>Ce<br>Cerium<br>140.116   | 59<br>Pr<br>Praseodymium<br>140.90766 | 60<br>Nd<br>Neodymium<br>144.242 | 61<br>Pm<br>Promethium<br>(145) | 62<br>Sm<br>Samarium<br>150.36 | 63<br>Eu<br>Europium<br>151.964 | 64<br>Gd<br>Gadolinium<br>157.25 | 65<br>Tb<br>Terbium<br>158.92535 | 66<br>Dy<br>Dysprosium<br>162.500 | 67<br>Ho<br>Holmium<br>164.93033 | 68<br>Er<br>Erbium<br>167.259 | 69<br>Tm<br>Thulium<br>168.93422  | 70<br>Yb<br>Ytterbium<br>173.045 | 71<br>Lu<br>Lutetium<br>174.9668 |
| 89<br>Ac<br>Actinium<br>(227)      | 90<br>Th<br>Thorium<br>232.0377 | 91<br>Pa<br>Protactinium<br>231.03688 | 92<br>U<br>Uranium<br>238.02891  | 93<br>Np<br>Neptunium<br>(237)  | 94<br>Pu<br>Plutonium<br>(244) | 95<br>Am<br>Americium<br>(243)  | 96<br>Cm<br>Curium<br>(247)      | 97<br>Bk<br>Berkelium<br>(247)   | 98<br>Cf<br>Californium<br>(251)  | 99<br>Es<br>Einsteinium<br>(252) | 100<br>Fm<br>Fermium<br>(257) | 101<br>Md<br>Mendelevium<br>(258) | 102<br>No<br>Nobelium<br>(259)   | 103<br>Lr<br>Lawrencium<br>(266) |

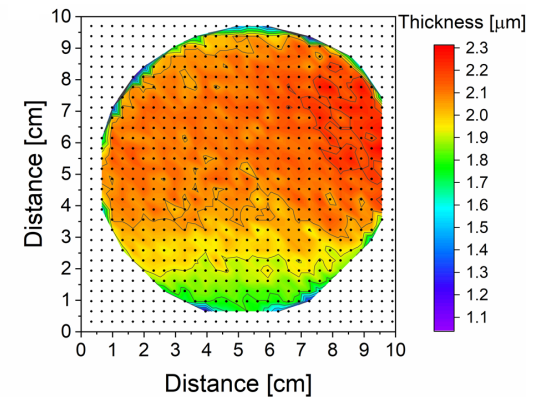
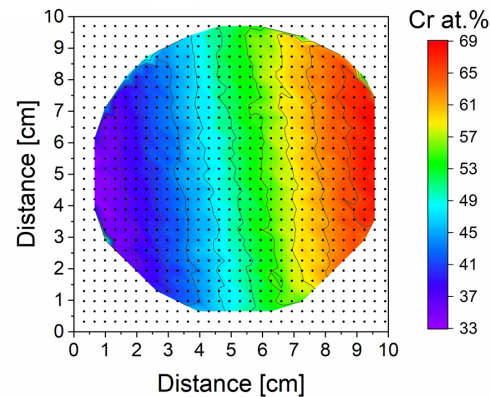
# Composition mapping



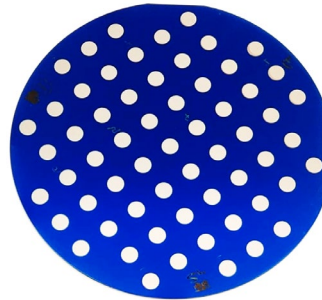
Fischerscope X-Ray XDV-SDD

XRF mapping on each patch:

- Chemical composition
- Coating thickness

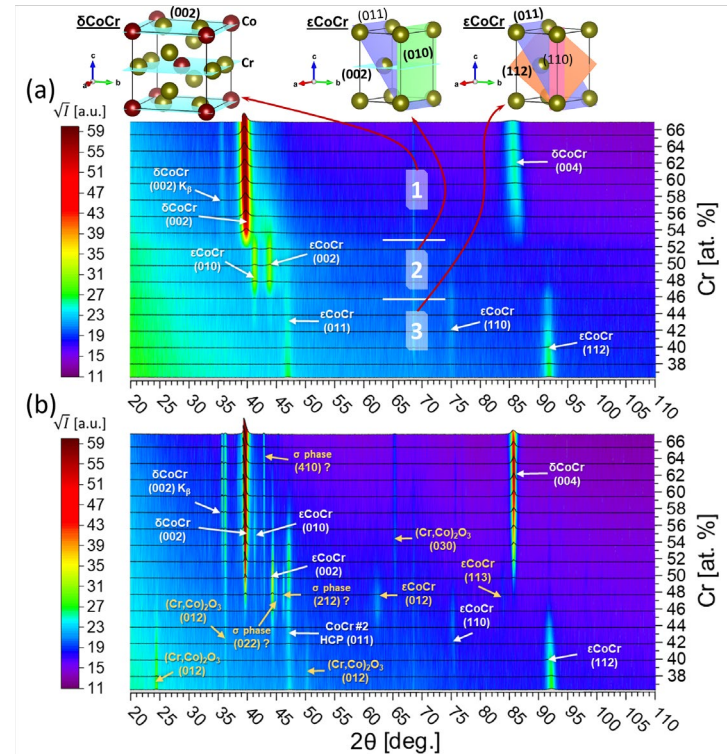


# Microstructure mapping

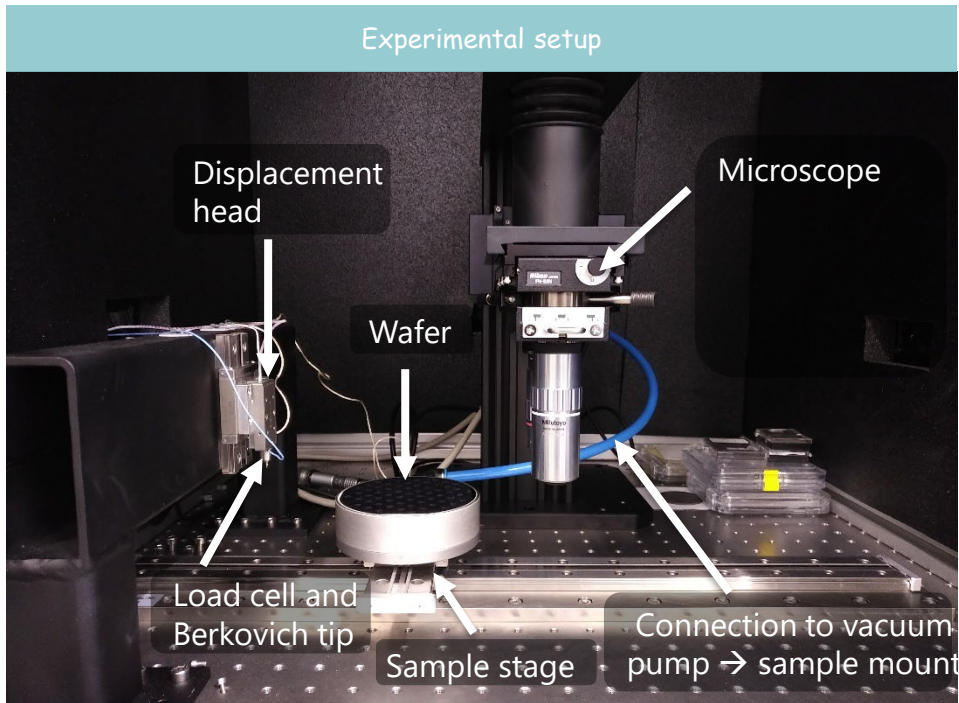


XRD mapping on each patch:

- Identification of phases
- Grain size analysis
- Correlation with composition

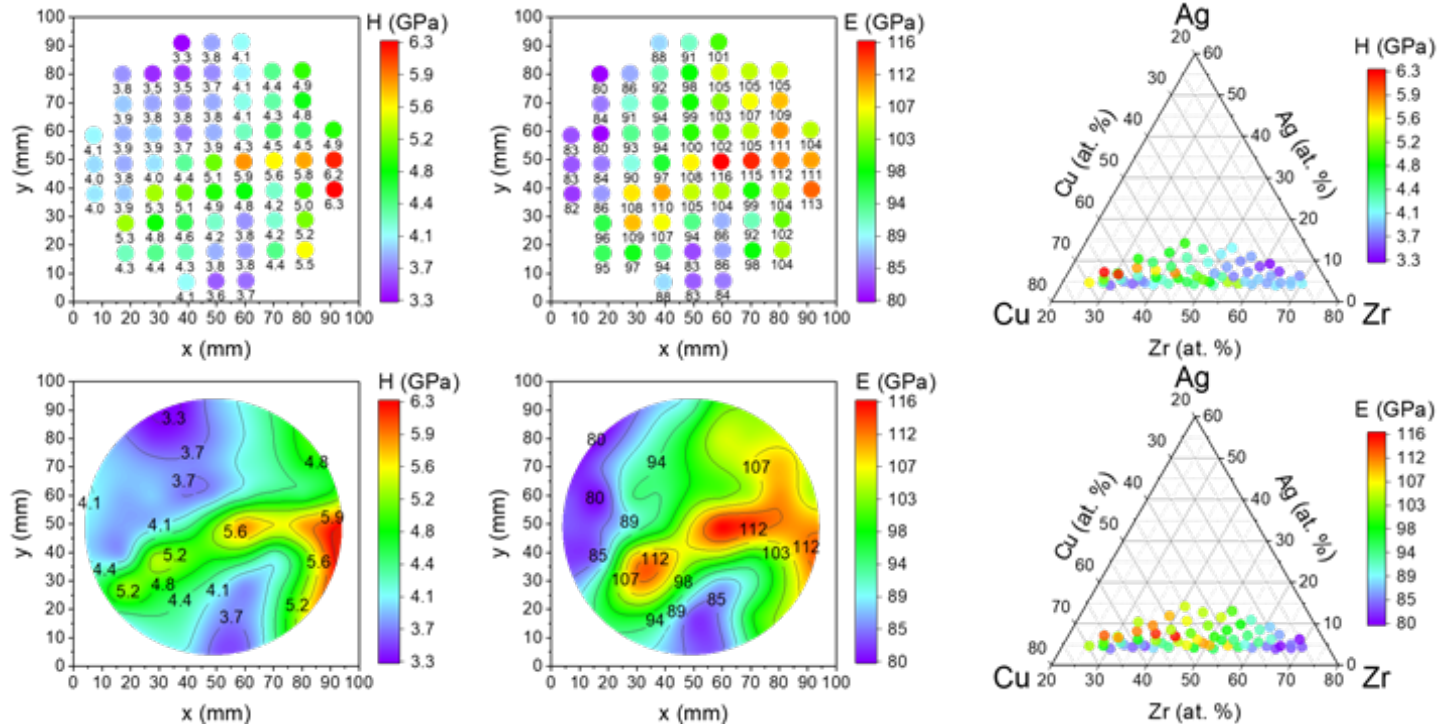


# Mechanical property mapping



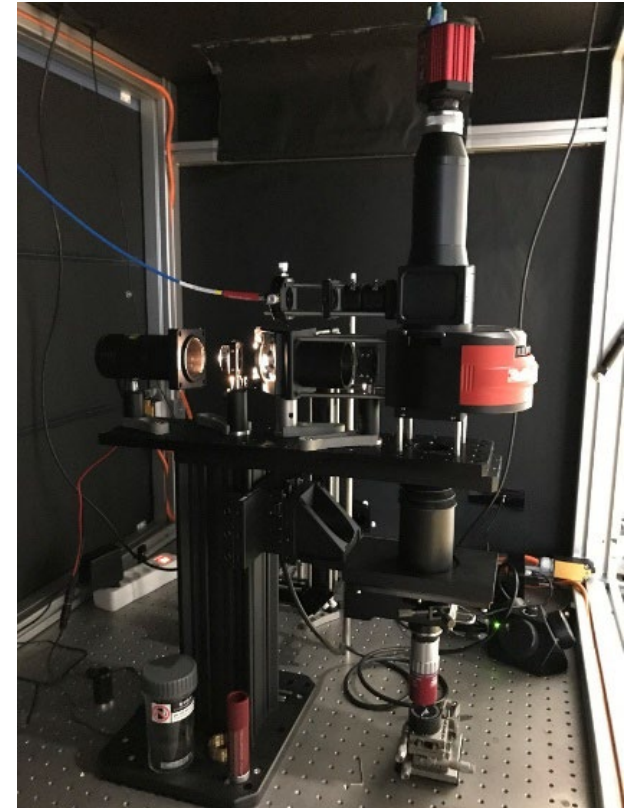
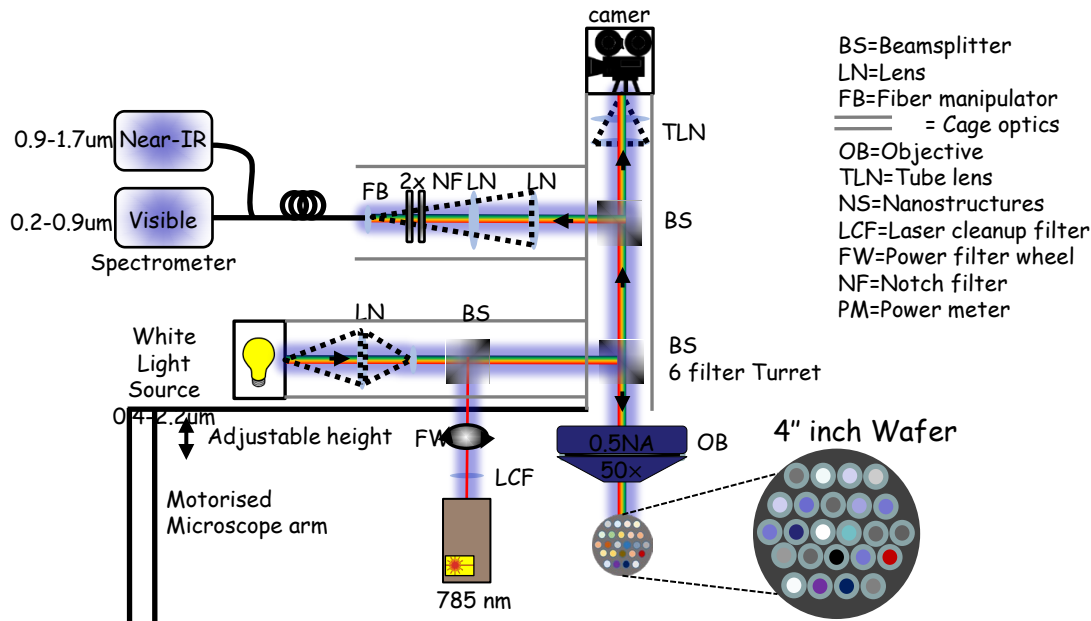
- High accuracy, low noise for thin film mechanical property measurements
- Automatic mapping of mechanical properties on 4in wafers
- Constant machine compliance
  - Guarantees consistent results over whole wafer
- Nanoindentation for measuring hardness, modulus, coating adhesion
- Scratch testing

# Mechanical property mapping - CuZrAg



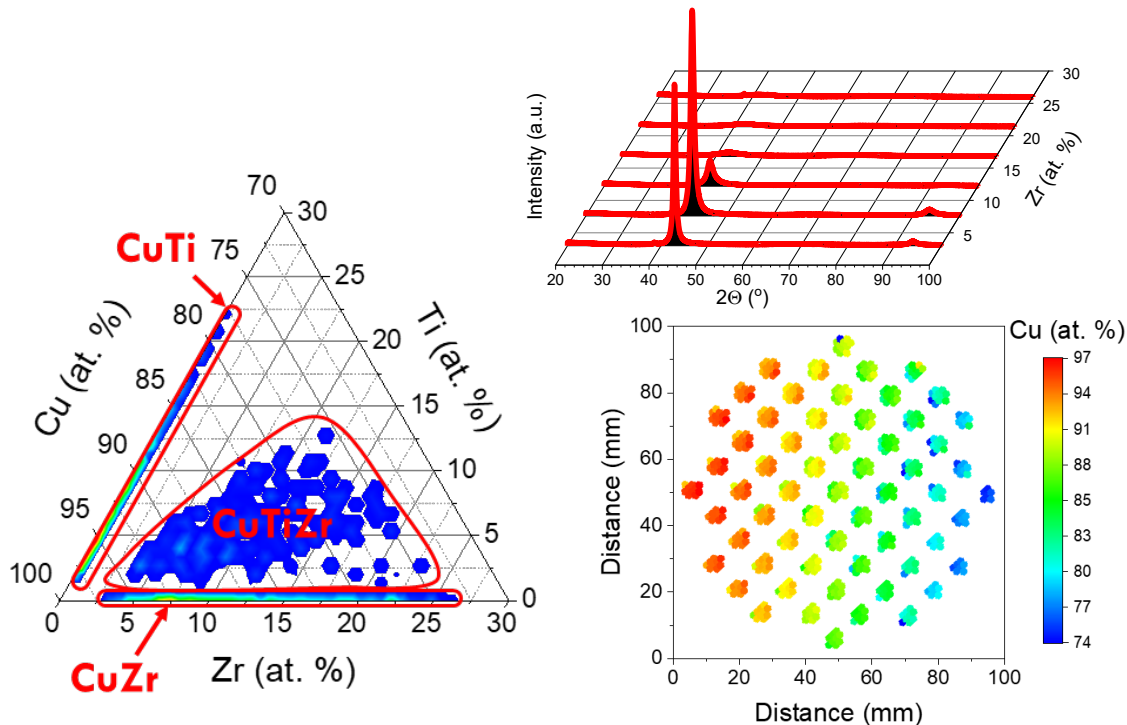
Hardness and modulus correlated to composition

# Optical property mapping

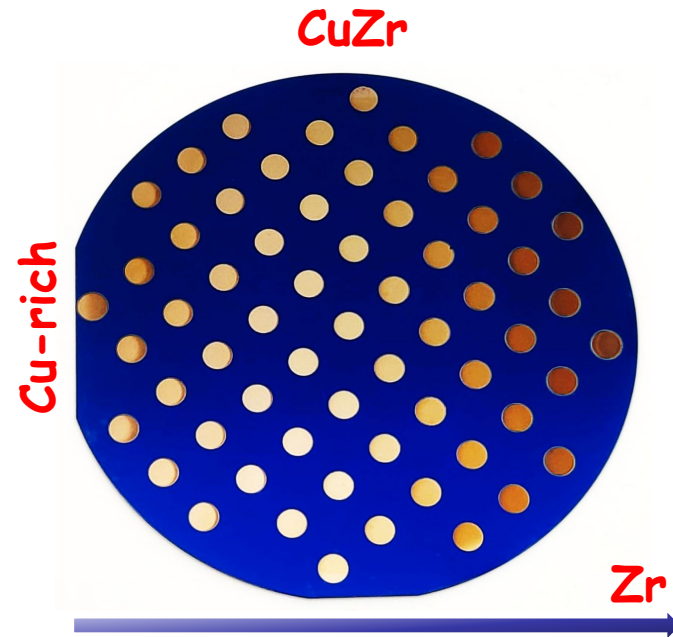


- Reflectivity: 300nm to 1800nm
- Raman spectroscopy (785nm laser)

# Optical property mapping - CuZrTi

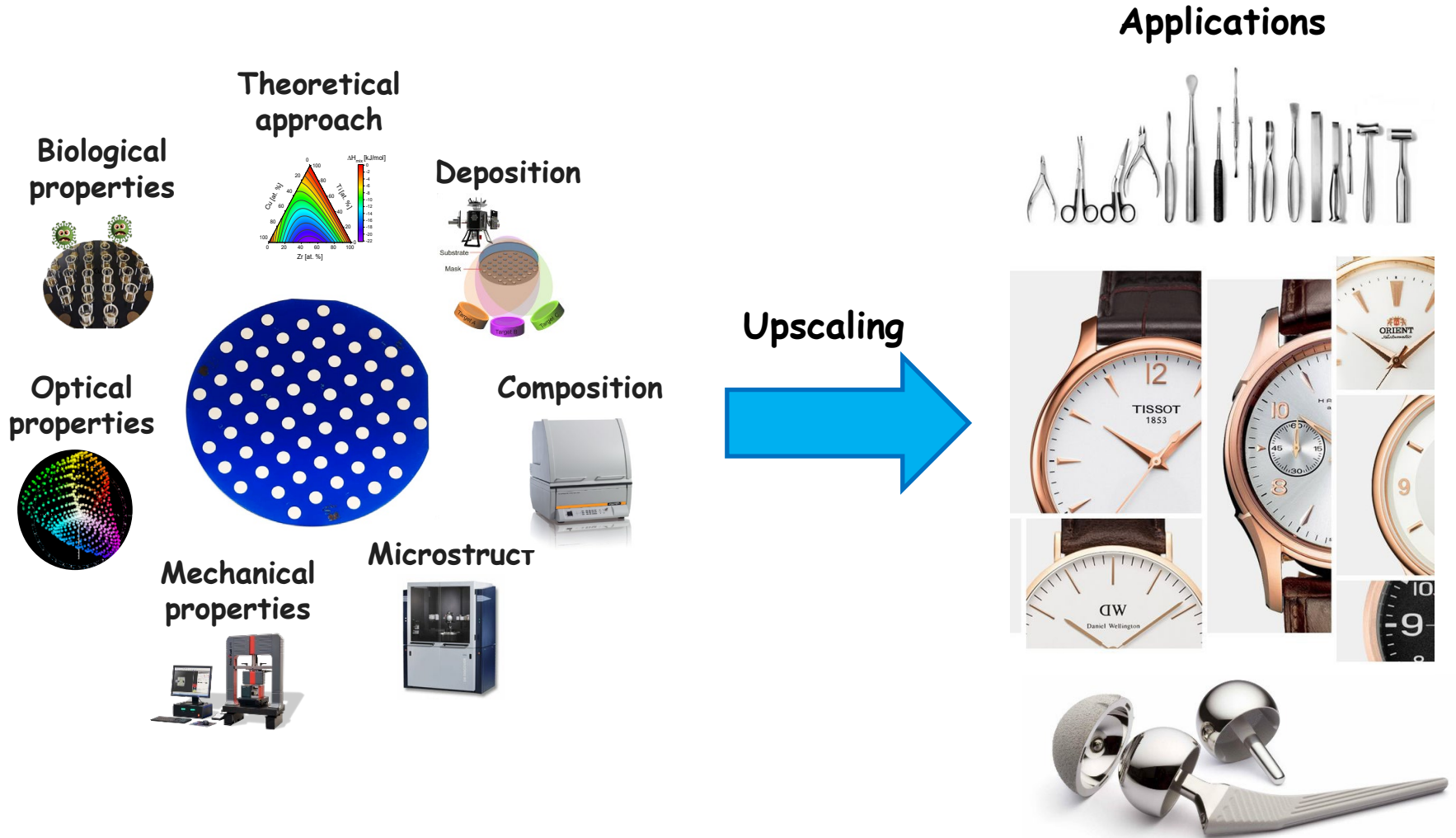


Heat treatment: 200°C / 10 min  
Atmosphere: air

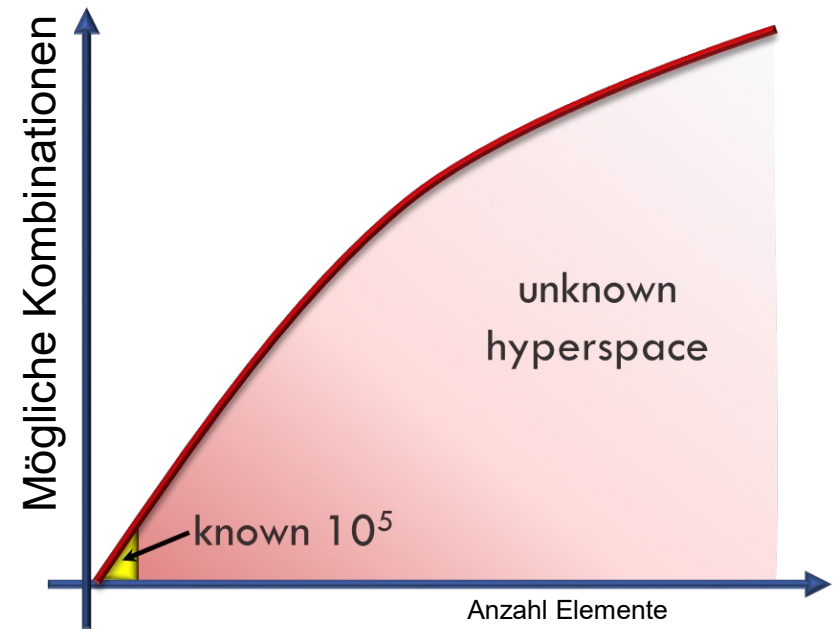
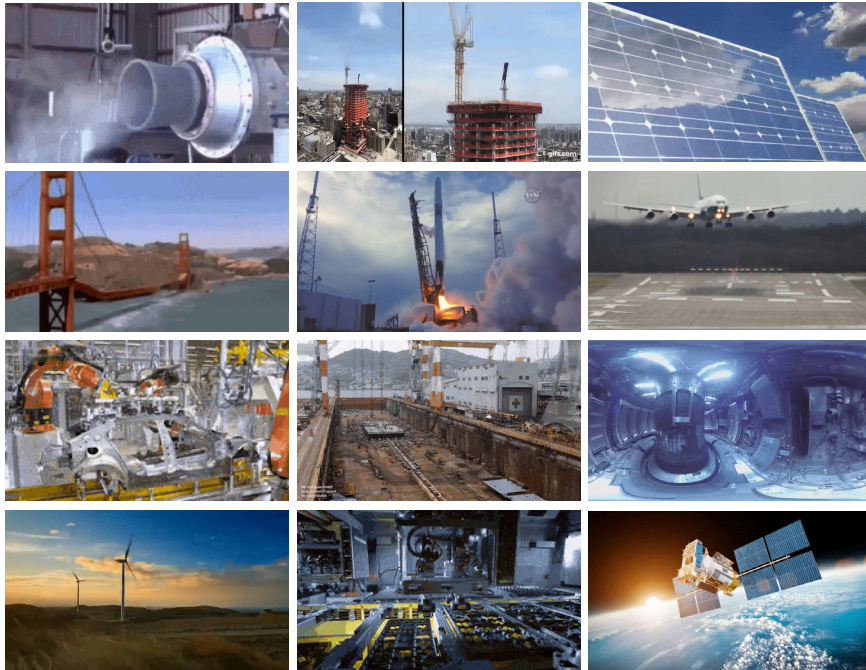


Note: Colour of the thin film changes significantly with the gradient of the chemical composition

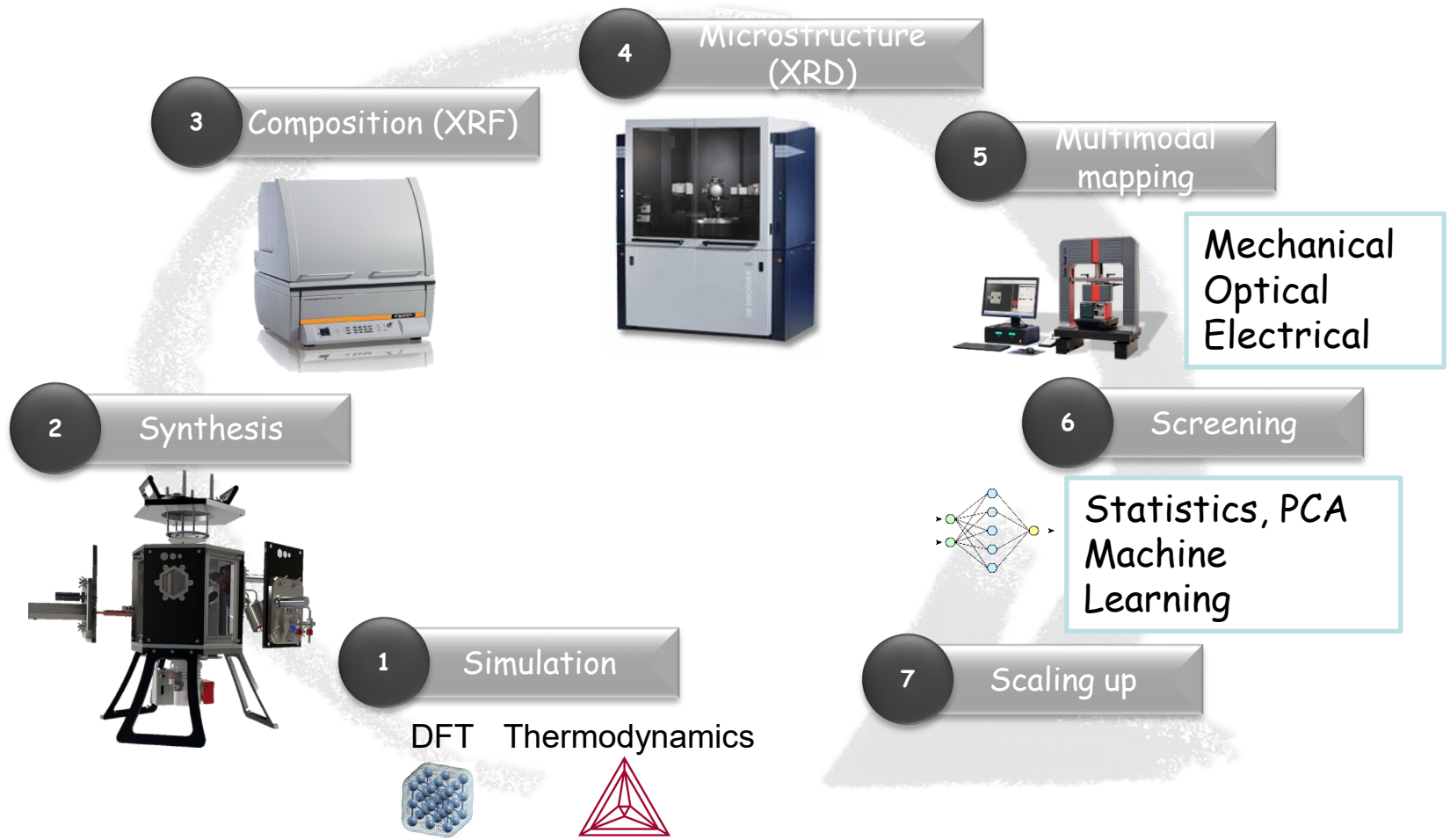
# Combinatorial materials discovery - outline



# Motivation - Warum ~~Hochdurchsatz?~~



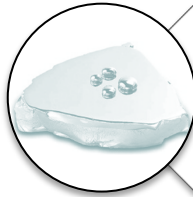
# Method - combinatorial thin film libraries



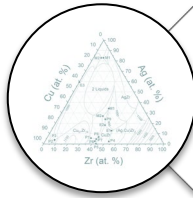


# Why CuZrAg?

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**High glass forming ability**



**Portion of the phase diagram where glasses are forming is known**

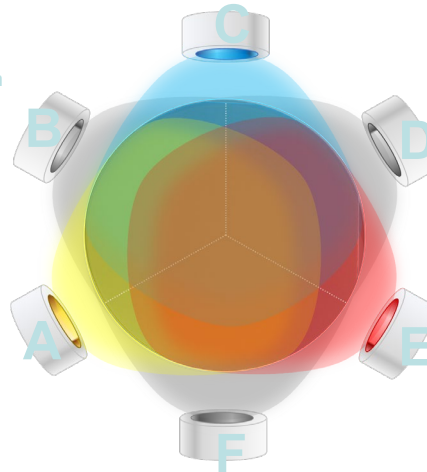
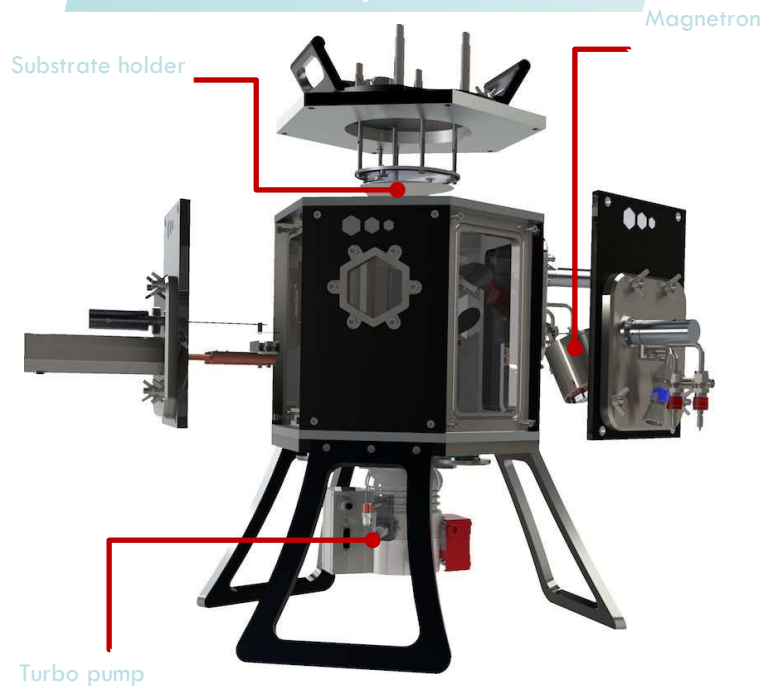


**Cu and Ag possess antimicrobial properties**

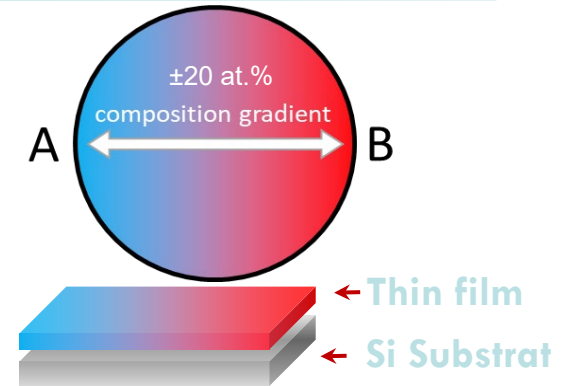
# Deposition of thin film libraries



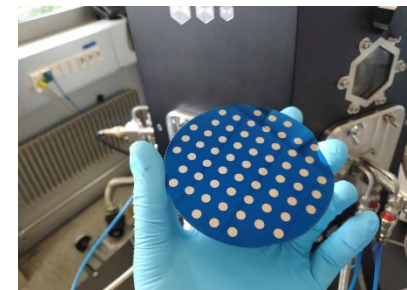
## PVD deposition



## Material library



Deposition process

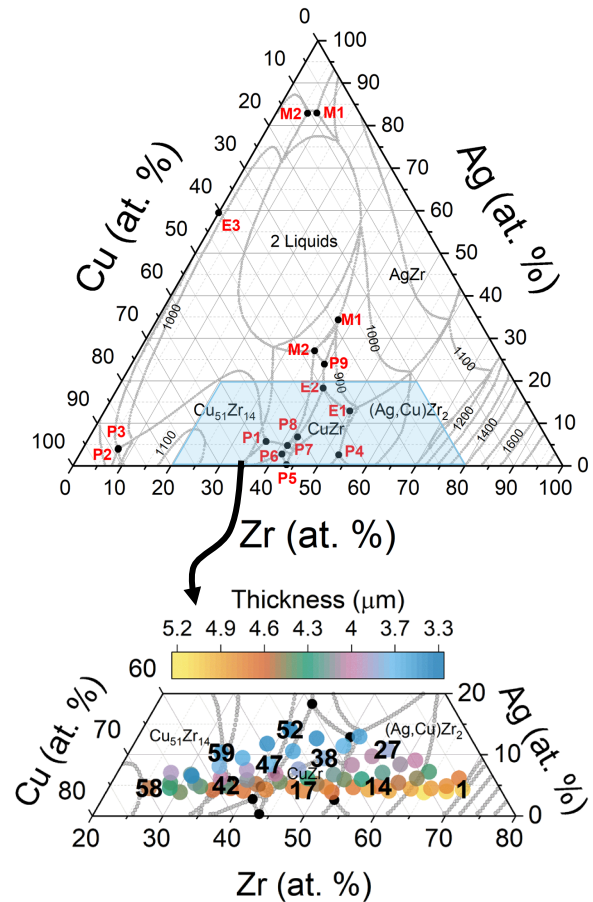
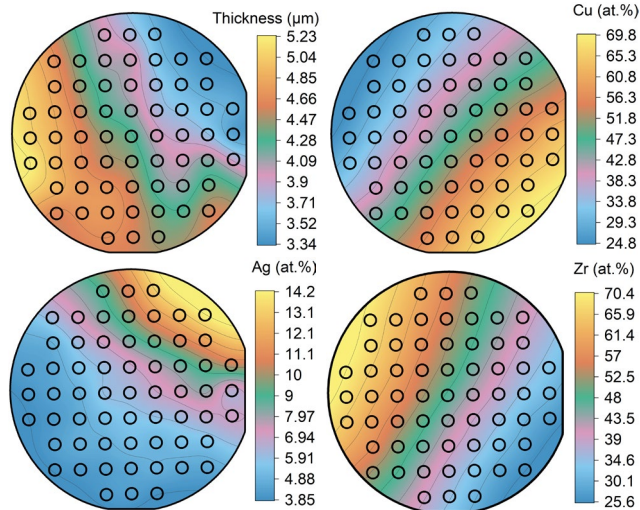


Thin film library

# Chemical composition



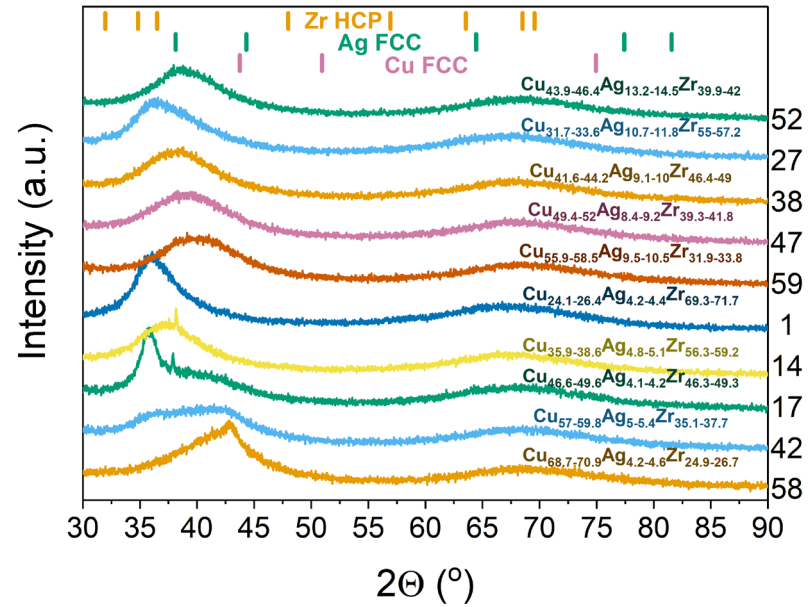
Fischerscope X-Ray XDV-SDD



XRF mapping on every patch:

- Chemical composition
- Film thickness

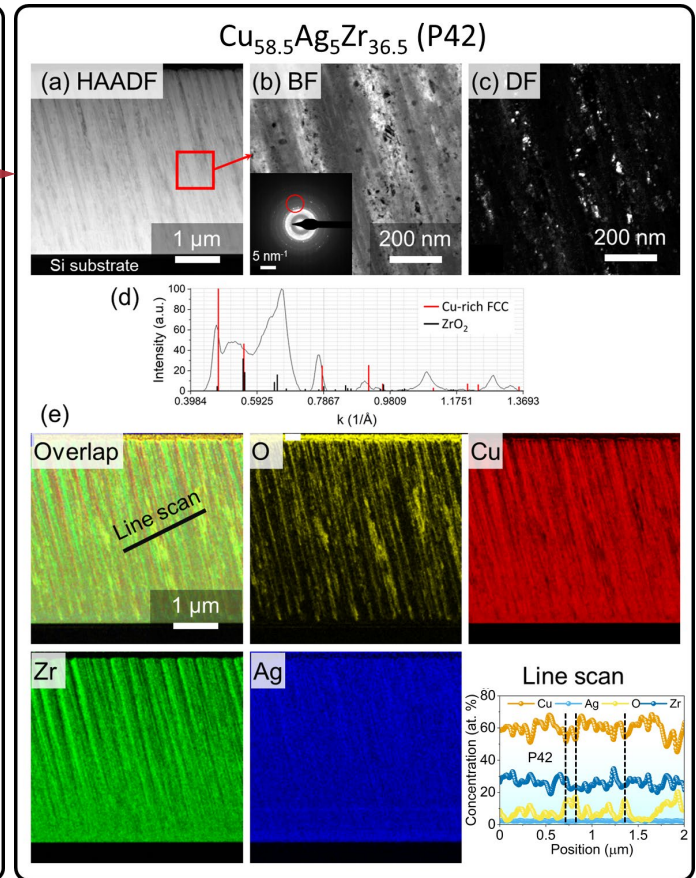
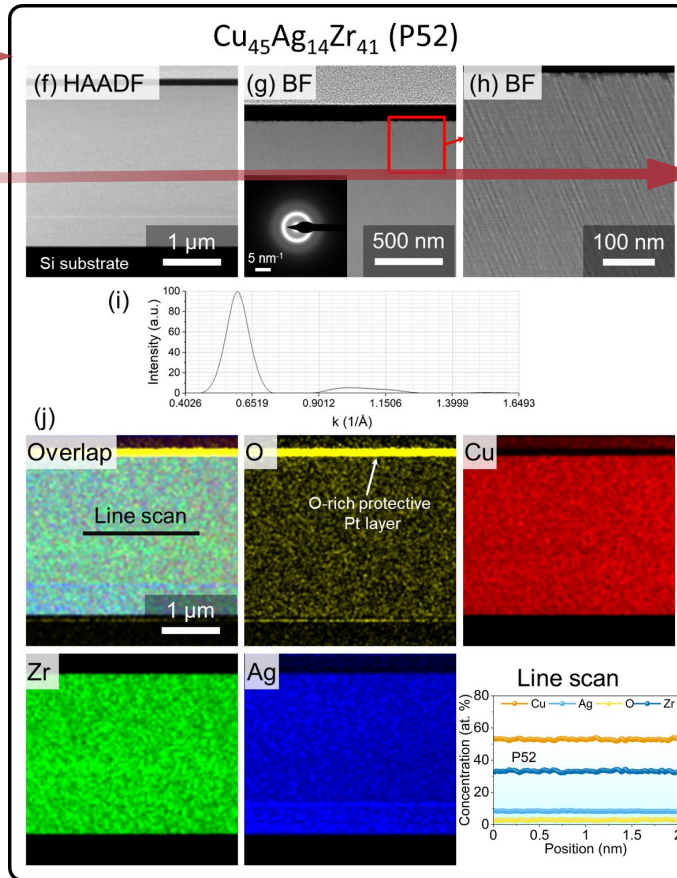
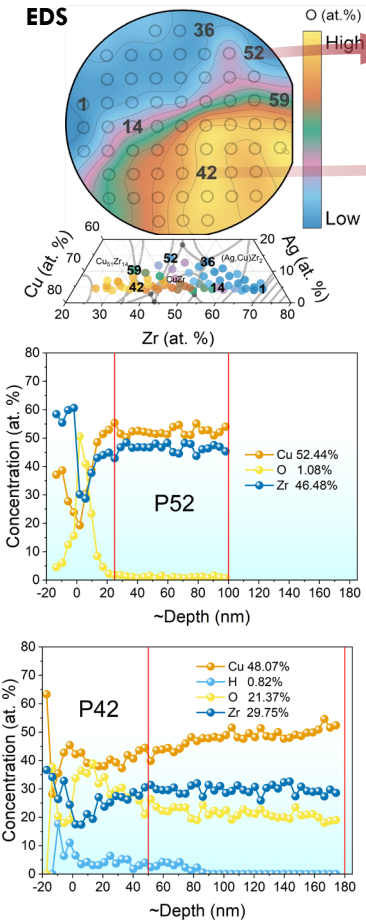
# Microstructure



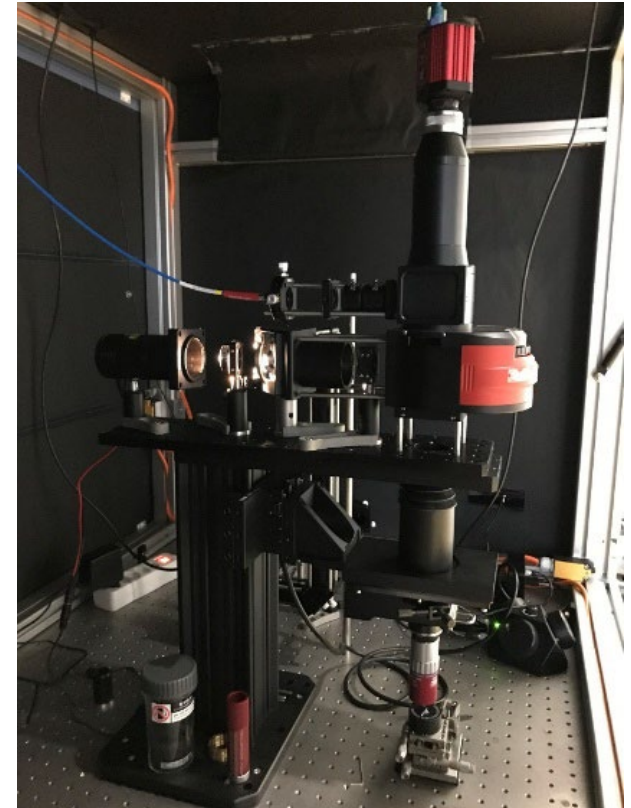
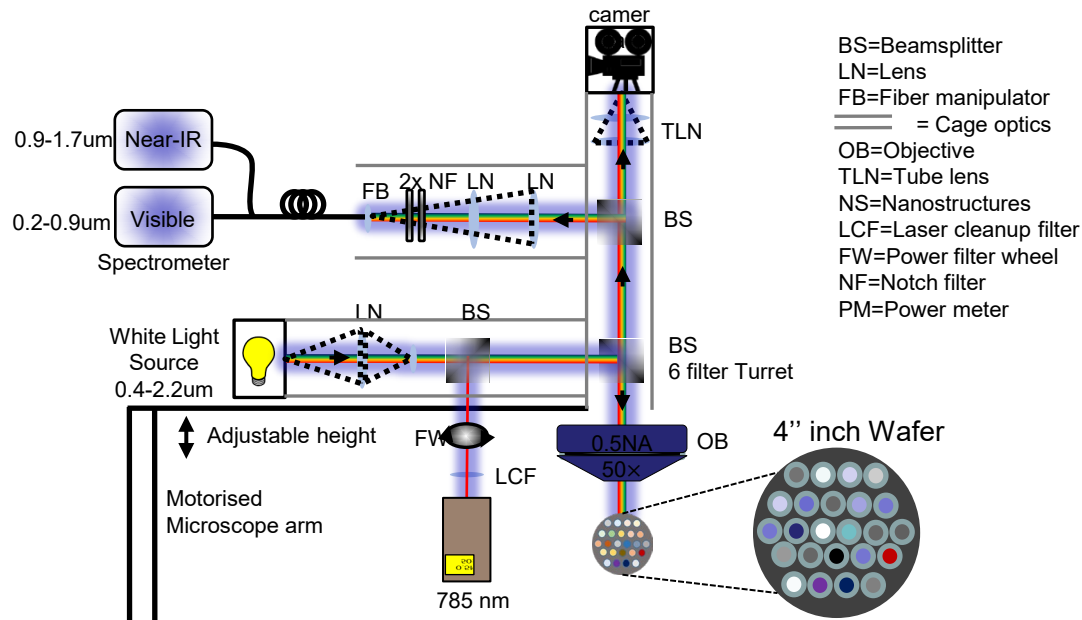
XRD on each patch:

- Amorphous structure

# Defects and oxygen content



# Instrument development: optical properties

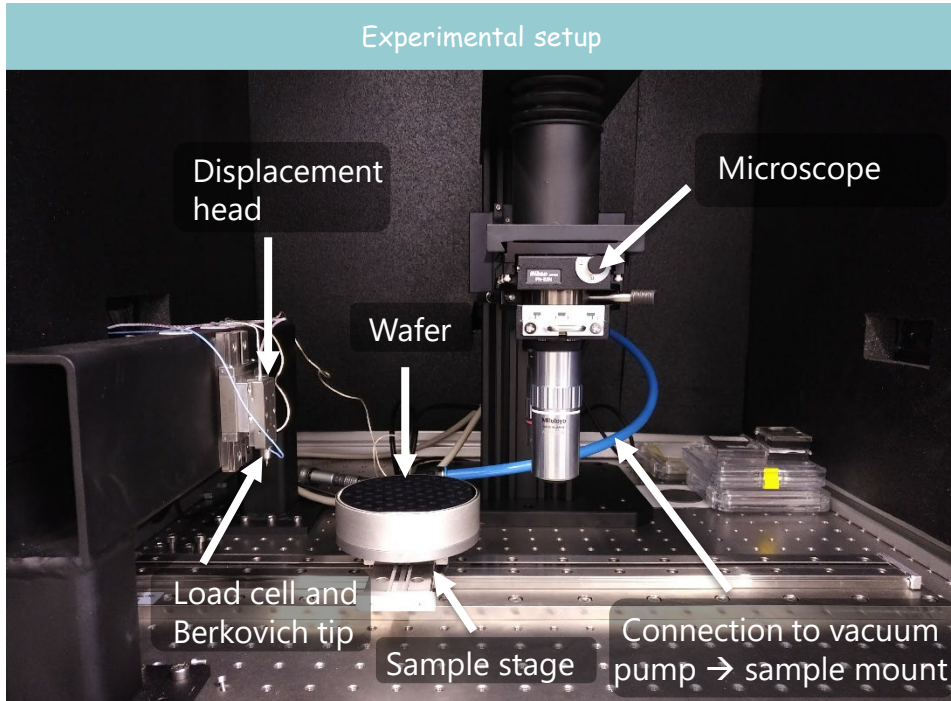


- Reflectivity: 300nm to 1800nm
- Raman Spectroscopy (785nm laser)

# Instrument development: Nanoindentation



**alemnis**  
engineering your ideas



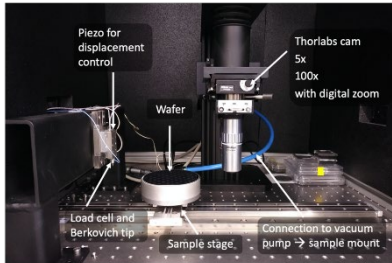
- High accuracy, low noise for thin film mechanical property measurements
- Automatic mapping of mechanical properties on 4in wafers
- Constant machine compliance
  - Guarantees consistent results over whole wafer
- Nanoindentation for measuring hardness, modulus, coating adhesion
- Scratch testing

# Nanomechanical properties



## Scanning Indenter

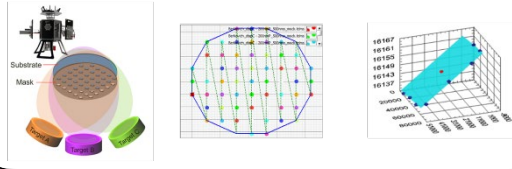
Automatische Messung auf 4 in Wafern



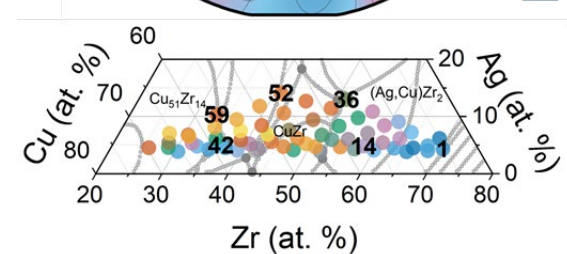
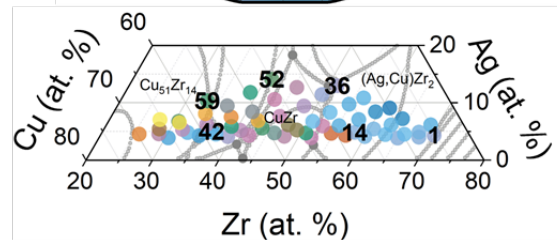
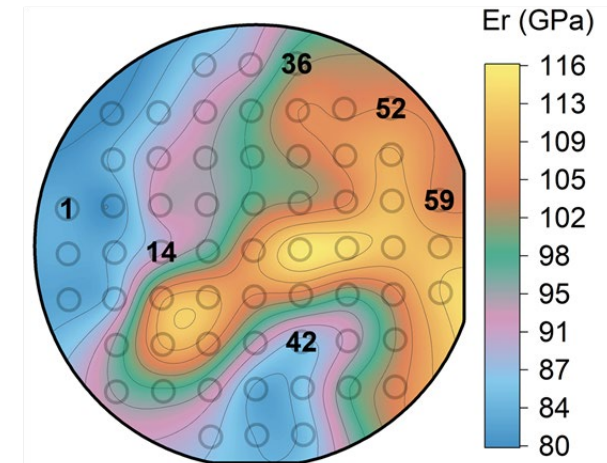
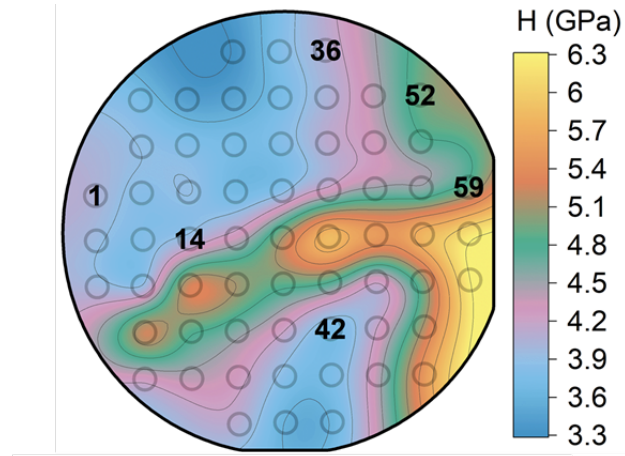
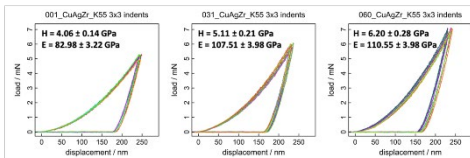
Chemische Gradienten

Automatisiertes Mapping

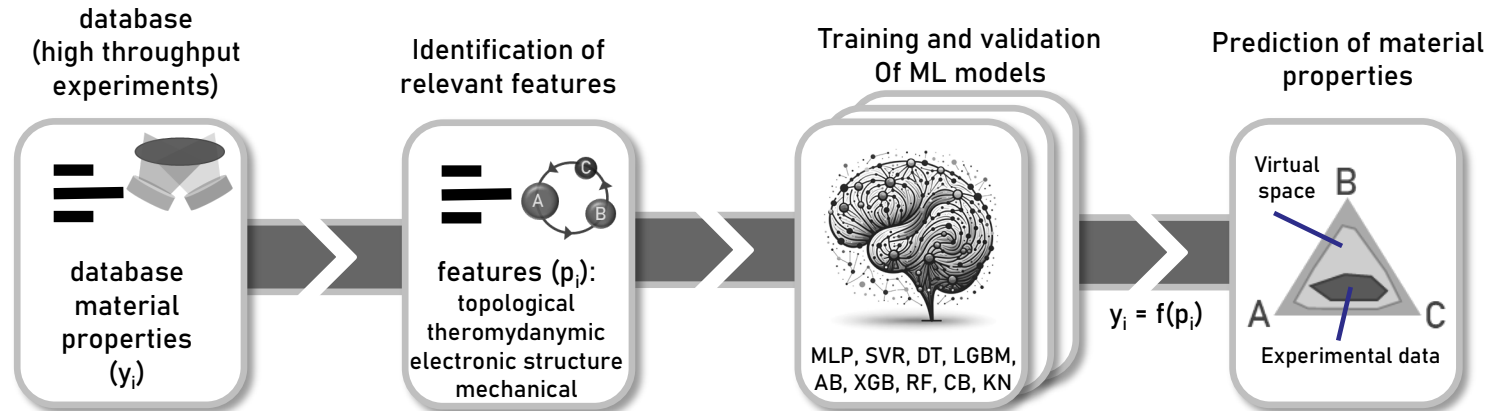
Oberflächendetektion



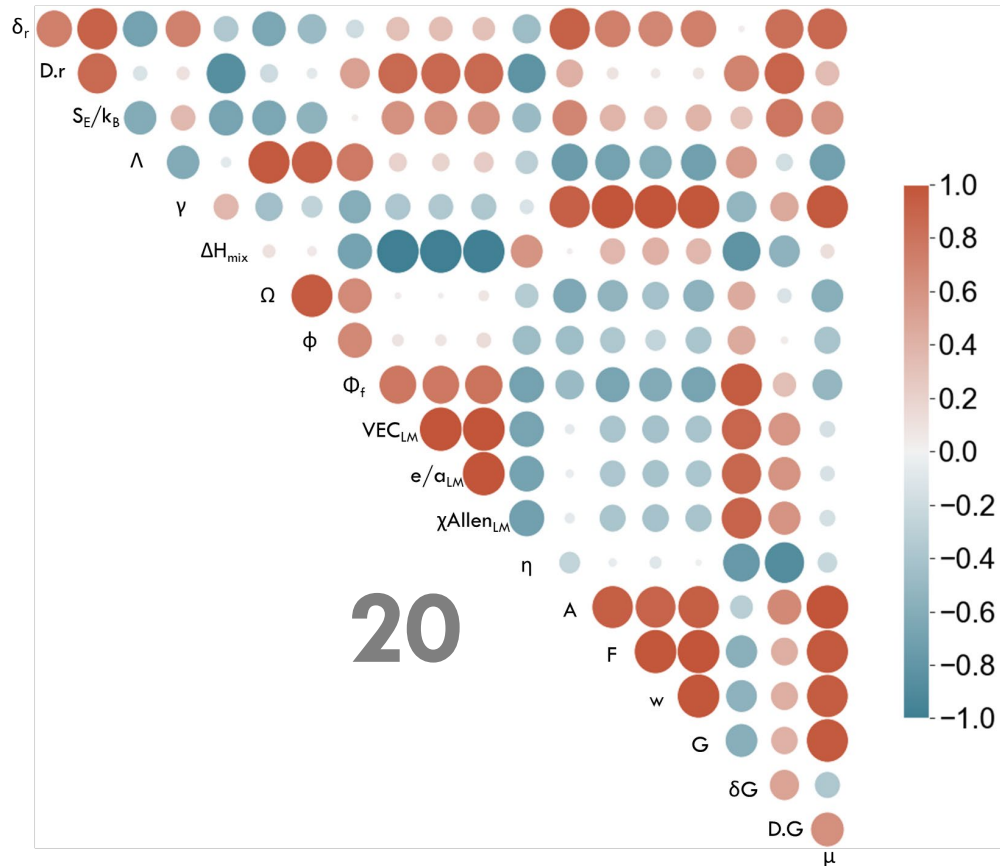
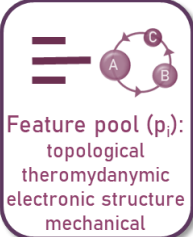
Messung von Härte und Modul der 61 Compositionen



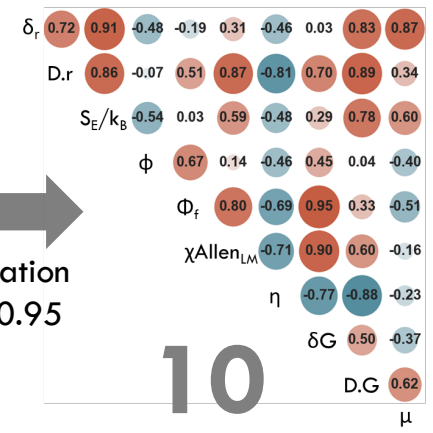
# Data analysis using machine learning



# Data analysis using machine learning



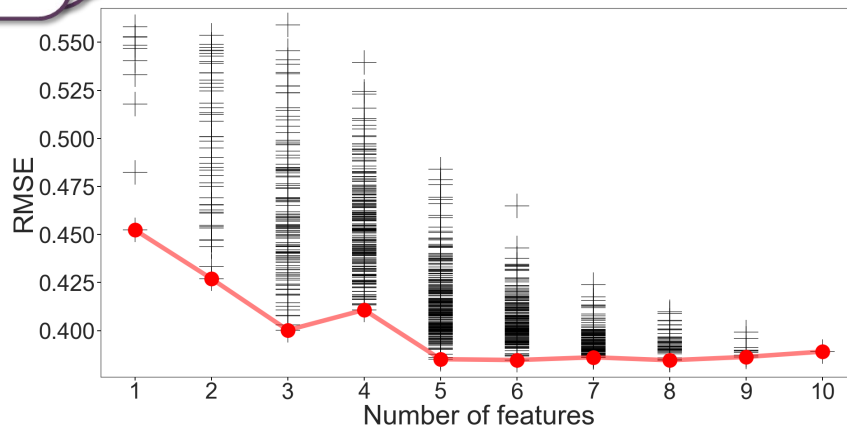
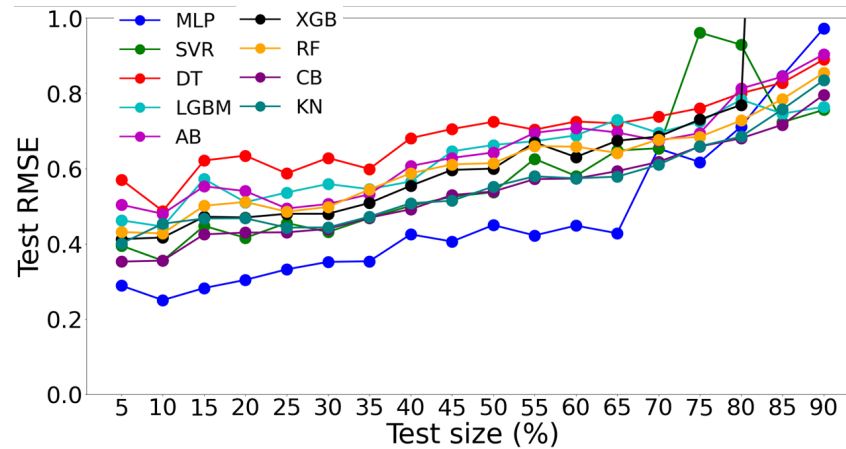
Correlation  
 max: 0.95



# Data analysis using machine learning



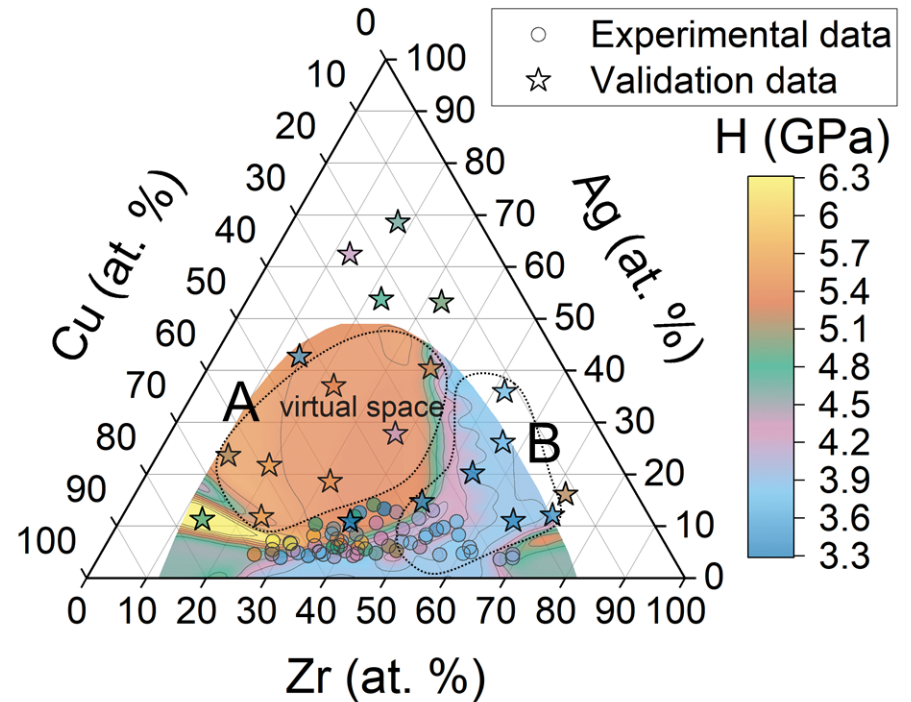
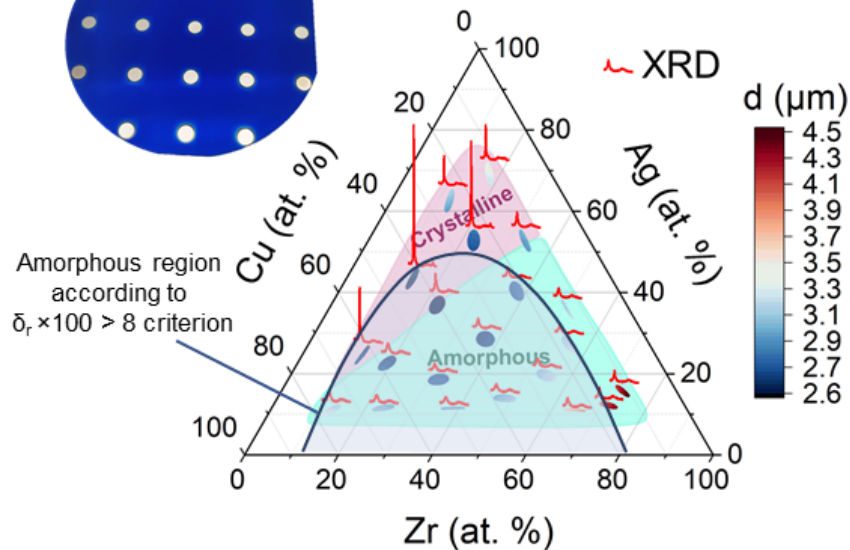
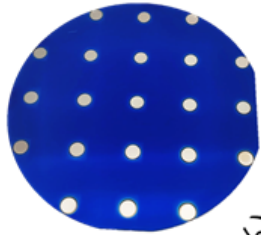
Feature pool ( $p_i$ ):  
topological  
thermodynamic  
electronic structure  
mechanical



| # feature | Best set of features  | RMSE   |
|-----------|---|--------|
| 1         | $\mu$   | 0.4524 |
| 2         | $\Phi_{fr}, \mu$  | 0.4270 |
| 3         | $\Phi_{fr}, \eta, \mu$  | 0.4002 |
| 4         | $\Phi_{fr}, \chi_{All_{LM}}, D.G, \mu$  | 0.4108 |
| 5         | $\Phi_{fr}, \chi_{All_{LM}}, \eta, D.G, \mu$  | 0.3851 |
| 6         | $\delta, \Phi_{fr}, \chi_{All_{LM}}, \eta, D.G, \mu$                                | 0.3847 |
| 7         | $\delta, D.r, \varphi, \Phi_{fr}, \chi_{All_{LM}}, D.G, \mu$                        | 0.3861 |
| 8         | $\delta, D.r, \Phi_{fr}, \chi_{All_{LM}}, \eta, \delta G, D.G, \mu$                 | 0.3846 |
| 9         | $\delta, D.r, SE/kB, \Phi_{fr}, \chi_{All_{LM}}, \eta, \delta G, D.G, \mu$          | 0.3863 |
| 10        | $\delta, D.r, SE/kB, \varphi, \Phi_{fr}, \chi_{All_{LM}}, \eta, \delta G, D.G, \mu$ | 0.3891 |

# Data analysis using machine learning

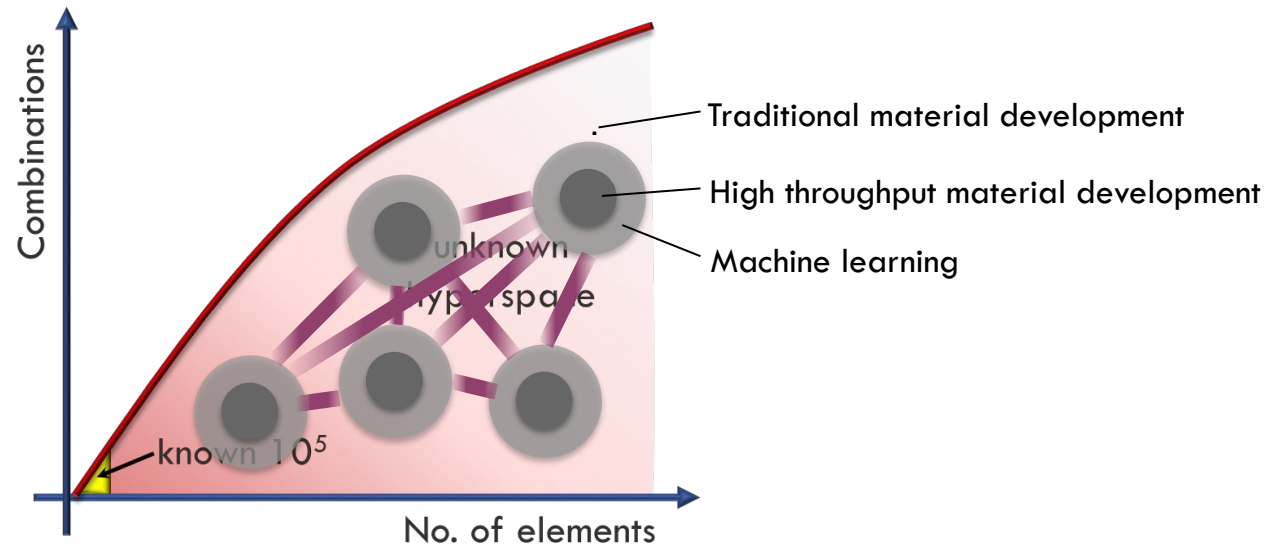
## Machine learning



# Summary



- ✓ Combination of combinatorial material libraries, high throughput experiments, and machine learning can significantly speed up the material development process
- ✓ The methods used in this study can be generalized and used for other material systems.
- ✓ The investigation of the CuAgZr system using our methods allows identifying compositions with high potential for biomedical applications.



K. Wiczerzak et al.: Unlocking the potential of CuAgZr metallic glasses: A comprehensive exploration with combinatorial synthesis, high-throughput characterization, and machine learning, Adv. Sci. (2023).