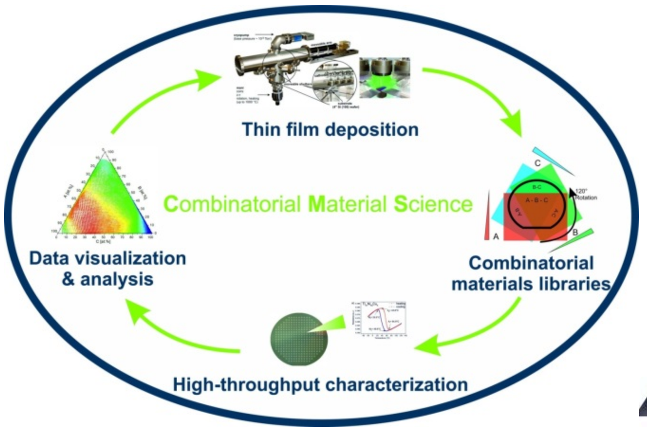
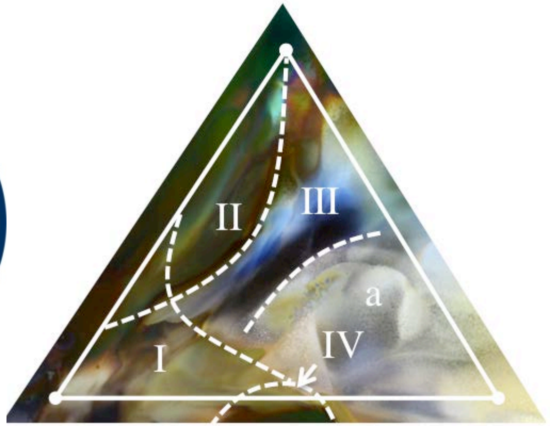
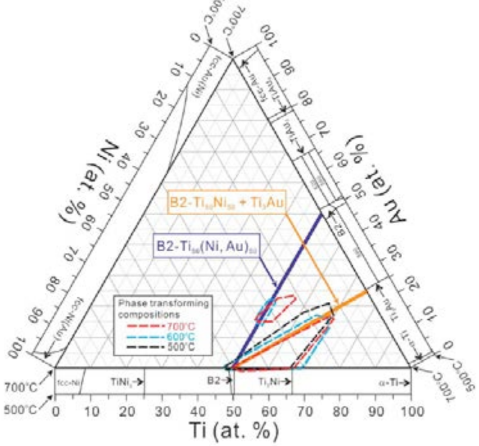






RUHR-UNIVERSITÄT BOCHUM

Fundamental Aspects of Materials Science and Engineering

Summer term 2020: Part 3 Combinatorial Materials Science and High-Throughput Experimenation

Prof. Dr.-Ing. Alfred Ludwig

Materials Discovery and Interfaces

Outline

- Materials discovery and optimization
- **Combinatorial synthesis of thin-film materials libraries**
- **High-throughput characterization**
- **Multifunctional existence diagrams** (Composition-Processing-Structure-Properties Maps)
- **Combinatorial thin-film libraries: Application examples**
  - Discovery of new phases
  - Verification of theoretical predictions: Shape memory alloys (SMA)
  - Examples of multifunctional existence diagrams
- **Combinatorial materials processing, libraries of nanostructured materials**
  - Nanostructured thin film oxides for solar water splitting
  - Multinary nanoscale films for atom probe tomography
  - Multinary nanoparticle libraries
- Conclusions and outlook

Materials discovery

Possibilities and challenges

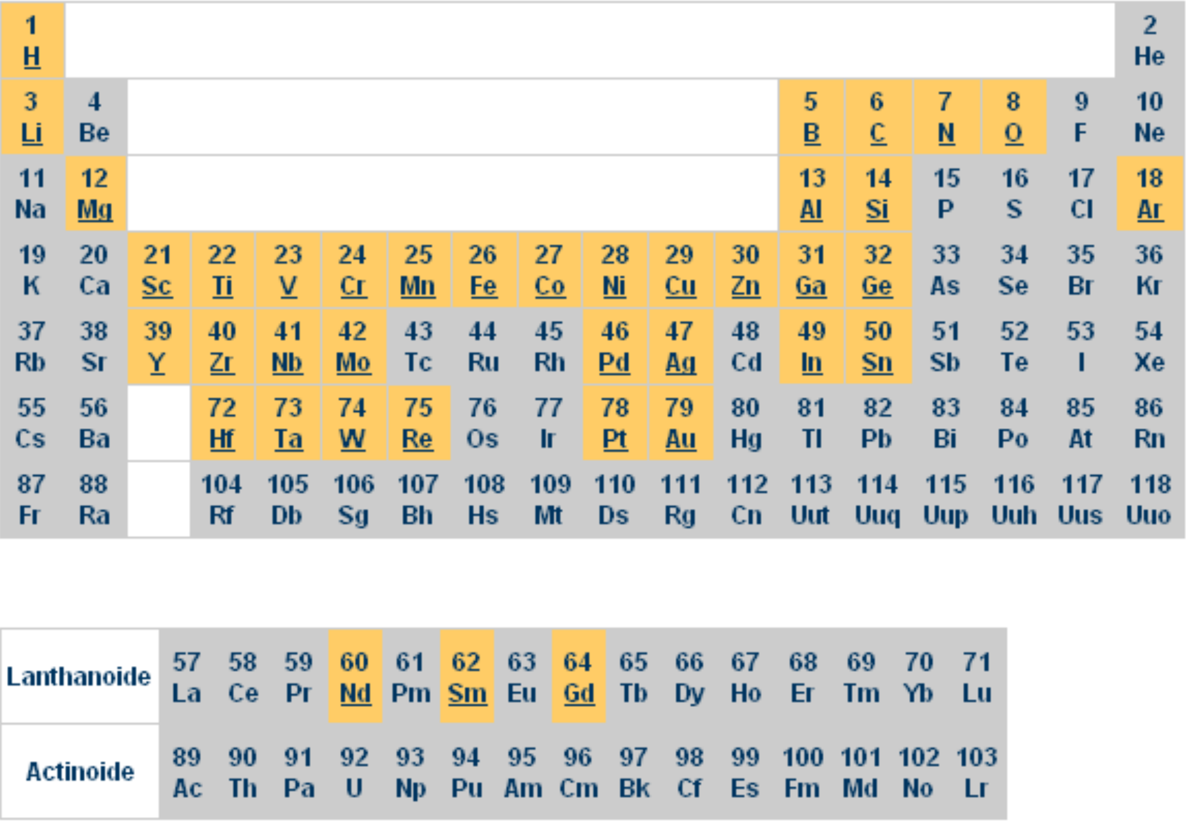
Number of combinations of n=50 elements

(n/k) = n!/(k!(n-k)!)

Binaries:
1225

Ternaries:
19600
(information on 7380 systems)

Quaternaries:
230000



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Lanthanoide	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinoide	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

+ compositional- and structural diversity
+ diversity of processing

A_1B_{99} to $A_{99}B_1$

$A_{50}B_{50}$(bulk) ≠ $A_{50}B_{50}$ (thin film)

Unexplored compositionally complex materials

Compositionally complex alloys: > 4 elements

Steels

Superalloys

High-entropy alloys

Multiple principal element alloys

Metallic glasses

….

Number of combinations of n=50 elements

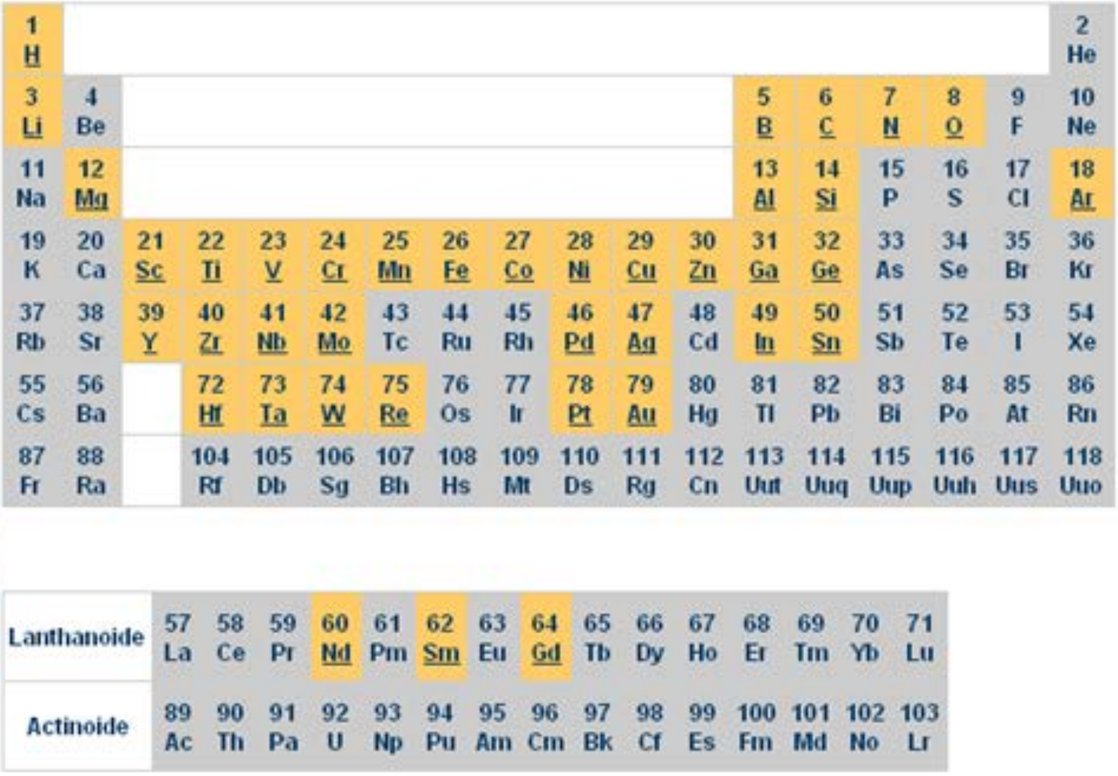
(n/k) = n!/(k!(n-k)!)

Binaries: 1225

Ternaries: 19600
(information on 7380 systems)

Quaternaries: 230000

Quinaries: 2.118.760



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

Lanthanoide	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinoide	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

"Combinatorial explosion" for multinary systems

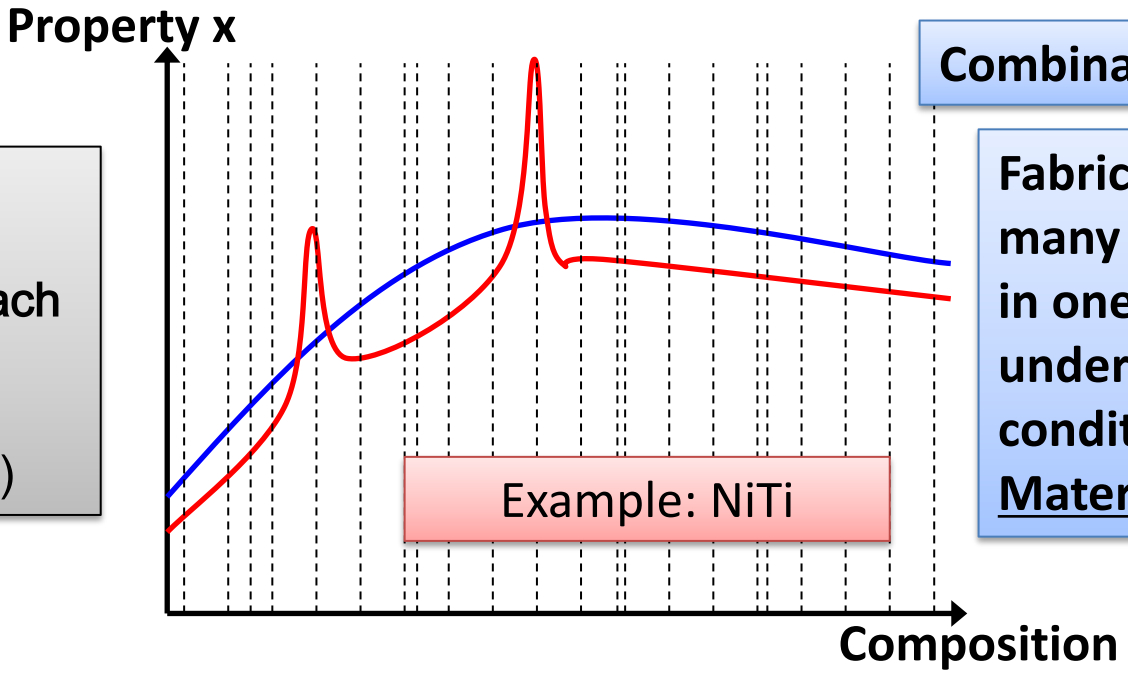
Compositional, process-related and structural complexity

High-throughput methods in materials science

Conventional and combinatorial material development

"Conventional" materials science: „one by one" approach → limited rate of discoveries (often serendipitous)

Mapping of physical properties versus composition



Example: NiTi

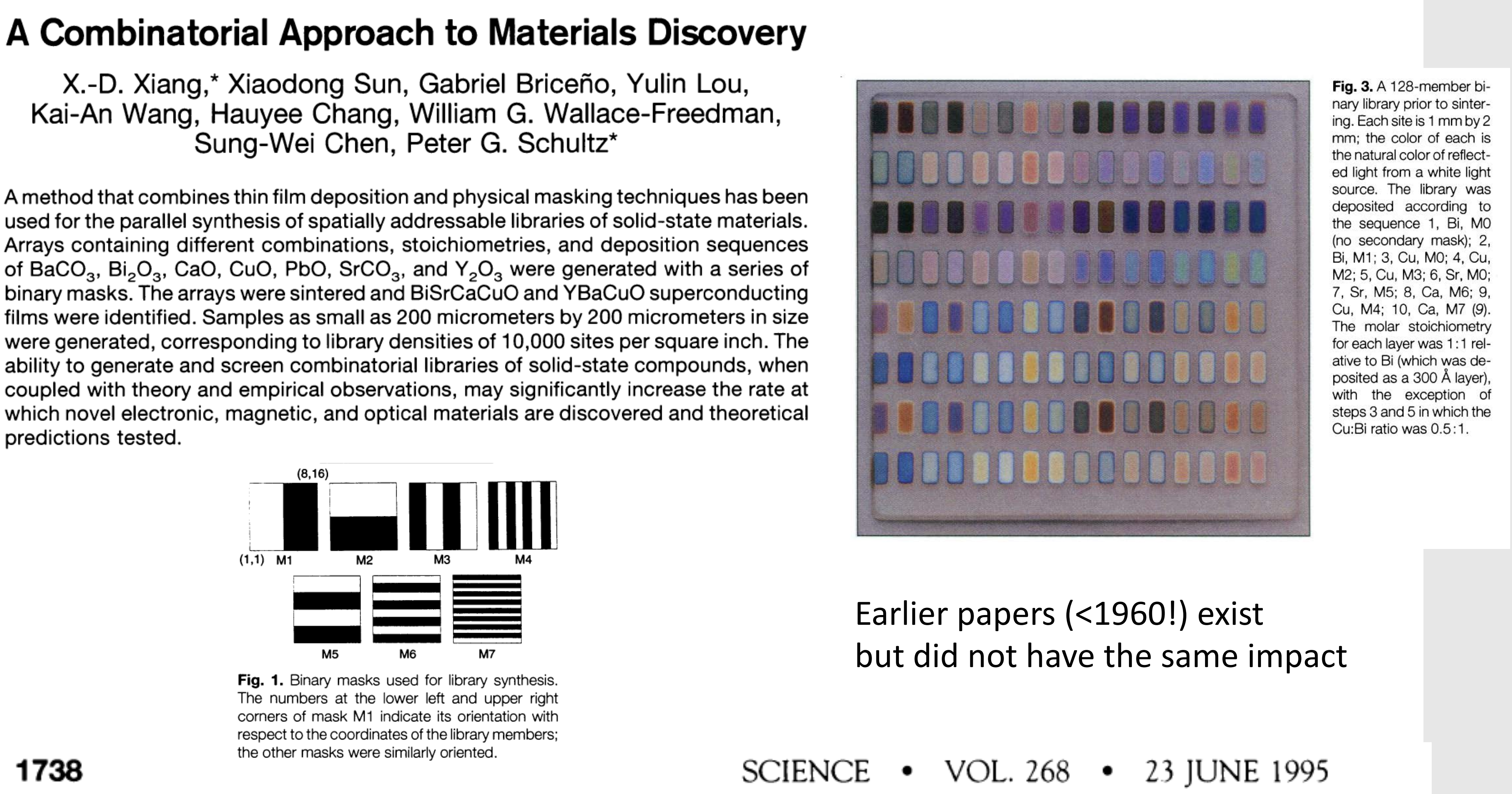
Combinatorial approach

Fabrication of many samples in one experiment under identical conditions: Materials Libraries

Fabricate
MATERIALS LIBRARIES
+
Use
HIGH-THROUGHPUT CHARACTERIZATION
„screening"

Materials library:
A well-defined set of materials
- *suitable for high-throughput characterization* -
produced in one experiment under identical conditions

Seminal paper in combinatorial materials science



A Combinatorial Approach to Materials Discovery

X.-D. Xiang,* Xiaodong Sun, Gabriel Briceño, Yulin Lou,
Kai-An Wang, Hauyee Chang, William G. Wallace-Freedman,
Sung-Wei Chen, Peter G. Schultz*

A method that combines thin film deposition and physical masking techniques has been used for the parallel synthesis of spatially addressable libraries of solid-state materials. Arrays containing different combinations, stoichiometries, and deposition sequences of $BaCO_3$, Bi_2O_3, CaO, CuO, PbO, $SrCO_3$, and Y_2O_3 were generated with a series of binary masks. The arrays were sintered and BiSrCaCuO and YBaCuO superconducting films were identified. Samples as small as 200 micrometers by 200 micrometers in size were generated, corresponding to library densities of 10,000 sites per square inch. The ability to generate and screen combinatorial libraries of solid-state compounds, when coupled with theory and empirical observations, may significantly increase the rate at which novel electronic, magnetic, and optical materials are discovered and theoretical predictions tested.

Fig. 1. Binary masks used for library synthesis. The numbers at the lower left and upper right corners of mask M1 indicate its orientation with respect to the coordinates of the library members; the other masks were similarly oriented.

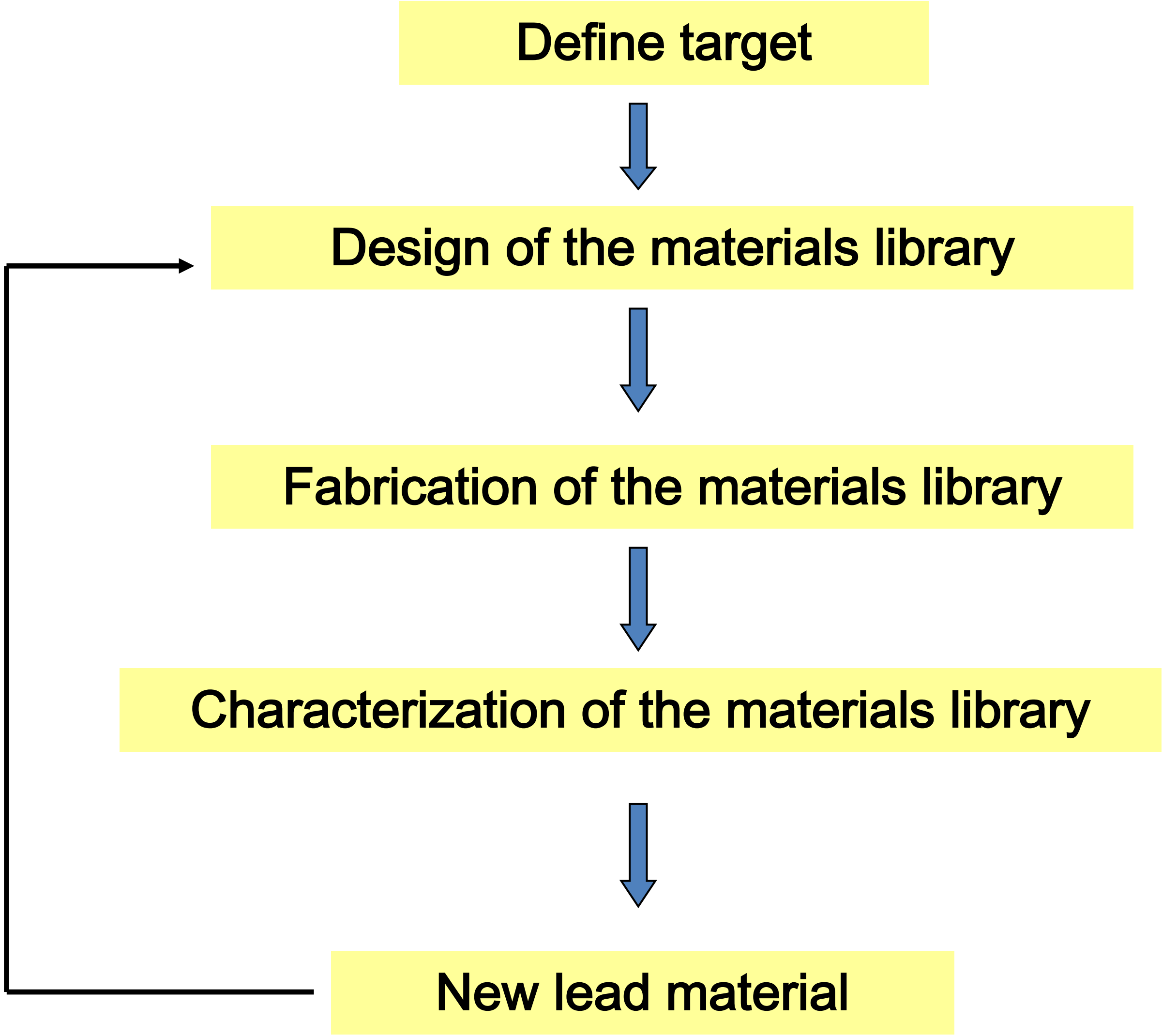
Fig. 3. A 128-member binary library prior to sintering. Each site is 1 mm by 2 mm; the color of each is the natural color of reflected light from a white light source. The library was deposited according to the sequence 1, Bi, M0 (no secondary mask); 2, Bi, M1; 3, Cu, M0; 4, Cu, M2; 5, Cu, M3; 6, Sr, M0; 7, Sr, M5; 8, Ca, M6; 9, Cu, M4; 10, Ca, M7 (9). The molar stoichiometry for each layer was 1:1 relative to Bi (which was deposited as a 300 Å layer), with the exception of steps 3 and 5 in which the Cu:Bi ratio was 0.5:1.

1738

SCIENCE • VOL. 268 • 23 JUNE 1995

Earlier papers (<1960!) exist
but did not have the same impact

Process flow



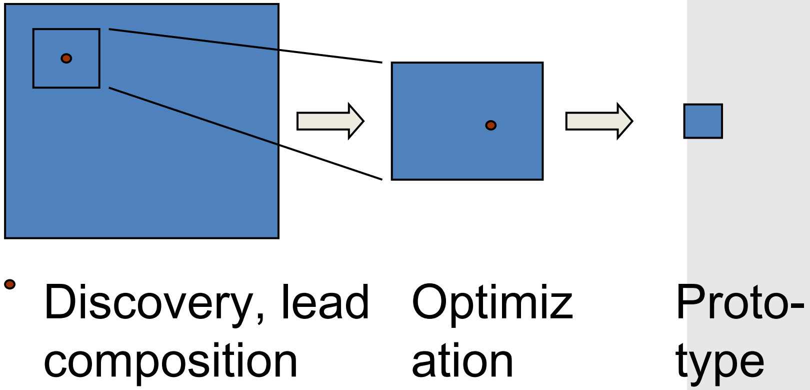
Define target

Design of the materials library

Fabrication of the materials library

Characterization of the materials library

New lead material



Synthesis of complete binary and ternary thin film materials libraries by magnetron sputtering

Establish

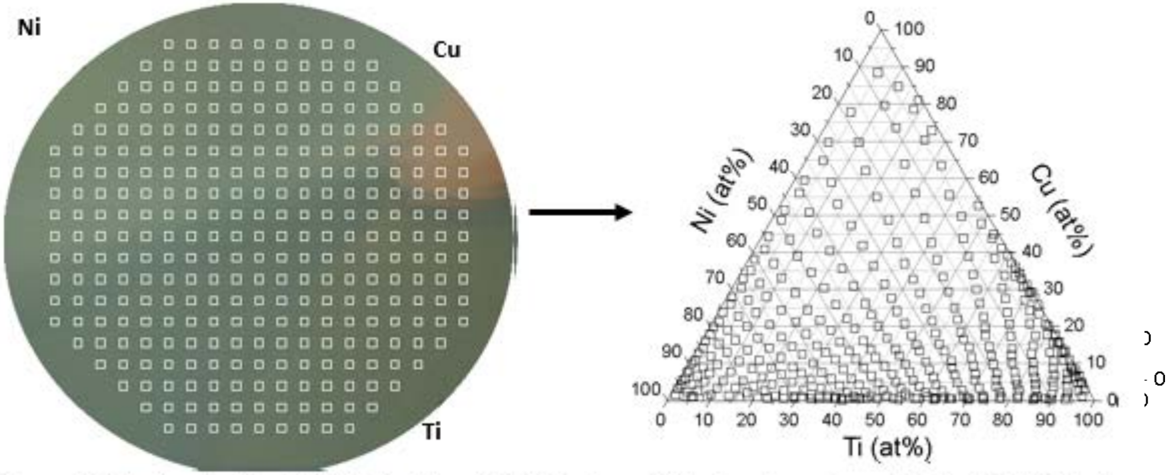
Composition-Structure-Property Correlation Maps

Trendlines: Property = f(composition)

Hits: compositions with unique properties

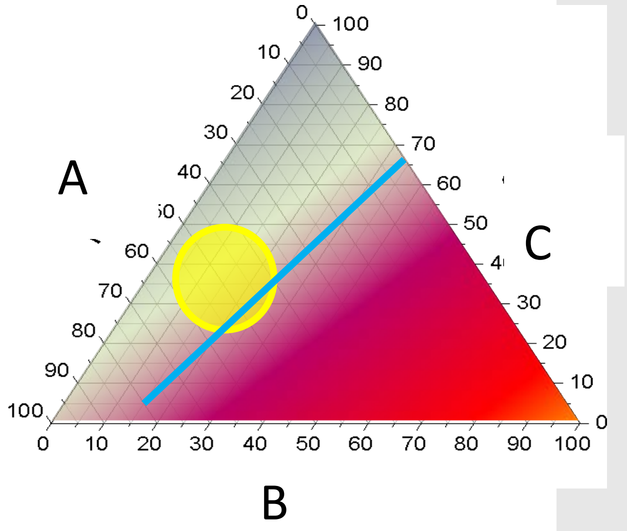
Composition: automated Energy Dispersive X-ray analysis (EDX)

- over-night measurements (90-120 s/point – # of points 301)
- spacing in x-, y- direction 4.5 mm



R. Löbel, A. Savan, S. Thienhaus, A. Ludwig (2008), *Combinatorial fabrication and high-throughput characterization of a Ti-Ni-Cu shape memory thin film composition spread*, Materials Science and Engineering A 481-482, 151-155.

Property I II



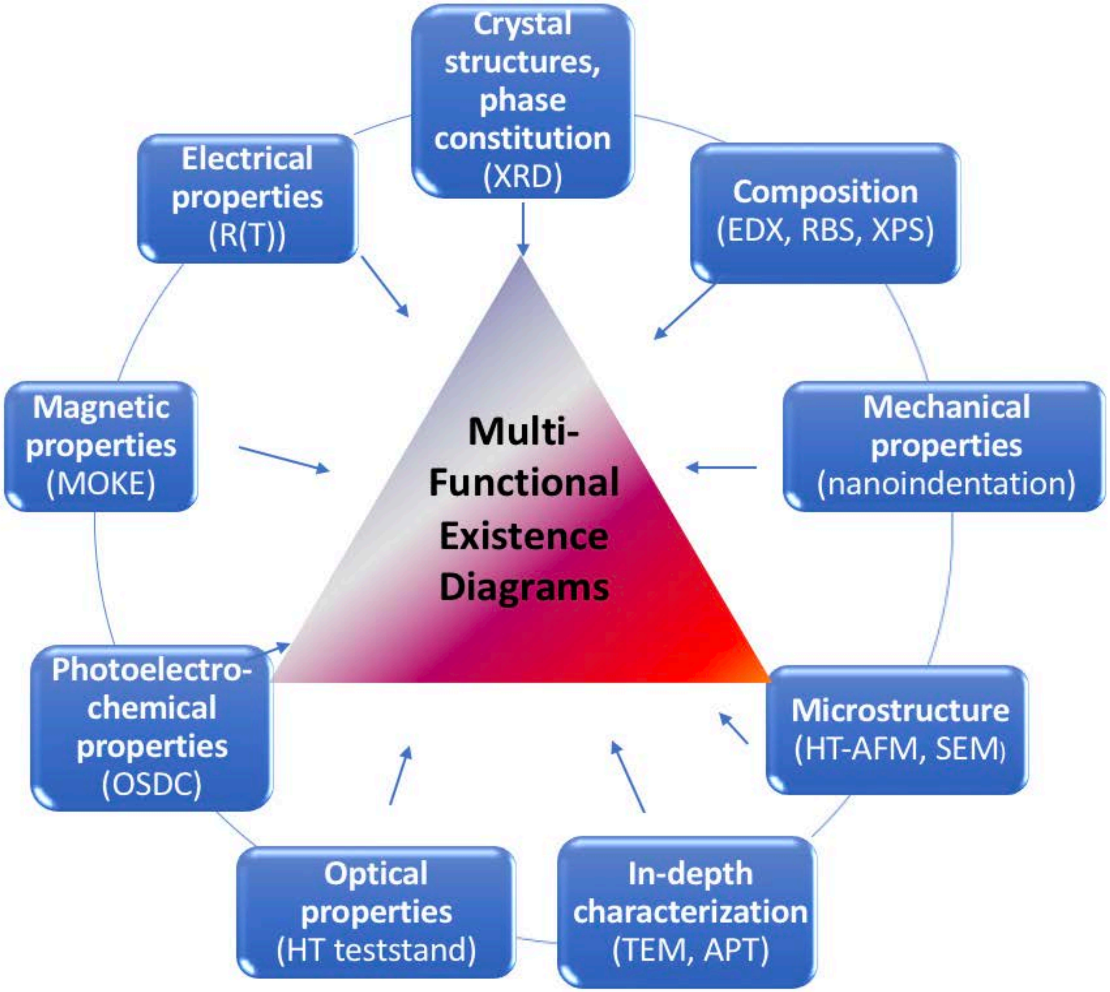
Fabricate materials library

High-throughput characterization

S. Thienhaus, S. Hamann, A. Ludwig (2011), *Modular high-throughput test-stand for versatile screening of thin-film materials libraries*, Sci. Technol. Adv. Mater. 12 054206

High-throughput Characterization for the creation of Multifunctional Existence Diagrams

Generation of **multidimensional datasets** by high-throughput characterization of materials libraries



Crystal structures, phase constitution (XRD)

Composition (EDX, RBS, XPS)

Mechanical properties (nanoindentation)

Microstructure (HT-AFM, SEM)

In-depth characterization (TEM, APT)

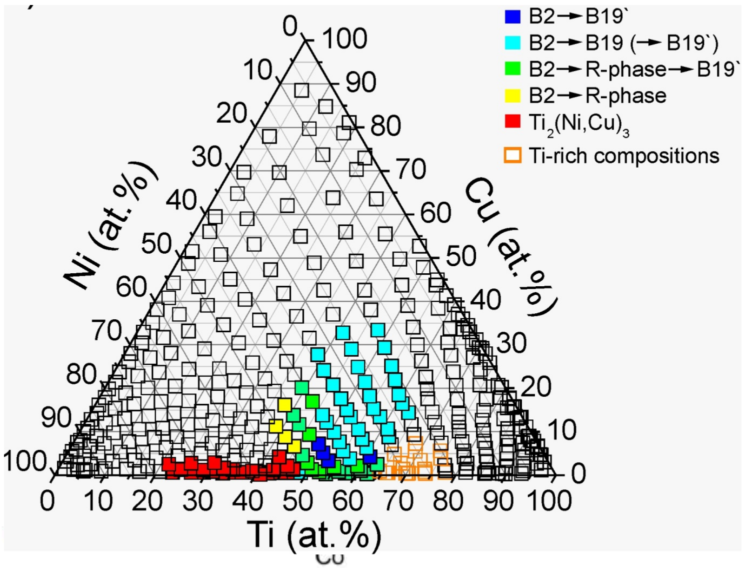
Optical properties (HT teststand)

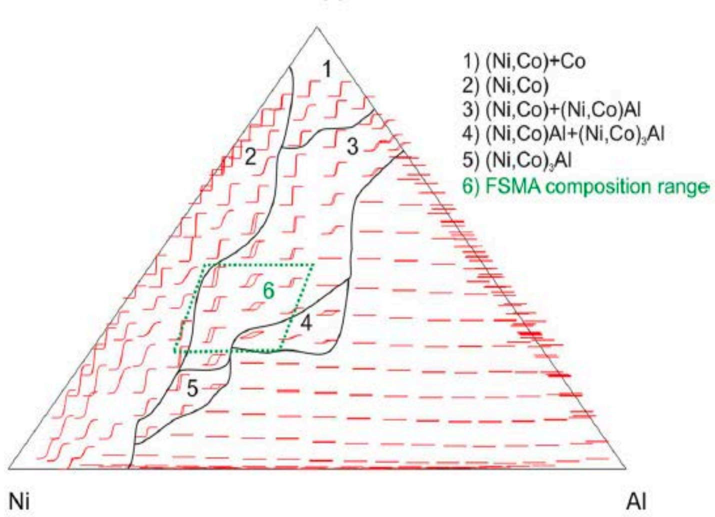
Photoelectro-chemical properties (OSDC)

Magnetic properties (MOKE)

Electrical properties (R(T))

Multi-Functional Existence Diagrams





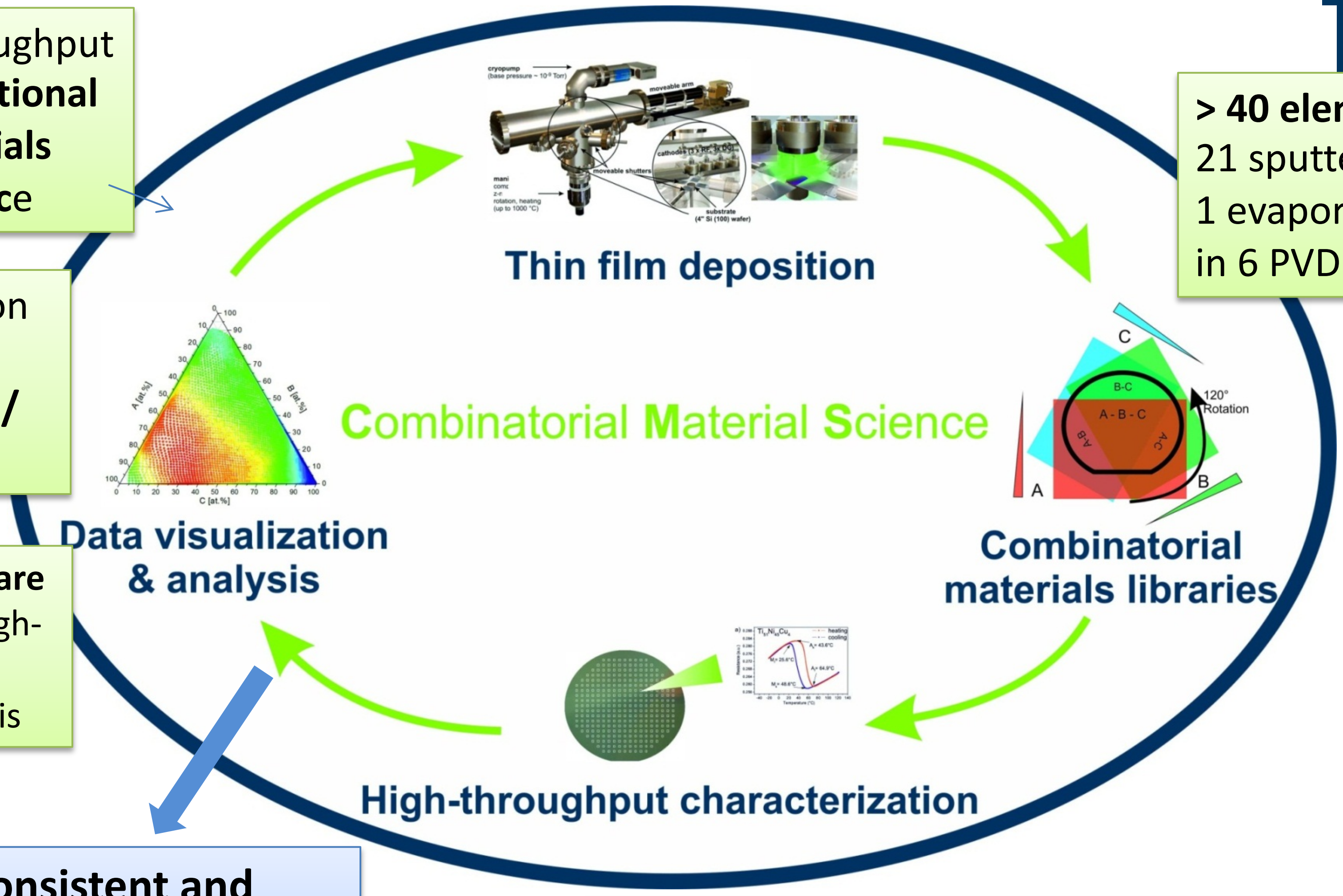
P. Decker, D. Naujoks, D. Langenkaemper, C. Somsen, A. Ludwig (2017) *High-throughput structural and functional characterization of the thin film materials system Ni-Co-Al,* ACS Combi. Sci. 19, 618-624

Combinatorial materials science approach

High-throughput **computational materials science**

Information from **databases/ literature**

New software tools for high-throughput data analysis



Thin film deposition

Combinatorial materials libraries

High-throughput characterization

Data visualization & analysis

Combinatorial Material Science

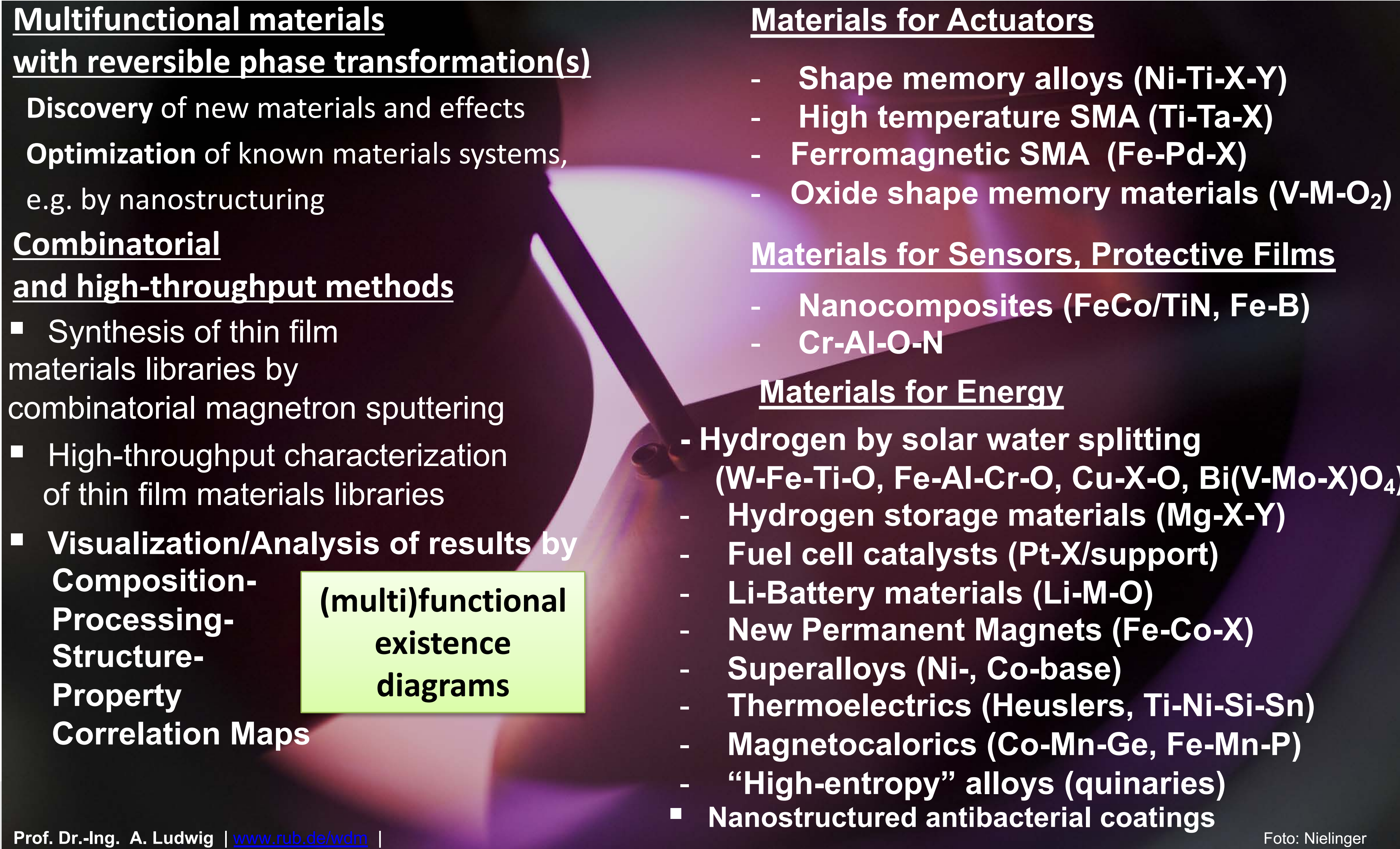
> 40 elements available
21 sputter sources
1 evaporation source
in 6 PVD systems

Consistent and complete data-sets on multinary material systems

Advantages of thin films

- tailorable composition and gradients
- high purity
- tailorable micro/nanostructure
- fabrication of metastable materials
- „artifical“ materials (e.g. nanoscale multilayers)
- design of precursor structures for tailored phase formation

Combinatorial material science in Bochum: Concepts and projects (since 2003)



Multifunctional materials with reversible phase transformation(s)

Discovery of new materials and effects

Optimization of known materials systems, e.g. by nanostructuring

Combinatorial and high-throughput methods

- Synthesis of thin film materials libraries by combinatorial magnetron sputtering
- High-throughput characterization of thin film materials libraries
- **Visualization/Analysis of results by Composition-Processing-Structure-Property Correlation Maps**

(multi)functional existence diagrams

Materials for Actuators

- **Shape memory alloys (Ni-Ti-X-Y)**
- **High temperature SMA (Ti-Ta-X)**
- **Ferromagnetic SMA (Fe-Pd-X)**
- **Oxide shape memory materials (V-M-O_2)**

Materials for Sensors, Protective Films

- **Nanocomposites (FeCo/TiN, Fe-B)**
- **Cr-Al-O-N**

Materials for Energy

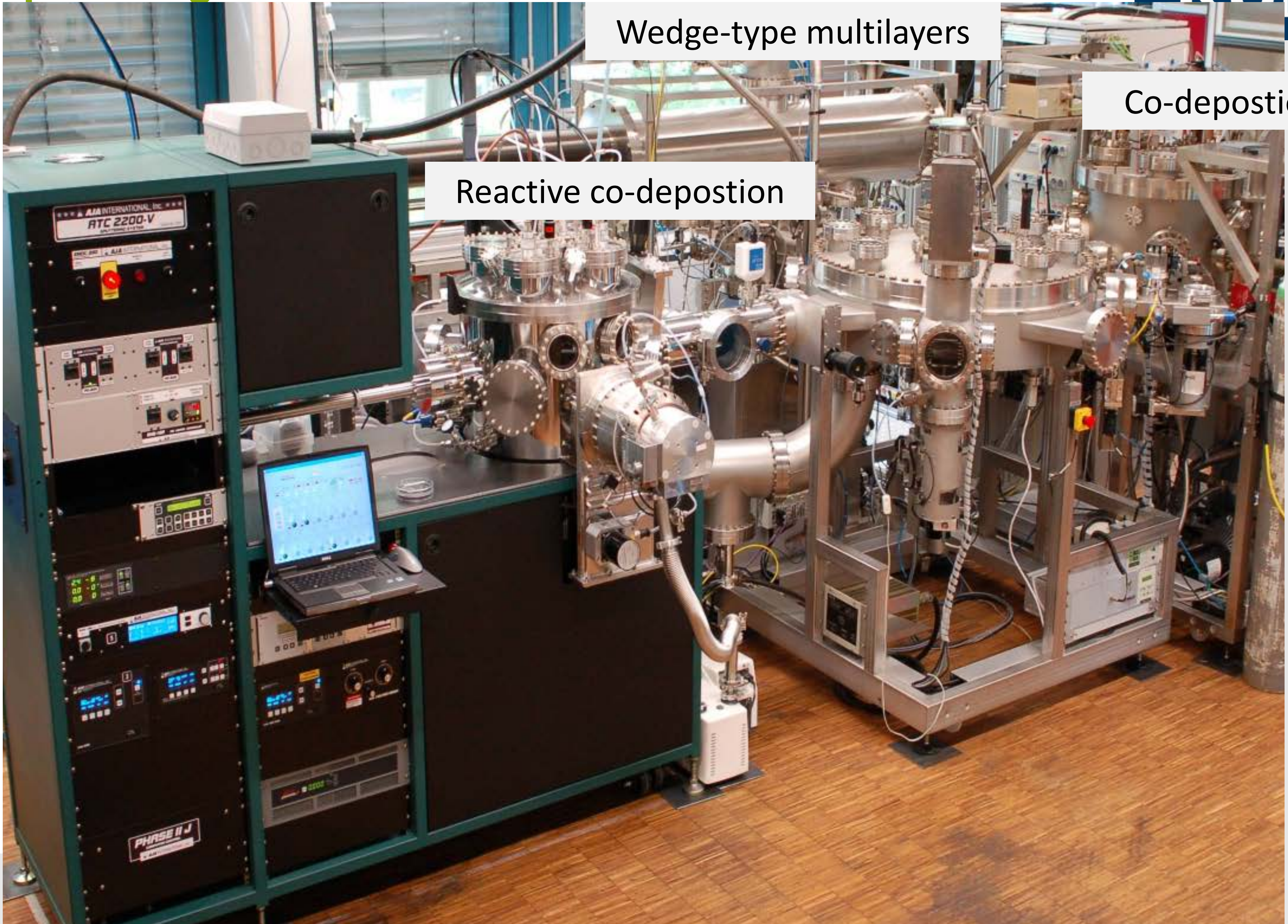
- **Hydrogen by solar water splitting (W-Fe-Ti-O, Fe-Al-Cr-O, Cu-X-O, Bi(V-Mo-X)O_4**
- **Hydrogen storage materials (Mg-X-Y)**
- **Fuel cell catalysts (Pt-X/support)**
- **Li-Battery materials (Li-M-O)**
- **New Permanent Magnets (Fe-Co-X)**
- **Superalloys (Ni-, Co-base)**
- **Thermoelectrics (Heuslers, Ti-Ni-Si-Sn)**
- **Magnetocalorics (Co-Mn-Ge, Fe-Mn-P)**
- **“High-entropy” alloys (quinaries)**

- **Nanostructured antibacterial coatings**

Foto: Nielinger

Synthesis of Thin Film Materials Libraries

Combinatorial synthesis of materials libraries using magnetron sputtering



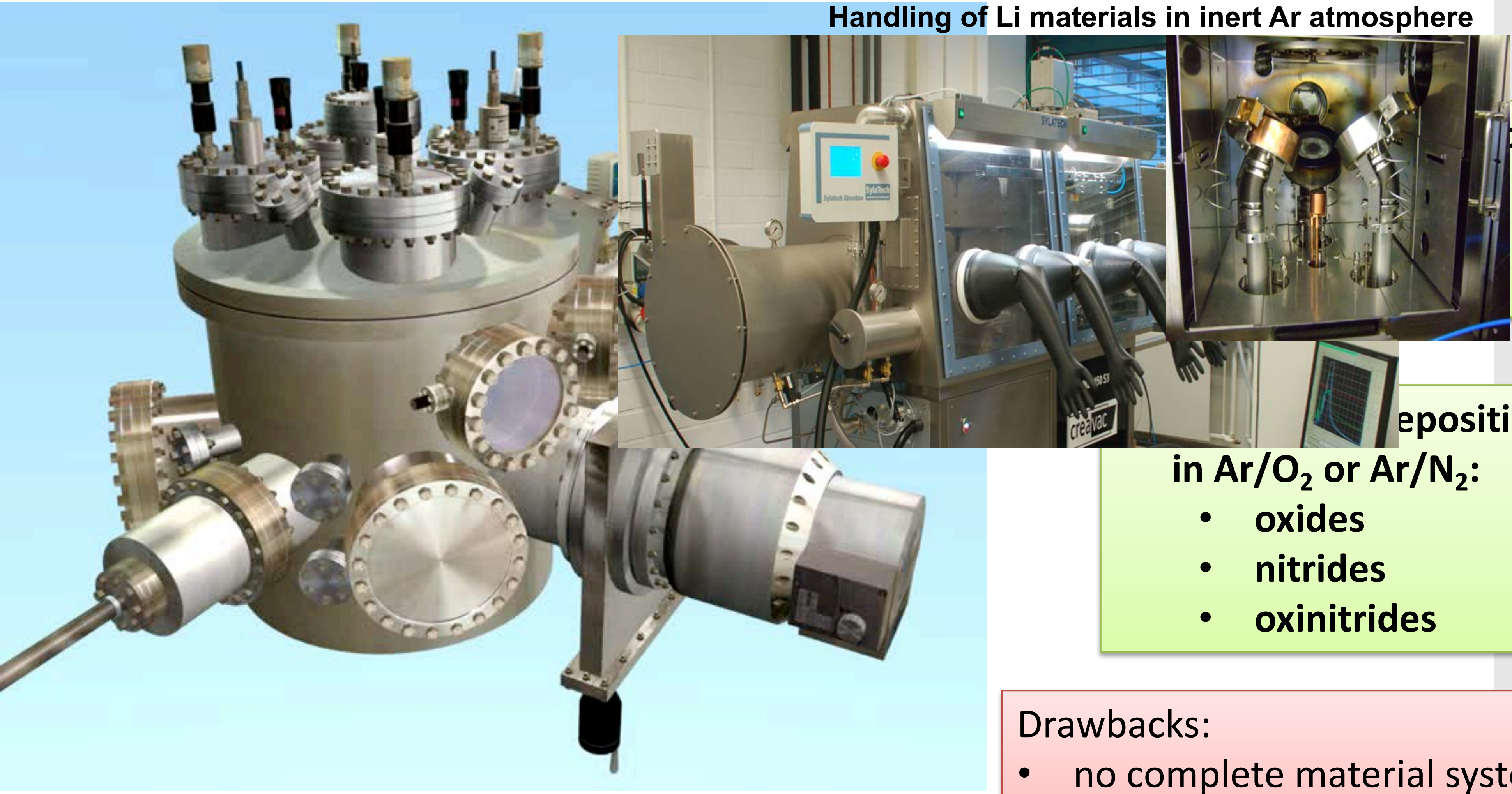
Wedge-type multilayers

Co-depostion

Reactive co-depostion

Co-sputter deposition of multinary materials libraries from up to 5 elemental targets

Handling of Li materials in inert Ar atmosphere

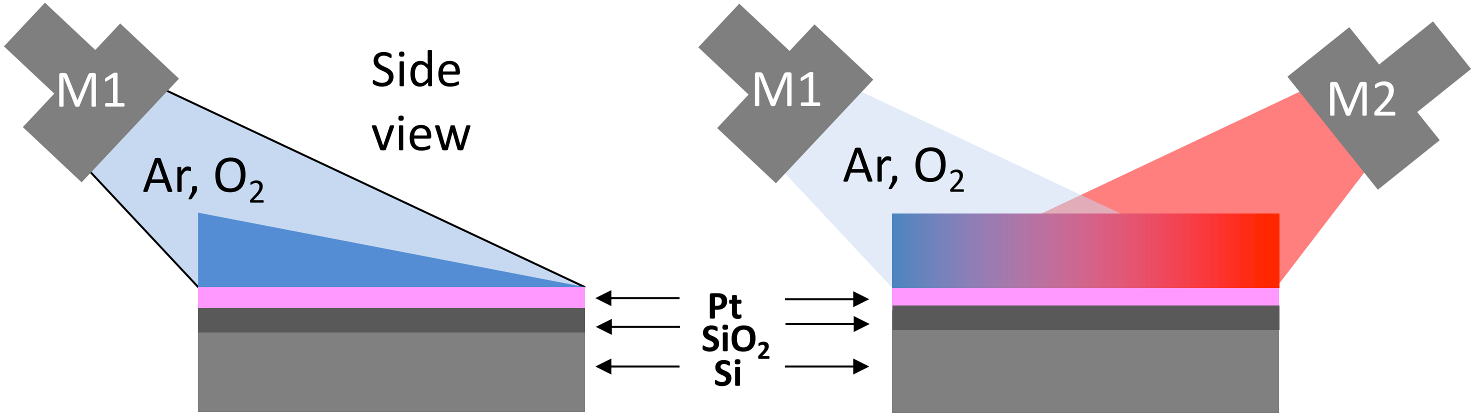


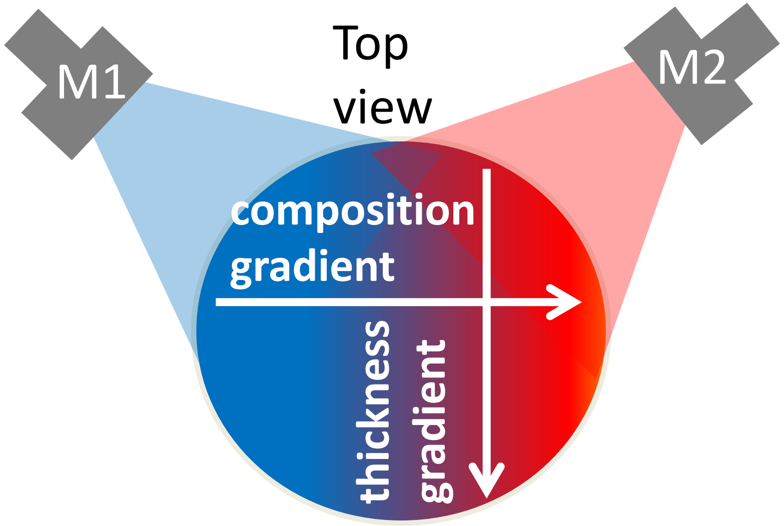
sition

eposition in Ar/O_2 or Ar/N_2:
- oxides
- nitrides
- oxinitrides

Drawbacks:
- no complete material system in one experiment
- limited gradients

Fabrication of Mixed Metal Oxide Thin Film Materials Libraries with Non-parallel Gradients





- Sputtering Parameters:

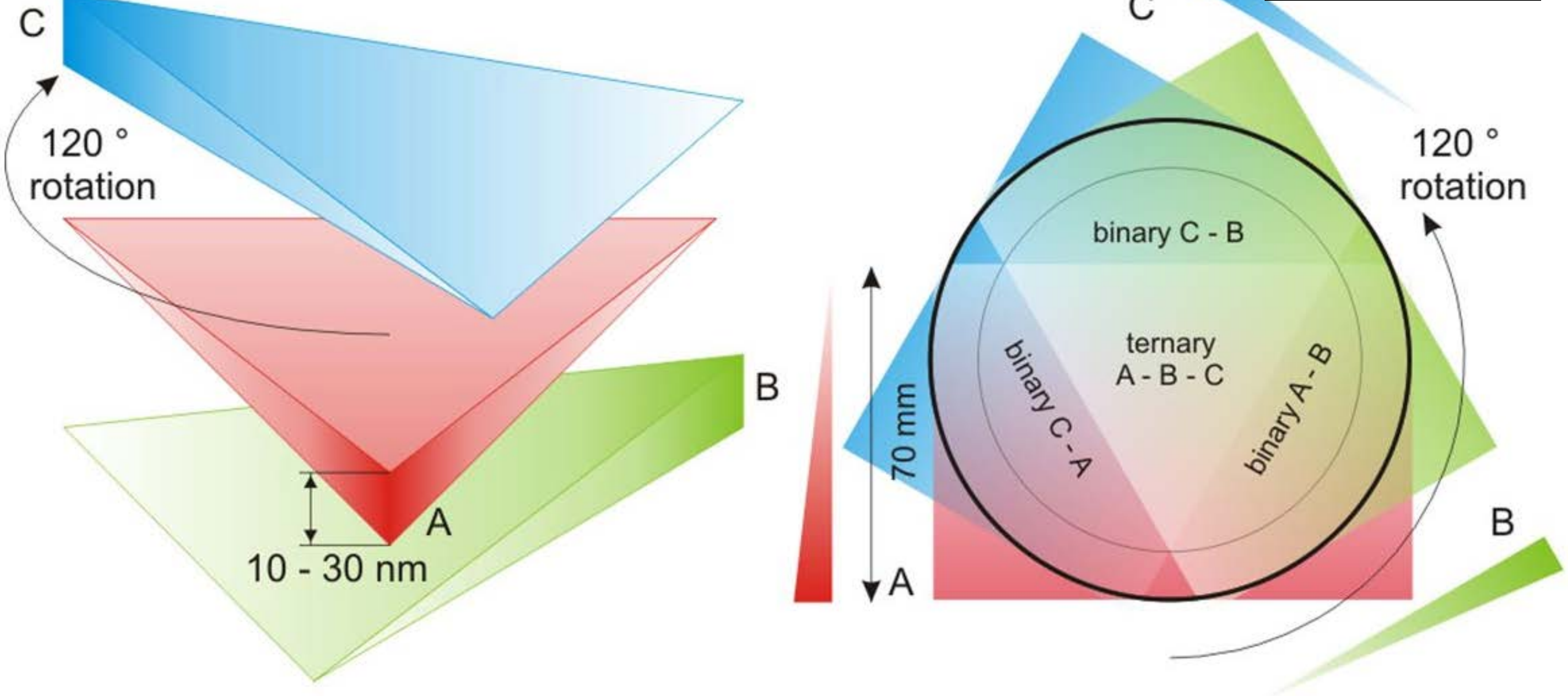
○ Temperature	400°C
○ Pressure	10 mTorr
○ Ar flow	30 sccm
○ O_2 flow	90 sccm
○ Power	70 – 400 W
○ Targets	Fe, W

SPP 1613

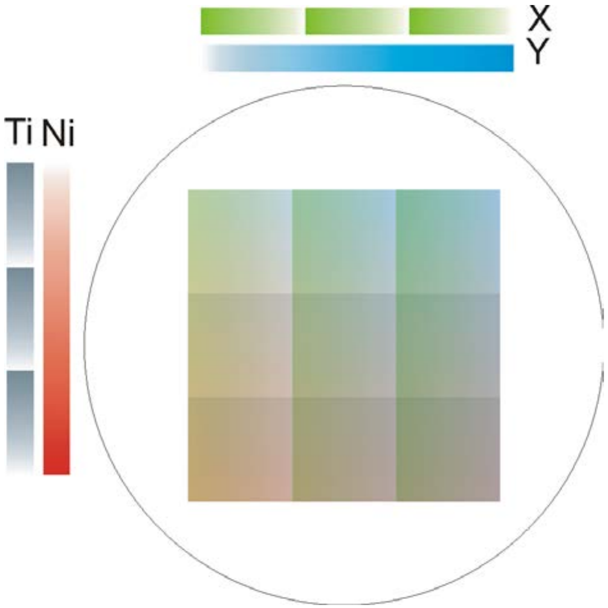
R. Meyer, K. Sliozberg, C. Khare, W. Schuhmann, A. Ludwig **High-Troughput screening of thin film semiconductor materials libraries II: Composition, crystallinity, morphology, thickness and photocurrent density of Fe-W-O libraries,** 2015 ChemSusChem

Synthesis of complete binary and ternary thin film materials libraries

Sequential deposition of nanoscale wedge-type thin films (multilayers)

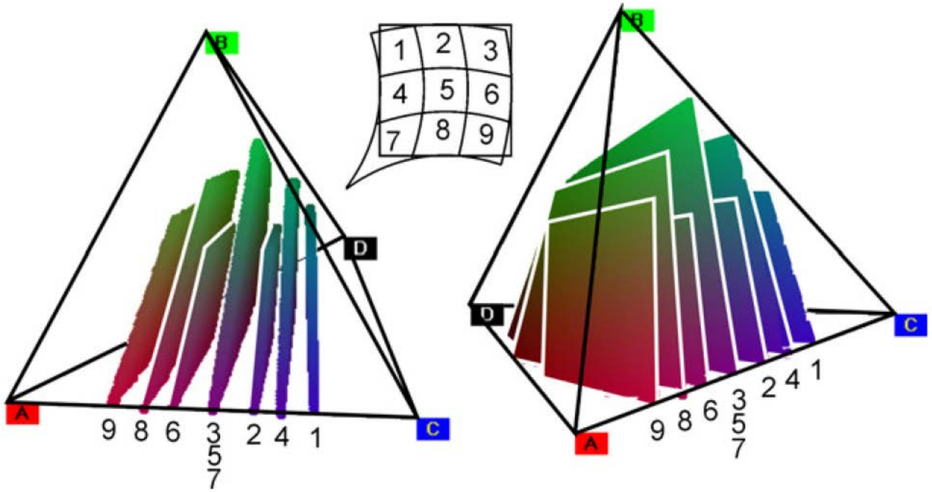


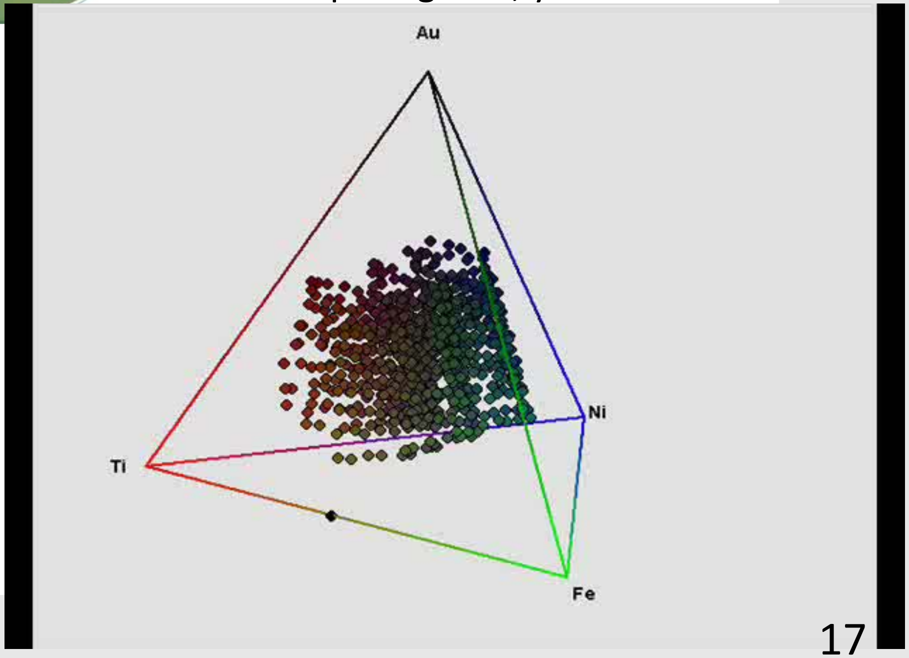
Fabrication and visualization of quaternary materials libraries: Ti-Ni-X-Y continuous composition spreads



Results of automated EDX

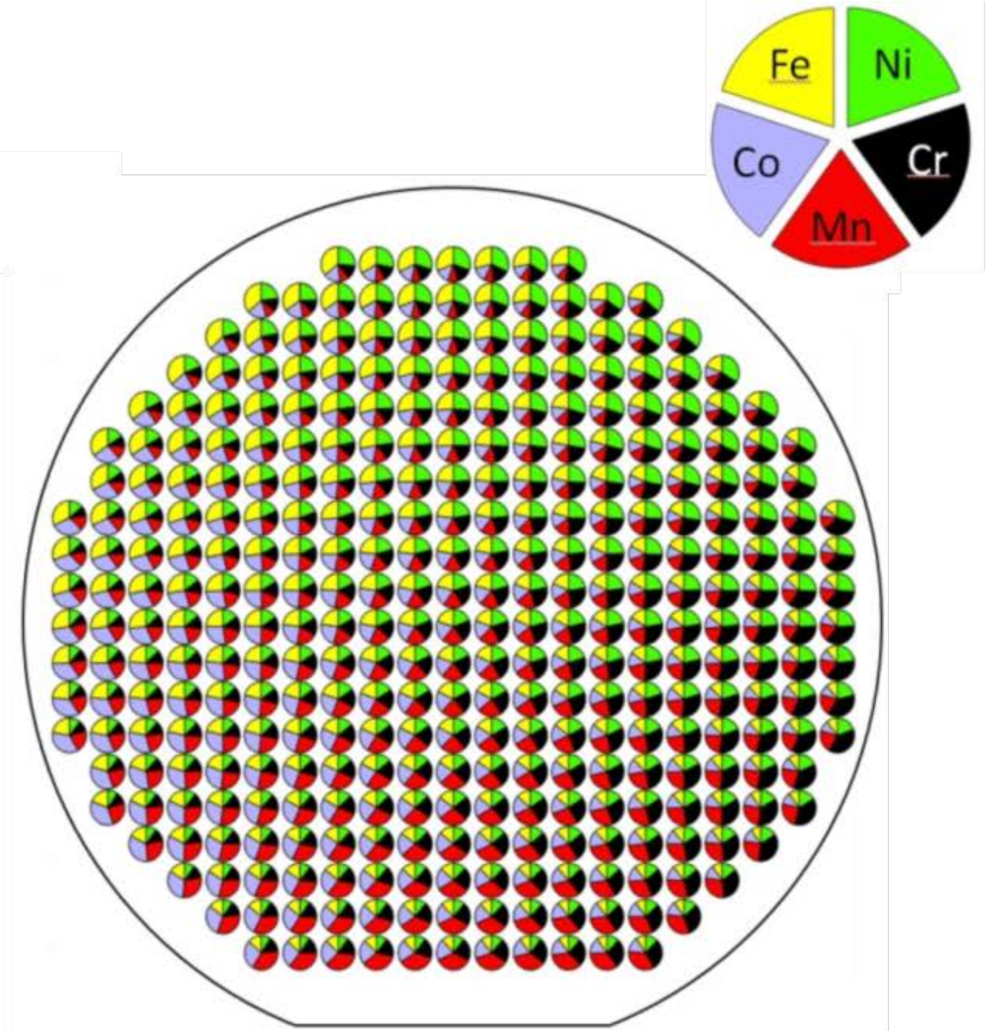
- weekend measurement
(100 s/point – 1024 points)
- spacing in x-, y- direction: 2.25 mm





[1] „Production and visualization of quaternary combinatorial thin films" Chevrier V, Dahn JR., Meas Sci Techno 2006;17:1399

Exploring quinary composition space: „high entropy“ alloys, multiple principal element alloys



Co-sputter deposition of multinary materials libraries from up to 5 elemental targets

Visualization of multidimensional data

Z. Li, A. Ludwig, A. Savan, H. Springer, D. Raabe (2018) *Combinatorial metallurgical synthesis and processing of high-entropy alloys*, accepted by Journal of Materials Research

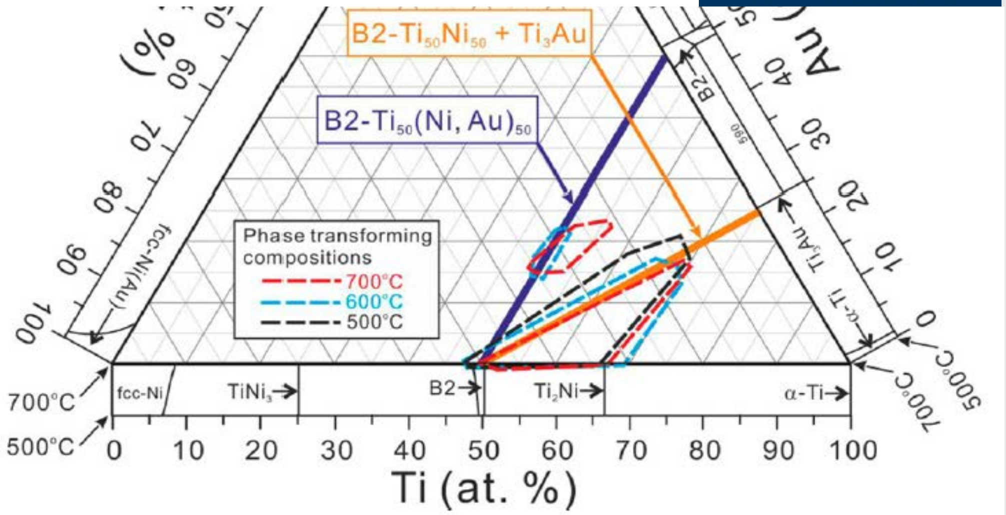
Combinatorial Processing

Next steps in combinatorial materials science: Combinatorial processing

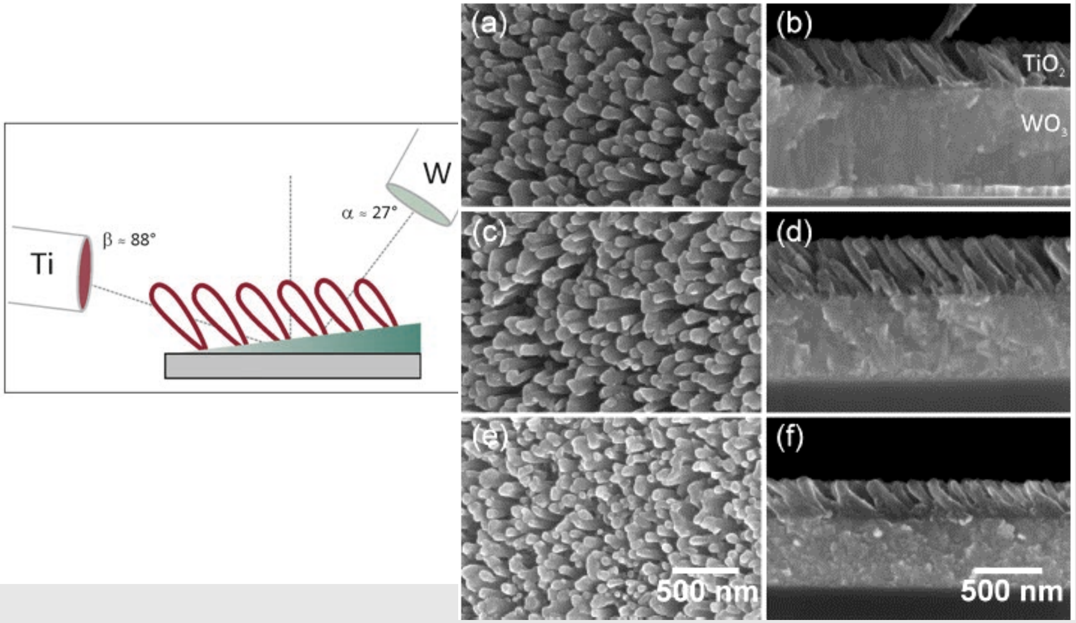
Establish
Composition-Processing-Structure-Property Correlation Maps

From compositional combinatorial material science **to micro/nanostructure** combinatorial material science using **combinatorial/high-throughput processing**

Which material
(*not only which composition and crystal structure*)
in which **(nanostructured) form** gives best properties?



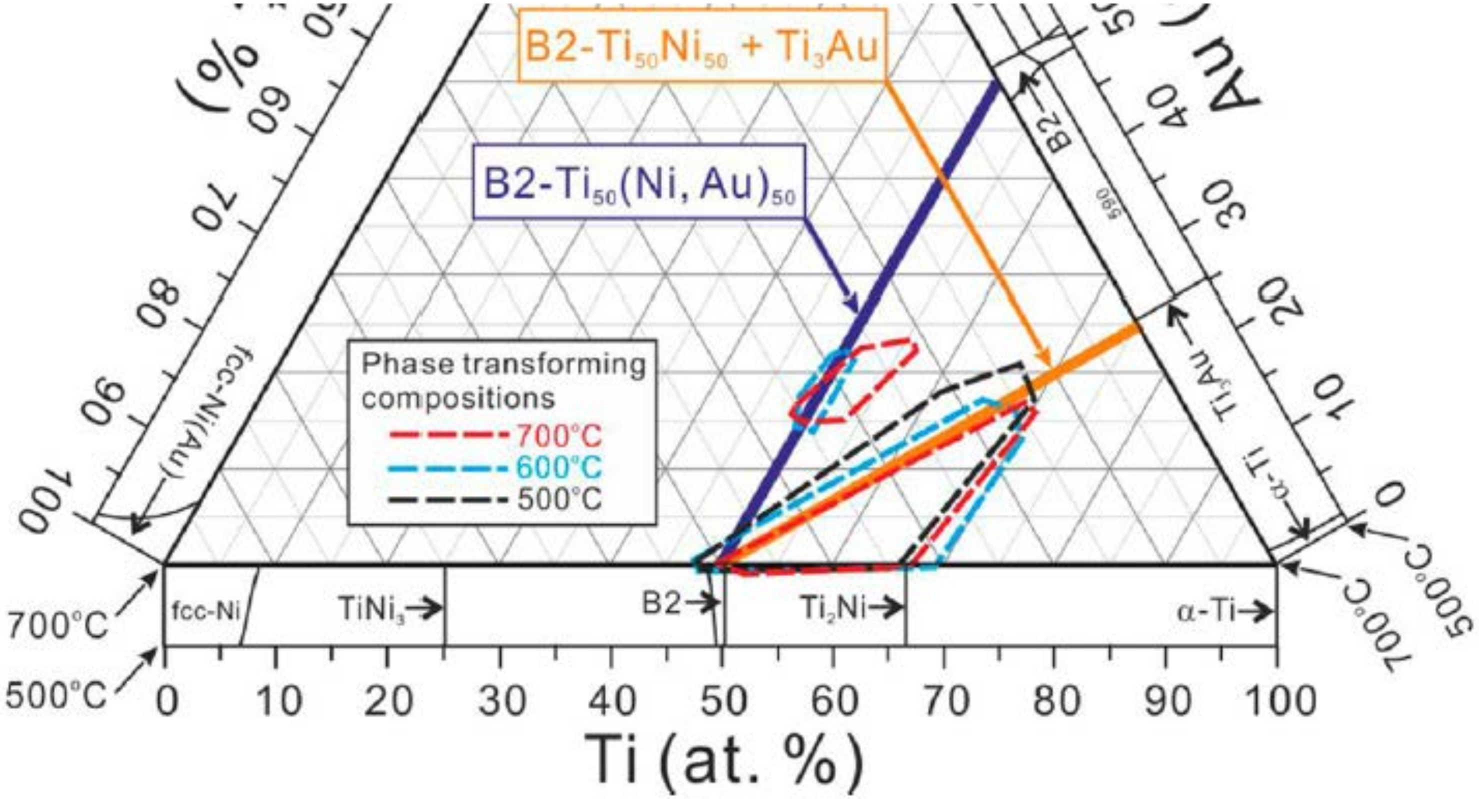
P. Buenconsejo, A. Ludwig (2014) *Composition-Structure-Function diagrams of Ti-Ni-Au thin film shape memory alloys,* ACS Comb. Sci. 16, 678–685



C. Khare, A. Ludwig et al., ***Int. J. of Hydrogen Energy*** (2013)

Combinatorial materials processing: temperature

Deposition/Annealing at different temperatures



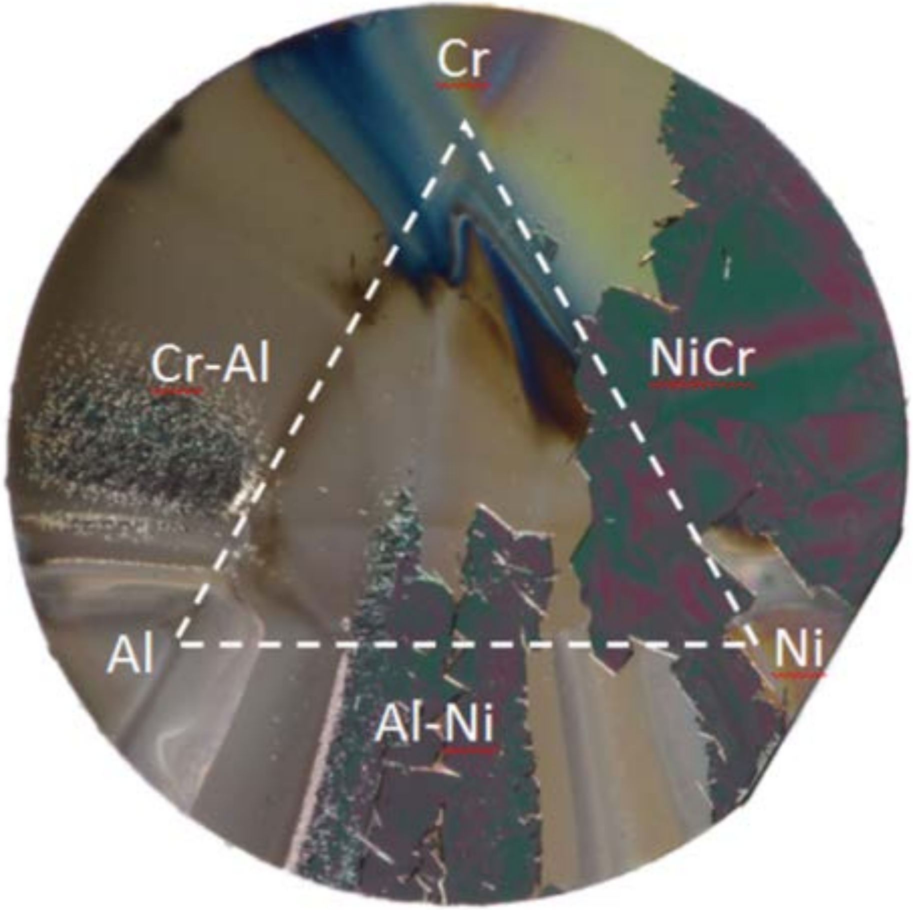
dx.doi.org/10.1021/co5000745 I *ACS Comb. Sci.* 2014, 16, 678–685

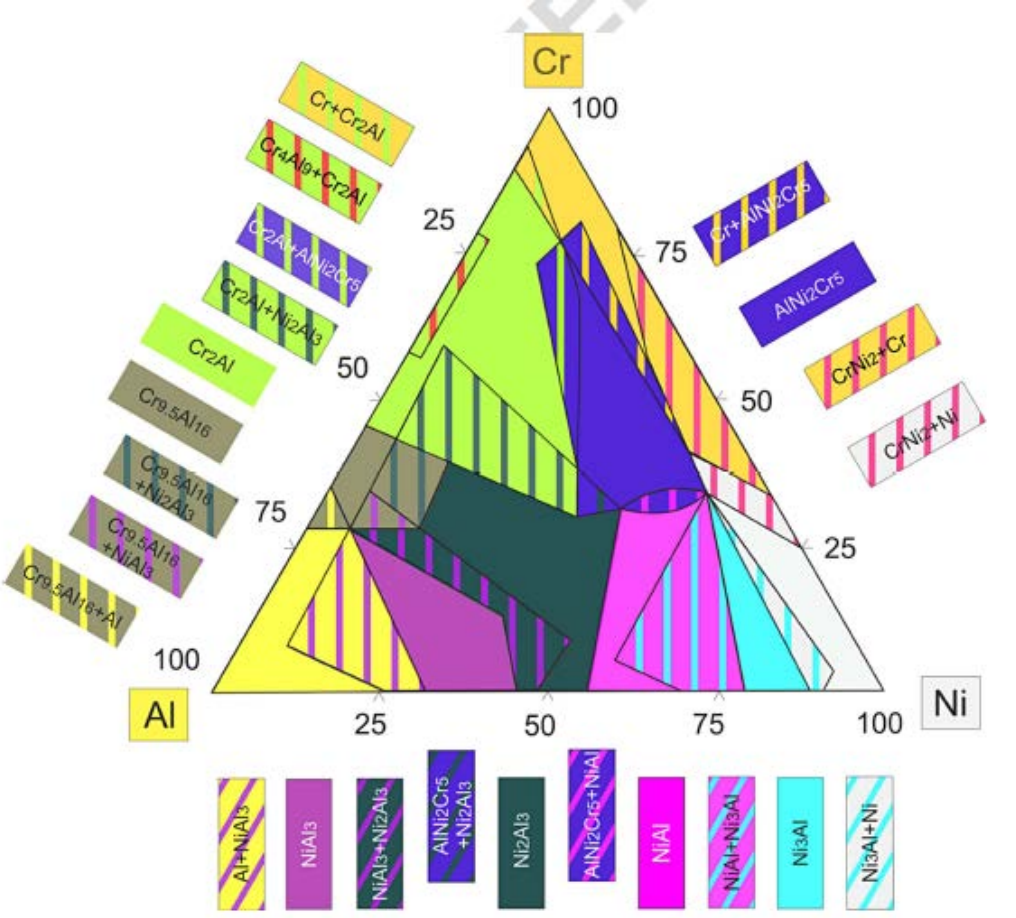
P. Buenconsejo, A. Ludwig (2014) *Composition-Structure-Function diagrams of Ti-Ni-Au thin film shape memory alloys,* ACS Comb. Sci. 16, 678–685

Combinatorial materials processing: high-throughput oxidation study (Ni-Al-Cr)

Thin film phase diagram after annealing in air at 500°C for 9h

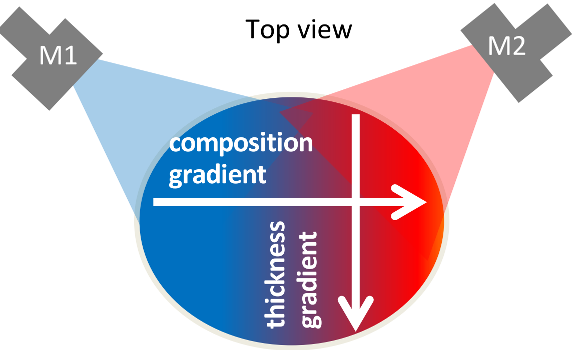
Ni_2AlCr_5

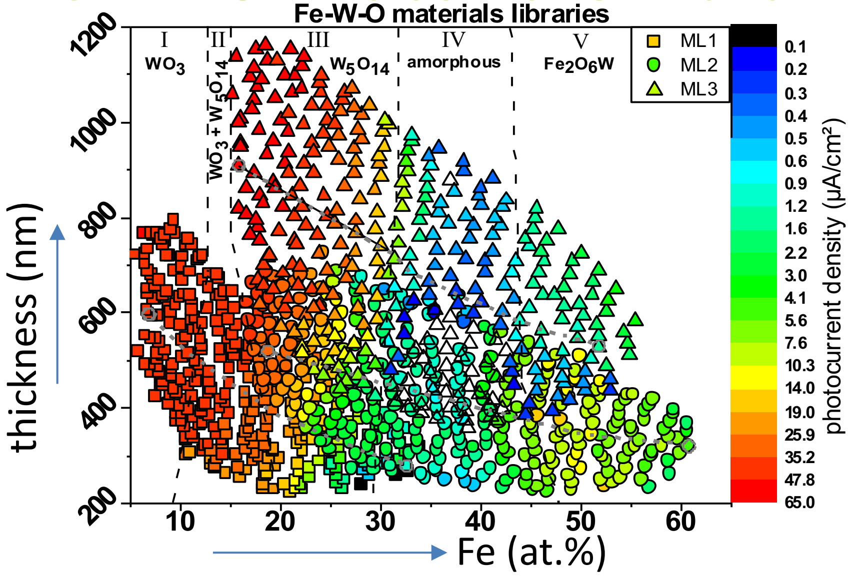




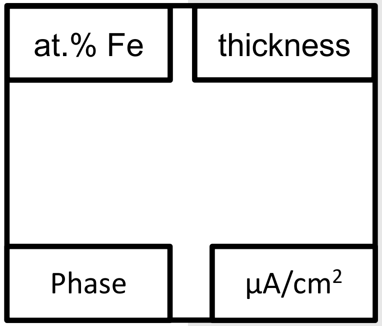
D. König, C. Eberling, M. Kieschnick, S. Virtanen, A. Ludwig (2015) *High-throughput investigation of the oxidation and phase constitution of thin film Ni-Al-Cr materials libraries, ,* Adv. Eng. Mat. 17, 1365-1373.

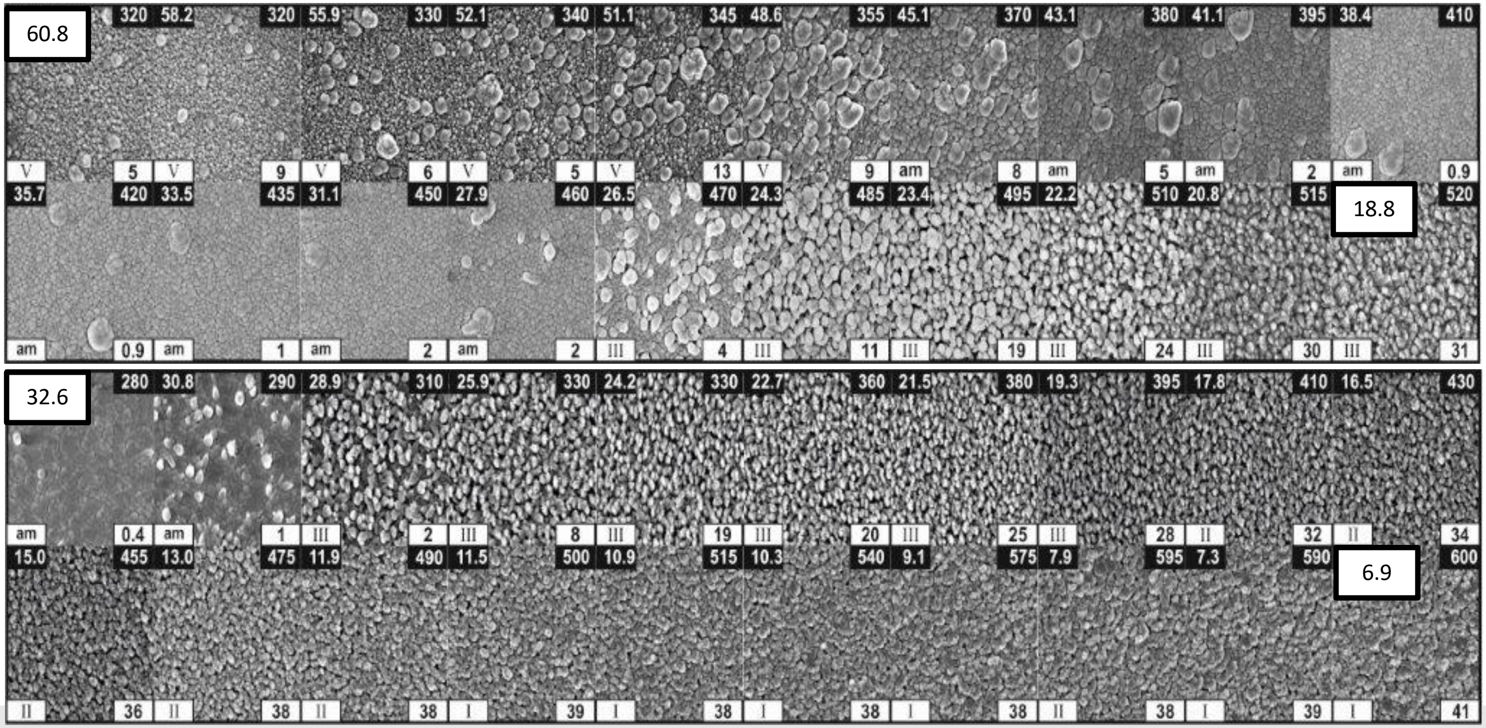
Morphology of Fe-W-O materials libraries





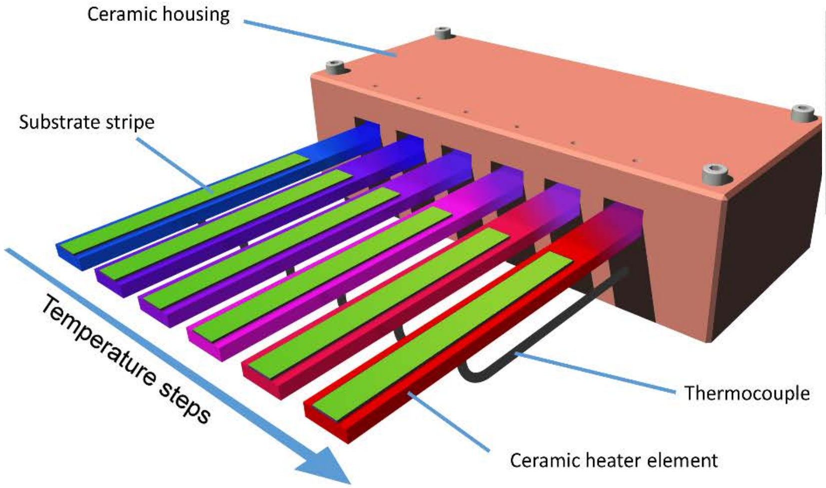
Fixed processing conditions

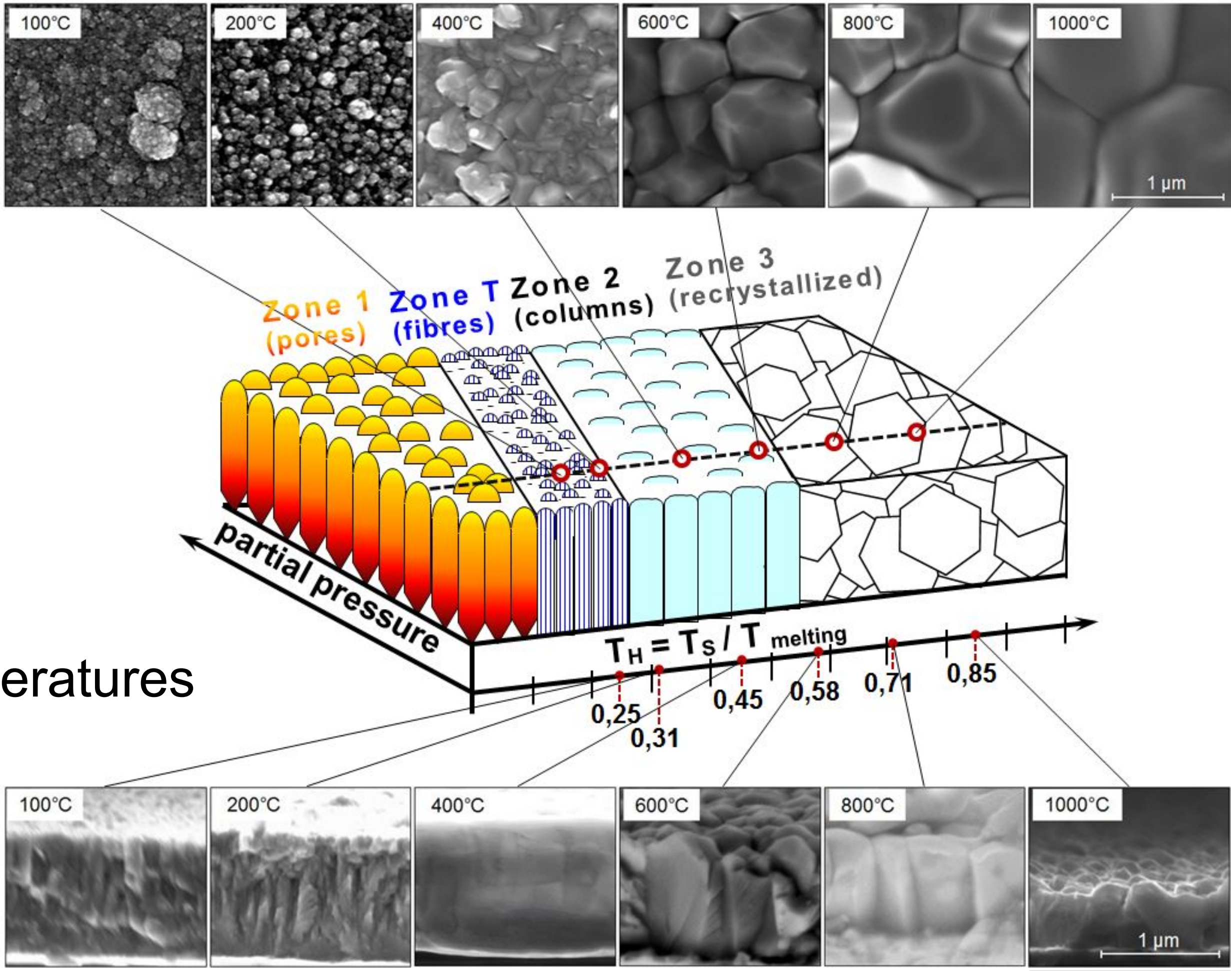




R. Meyer, K. Sliozberg, C. Khare, W. Schuhmann, A. Ludwig **High-Troughput screening of thin film semiconductor materials libraries II: Composition, crystallinity, morphology, thickness and photocurrent density of Fe-W-O libraries,** 2015 ChemSusChem

Step heater: Composition – morphology variations (structure zone diagrams)





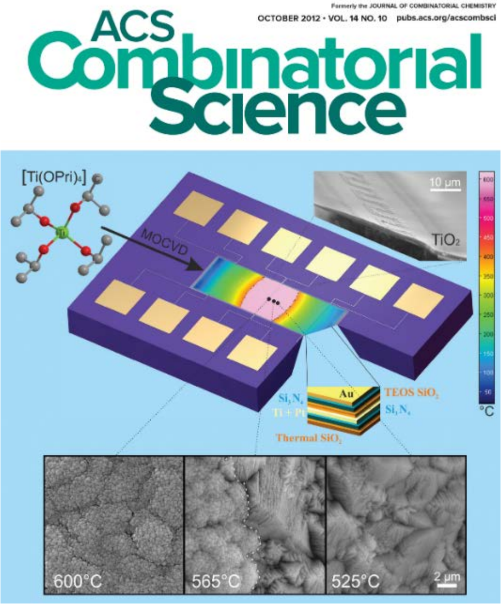
Combinatorial deposition of 6 (quasi)binary composition spread materials libraries at 6 different temperatures up to 1000°C

Controlled variation of composition and thin film morphology

Examples system: Cu$_2$O (cuprite) → Cu–O-based p-type materials

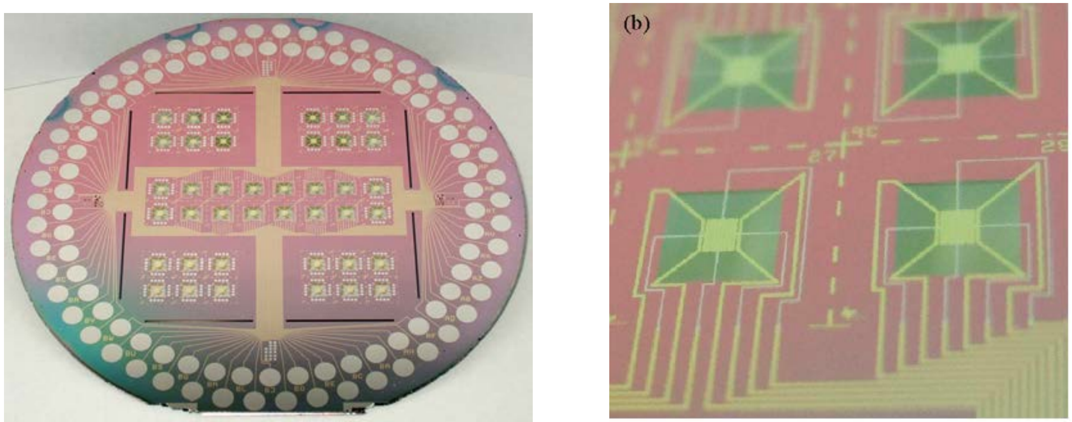
H. Stein, D. Naujoks, D. Grochla, C. Khare, R. Gutkowski, S. Grützke, W. Schuhmann and A. Ludwig (2015) A structure zone diagram obtained by simultaneous deposition on a novel step heater: a case study for Cu$_2$O thin films. *Physica Status Solidi A*, 212, 2798-2804

Combinatorial materials processing: MEMS Tools for high-throughput experimentation

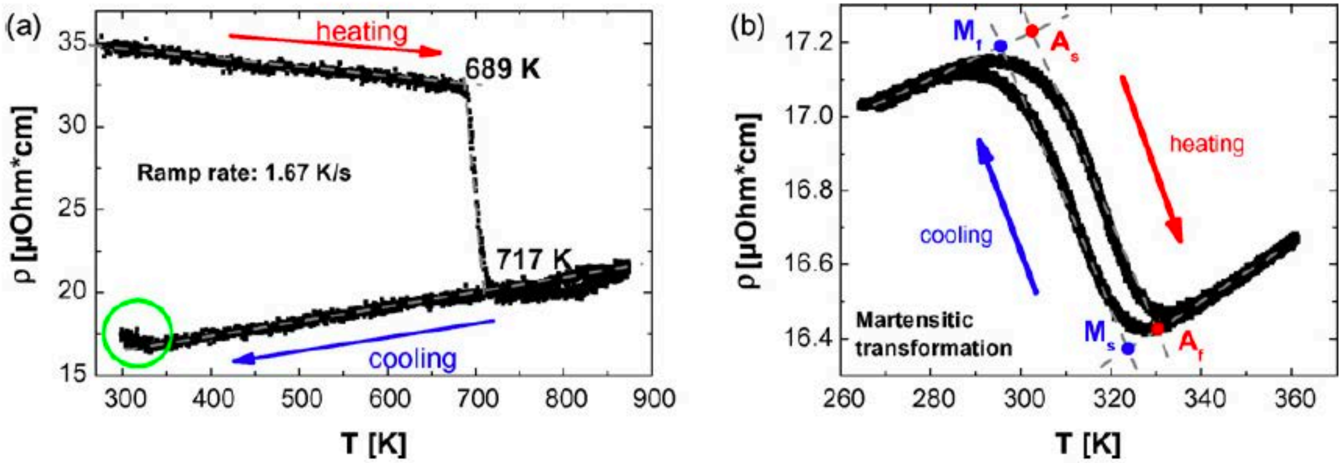


Microgradient-Heaters: micro/nanostructure libraries

Micro-Hotplate-Electrode-Array



- Controlled quenching of metastable phases
- In situ measurement of crystallization and martensitic phase transformation (e.g.: Ni-Ti-Cu)

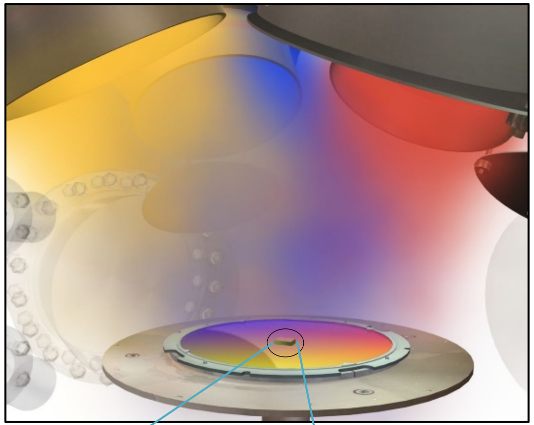


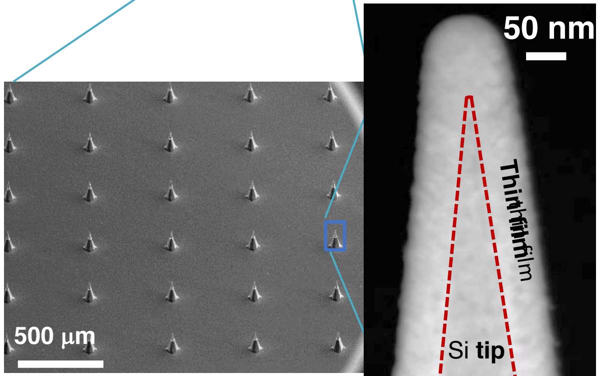
S. Hamann, M. Ehmann, S. Thienhaus, A. Savan, **A. Ludwig** (2008), *Micro-hotplates for high-throughput thin film processing and in situ phase transformation characterization*, Sensors and Actuators A, 147, 576 - 582.

Combinatorial processing platforms for accelerated phase evolution in CCAs

Fast synthesis of nc thin films (Combinatorial deposition)

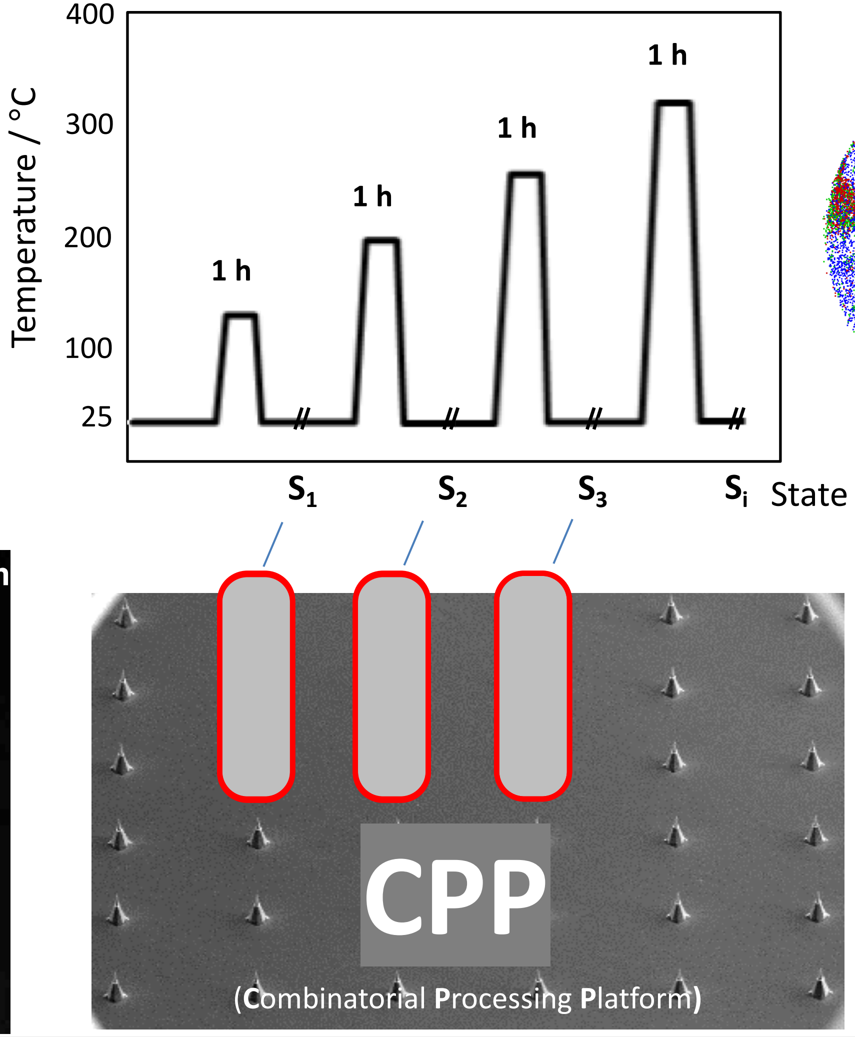
5 targets, rotated substrate
MnCrFeCoNi, Cantor alloy





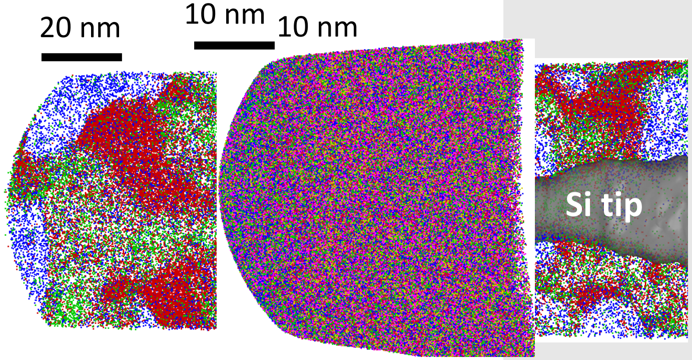
36 identical atomic-scale-mixed films

Fast annealing / oxidation (rapid phase evolution)

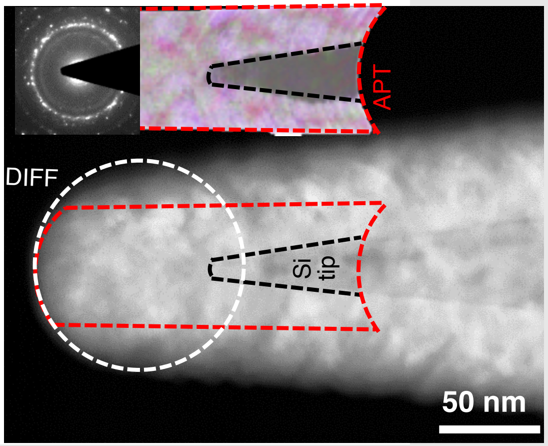


Direct atomic-scale analysis

APT
(chemical analysis)



TEM
(crystal structure)



Y. J. Li, A. Savan, A. Kostka, H. S. Stein, A. Ludwig (2018) ***Accelerated atomic-scale exploration of phase evolution in compositionally complex materials,*** **Materials Horizons 5, 86 - 92**

High-Throughput Characterization of Materials Libraries

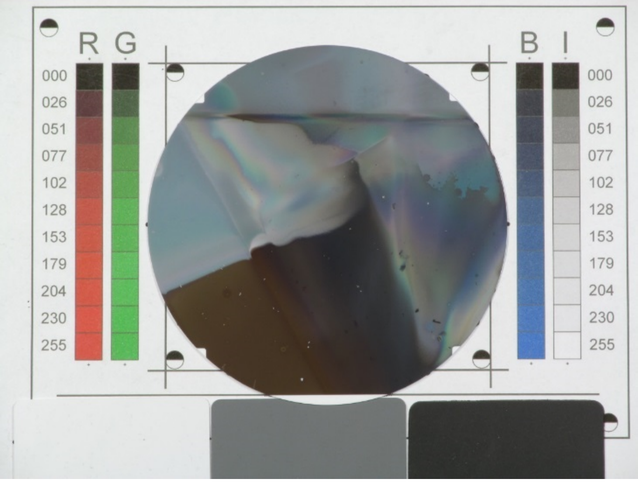
High-throughput characterization of materials libraries

Screening should be: automated, quick, quantitative, non-destructing

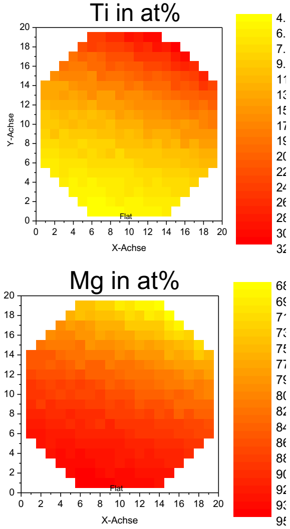
Parallel and sequential screening

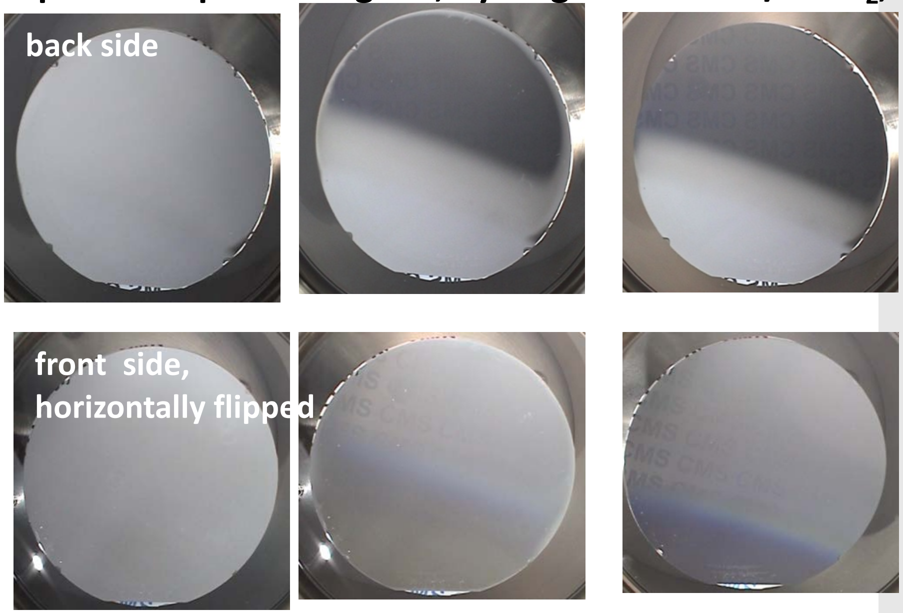
Parallel screening

- Optical properties (e.g. for chemical reactions)
- Si Cantilever libraries (SMA, stress, H_2, Li, …)



e.g.: **Mg-Ti** composition spread on glass, hydrogenation: Ar / 5%H_2, RT, 1 bar

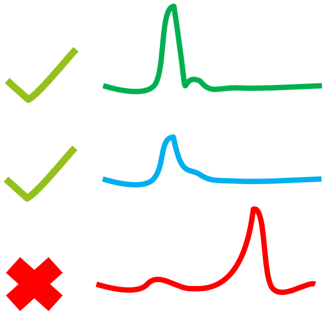


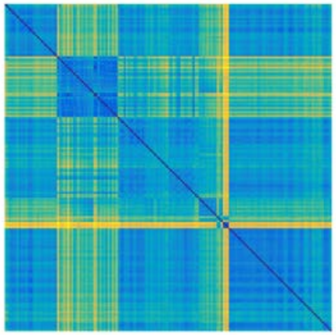


Materials informatics for high-throughput data analysis

Clustering

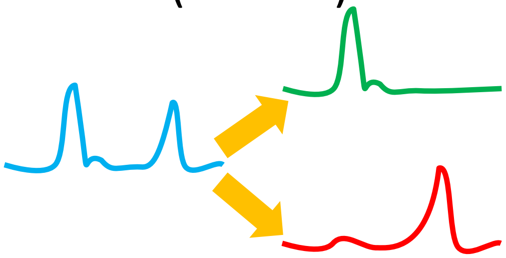
Clustering by „Similarity“

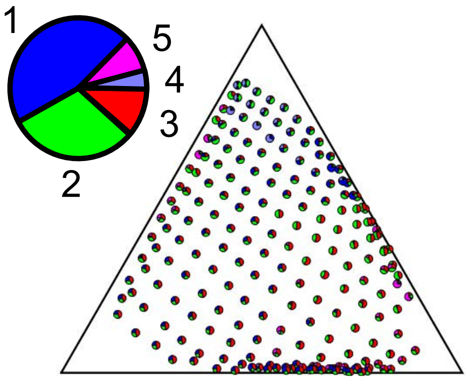




Factorization

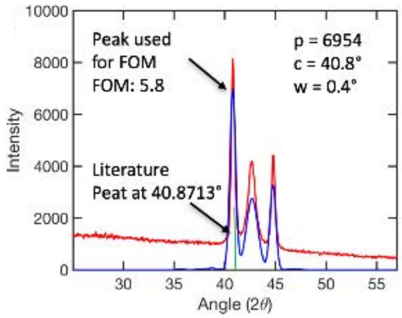
Splitting XRD patterns into components (factors)

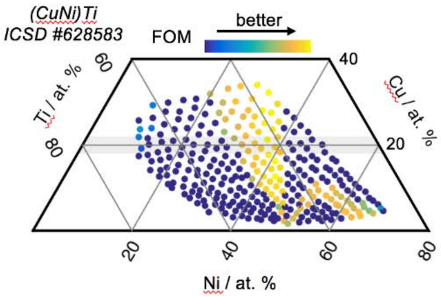




Matching

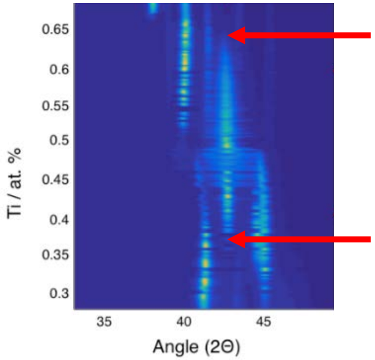
Comparing automatic fits to reference data

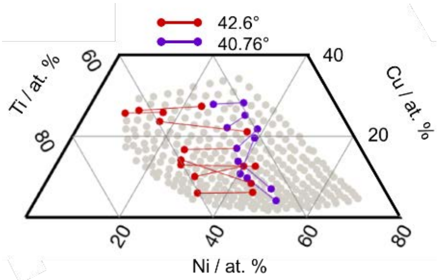




Reasoning

Human pattern recognition (& analysis)



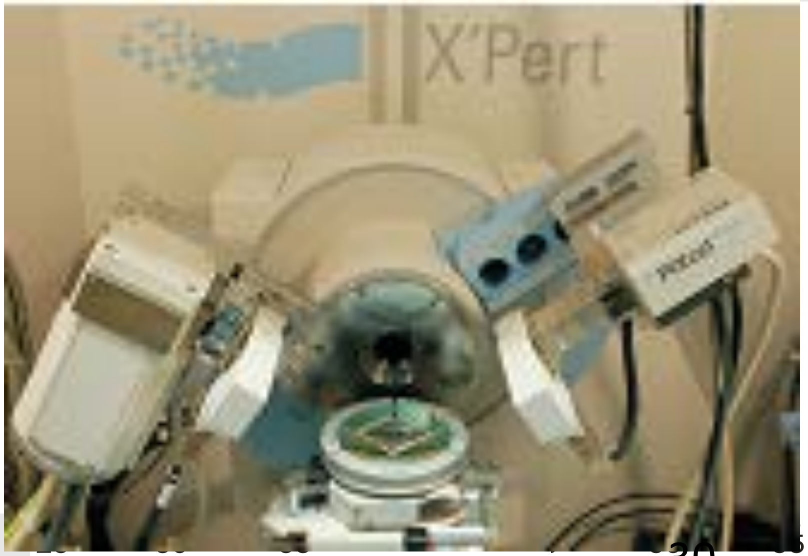


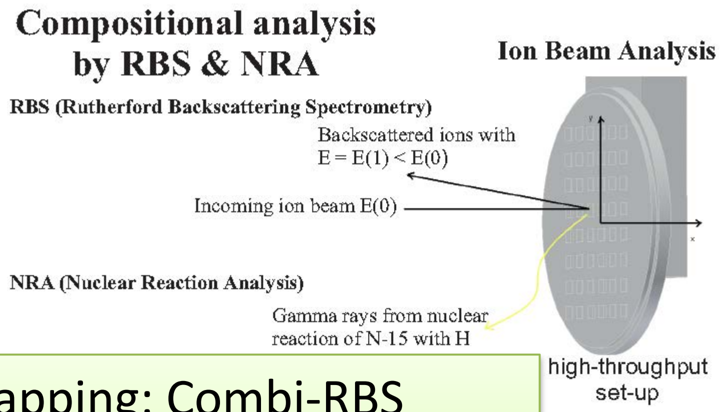
HS Stein, S Jiao, A Ludwig
ACS combinatorial science 19 (1), 1-8

High-throughput characterization of materials libraries

Automated wafer mapping systems

- thin film composition (**EDX**)
- thin film structure (**X-Ray Diffraction**)
- thin film thickness (**profilometer, DHM**)
- phases and phase changes
  (resistivity vs. temperature)





O-, N-mapping: Combi-RBS
H-, B-, Li-mapping: Combi-NRA
@RUBION, RUB, Bochum

High-throughput characterization of materials libraries: Definition of adequate screening parameters

At least one adequate screening parameter needs to be identified

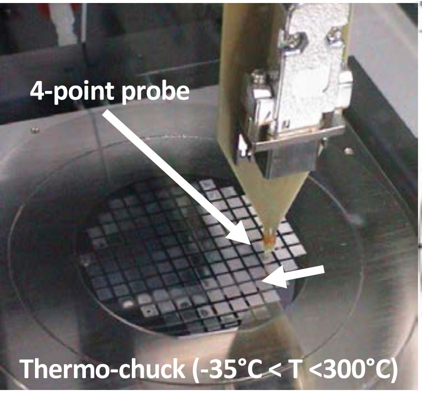
The design of the materials library has to enable the high-throughput characterization of one or more screening parameters

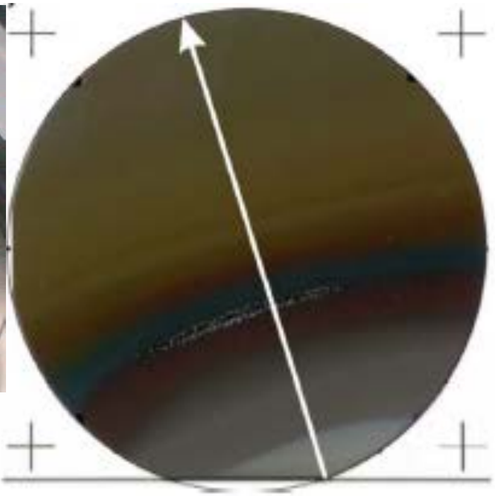
thermoelectrics → Seebeck coefficient

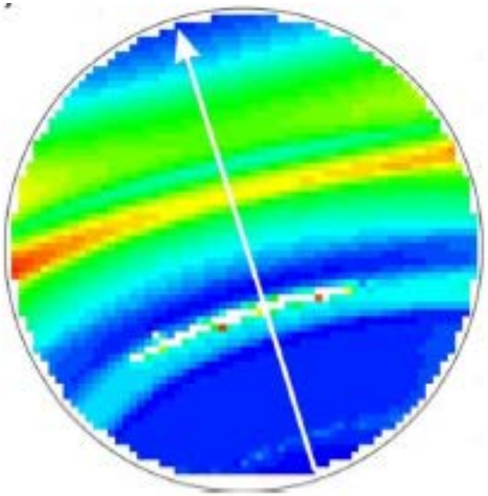
magnetocalorics → Temperatur change ΔT on magnetization change

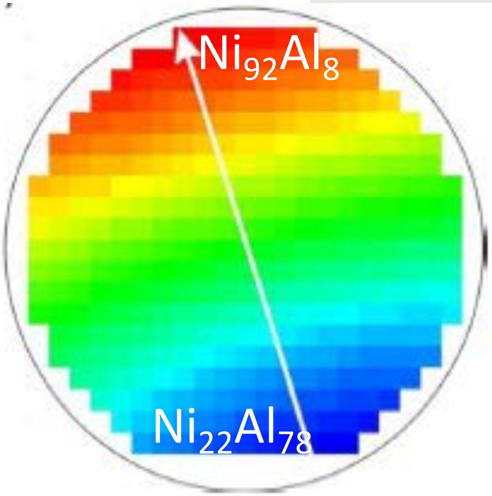
Solar water splitting materials → photocurrent

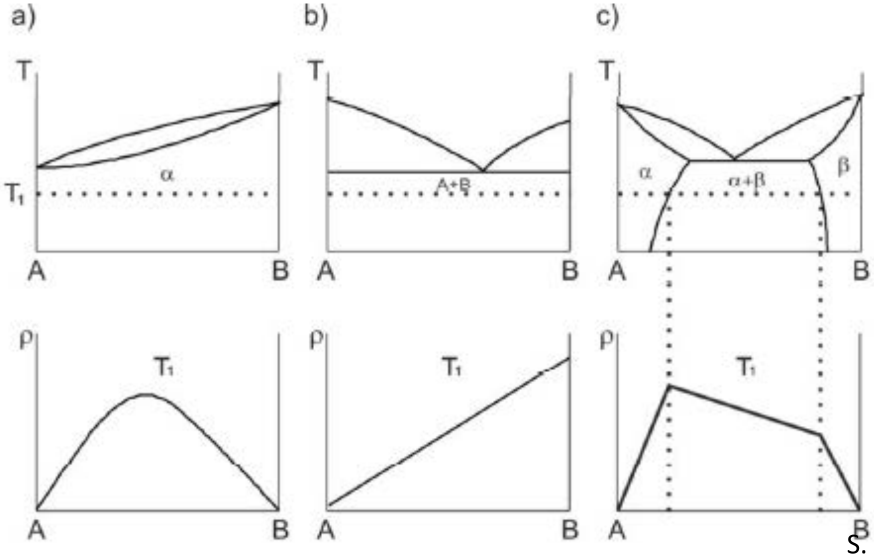
Resistivity screening as a discovery tool for phases and phase tranformations

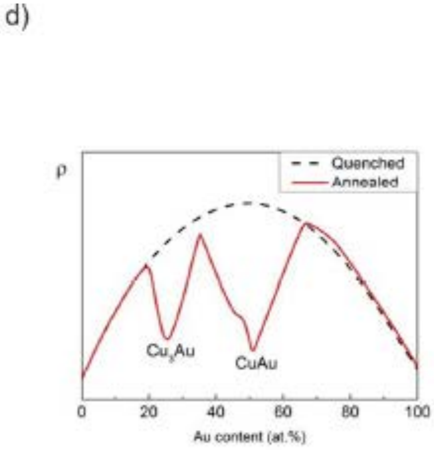


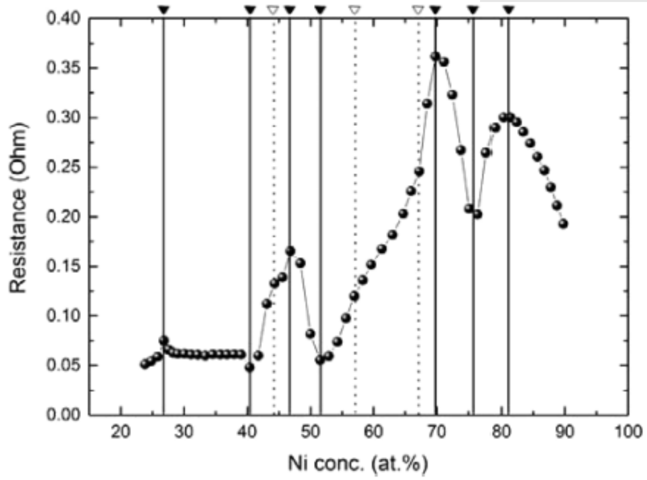




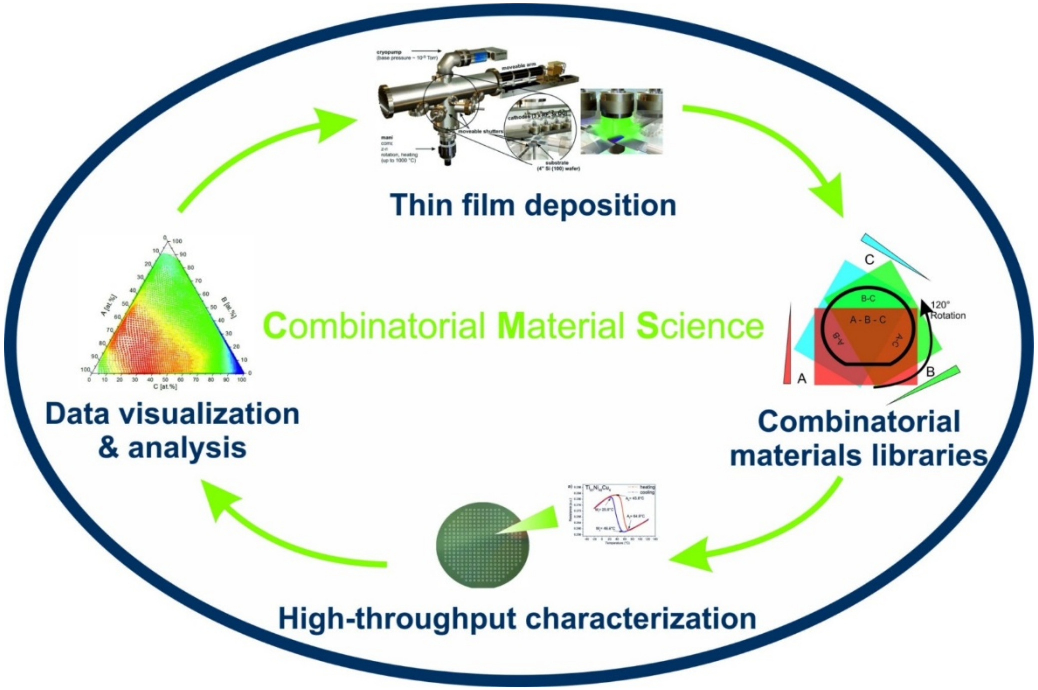








S. Thienhaus, D. Naujoks, J. Pfetzing-Micklich, D. König, A. Ludwig (2014) *Rapid Identification of Areas of Interest in Thin Film Materials Libraries by Combining Electrical, Optical, X-ray Diffraction, and Mechanical High-Throughput Measurements: A Case Study for the System Ni–Al*, ACS Comb. Sci. 16, 686



Thin film deposition

Combinatorial Material Science

Combinatorial materials libraries

High-throughput characterization

Data visualization & analysis

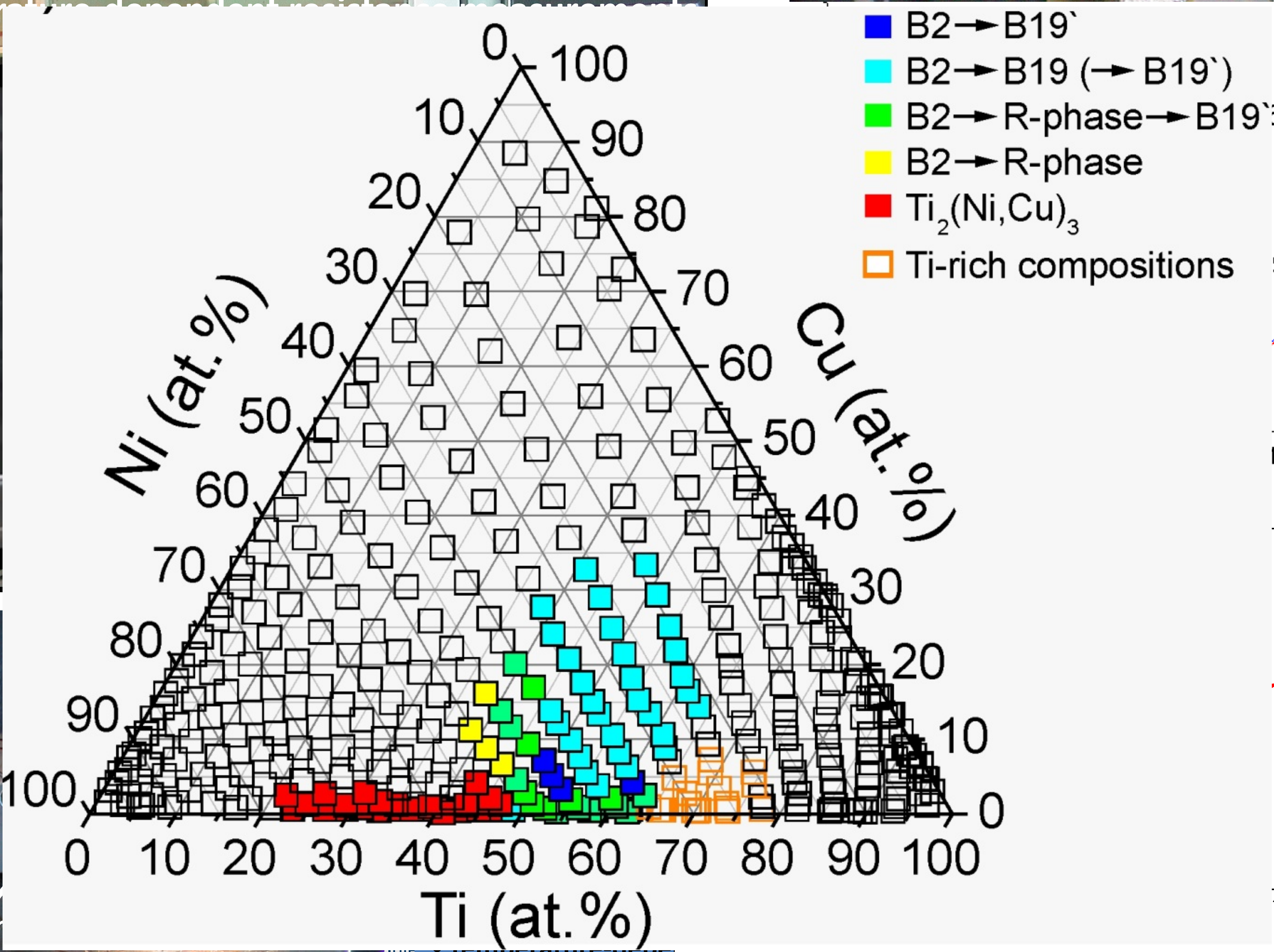
Searching new phases

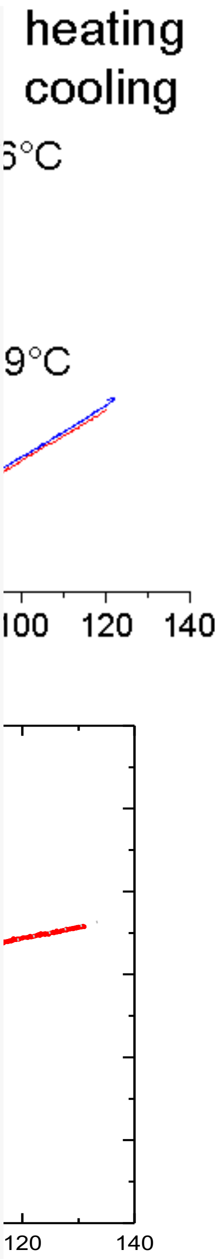
Shape Memory Alloys

High-throughput characterization of materials libraries: R(T)

Screening of phases, phase transformations, magnetism

Temperature-dependent resistance measurements





Electrom

inte

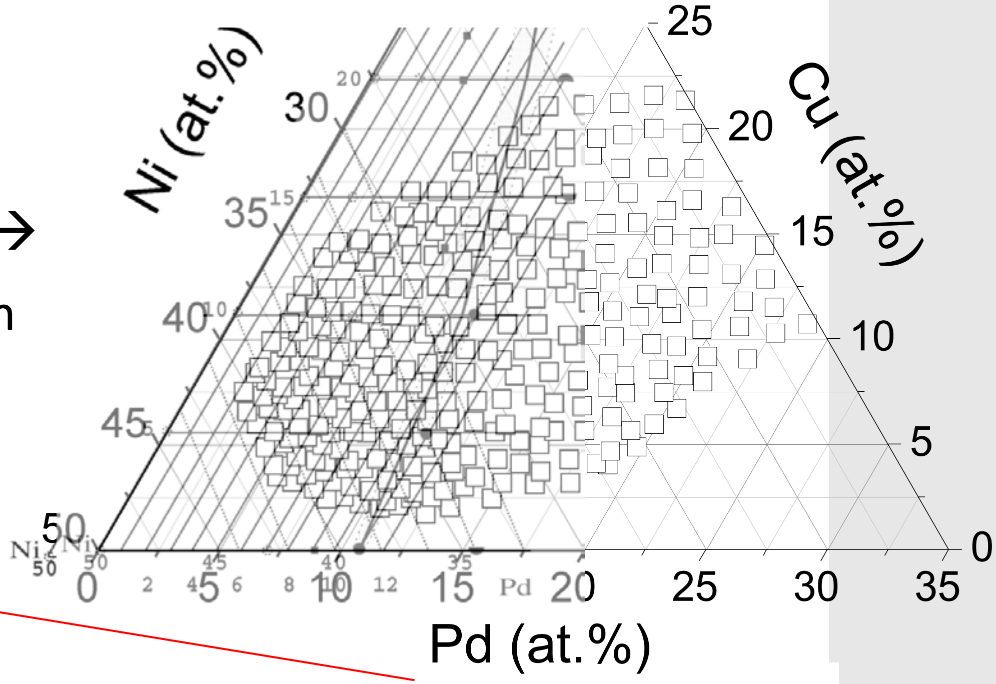
- temperature-depe

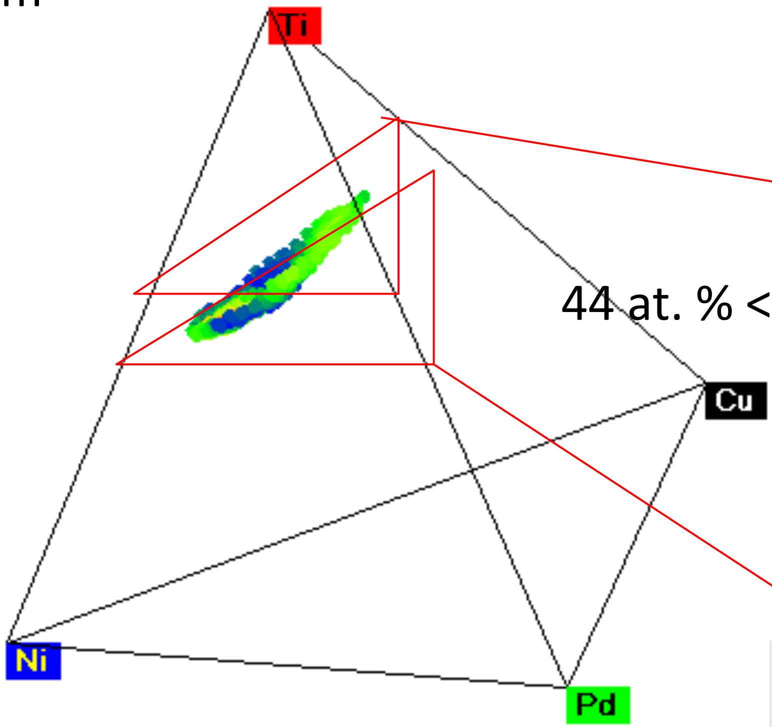
Exemplaric results for intermetallic systems: Theory verfication for quaternary shape memory alloys

Ti-Ni-Cu-Pd composition spread

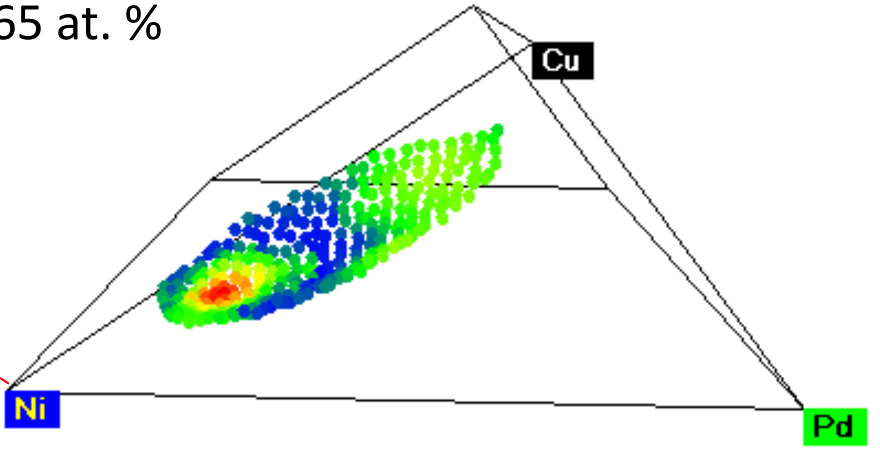
prediction of “zero hysteresis” by R.D. James

- fabricated using wedge-type thin film approach for ternary alloy systems (Ni-Pd-Cu)
+ additional homogenous deposition of Ti layers → *in situ* heating for alloy formation at 500°C / 1 h in vacuum

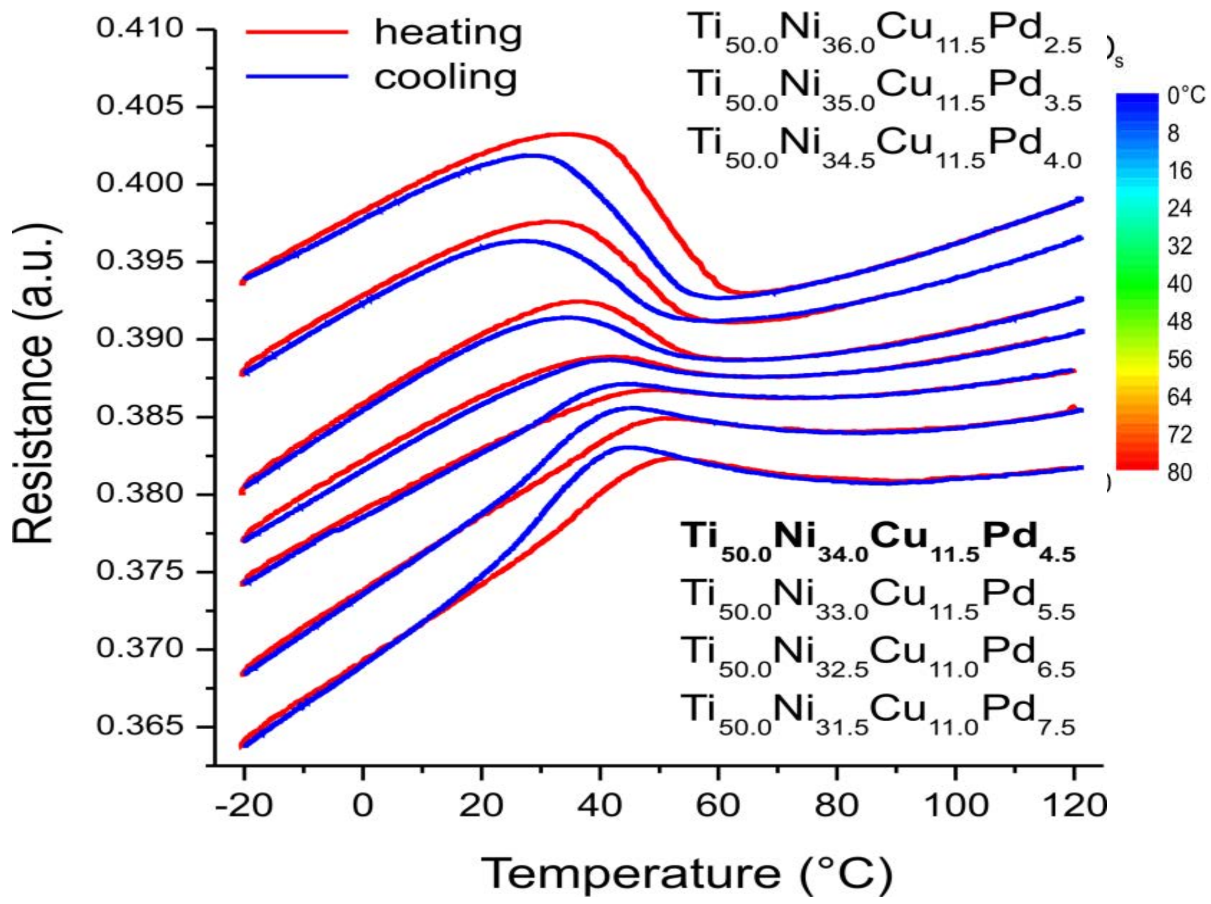


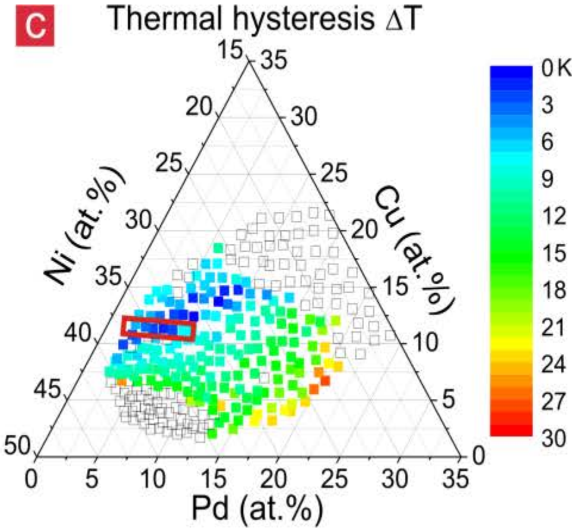


44 at. % < Ti < 65 at. %



Exemplaric results for intermetallic systems: Quaternary shape memory alloys





Vanishing hysteresis in SMA

Prof. Dr.-Ing. A. Ludwig | www.rub.de/wdm | R. Zarnetta, R. Takahash, V. Srivastava, M. L. Young, A. Savan, Y. Furuya, S. Thienhaus, B. Maaß, M. Rahim, J. Frenzel, H. Brunken, Y. S. Chu, R. D. James, I. Takeuchi, G. Eggeler, A. Ludwig (2010), *Identification of quaternary shape memory alloys with "zero" thermal hysteresis and unprecedented functional stability*, **Advanced Functional Materials**, 20, 1917 – 1923.

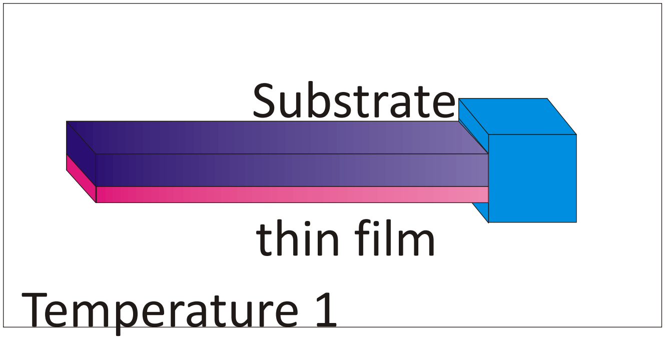
Si-cantilever arrays for high-throughput stress measurements (phase transformations)

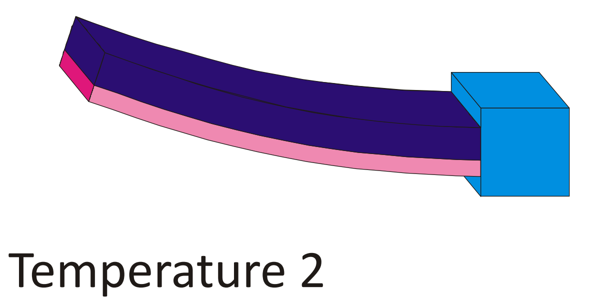
ls

Shape memory effect

Martensitic transformation:

Change of stress state between austenite and martensite





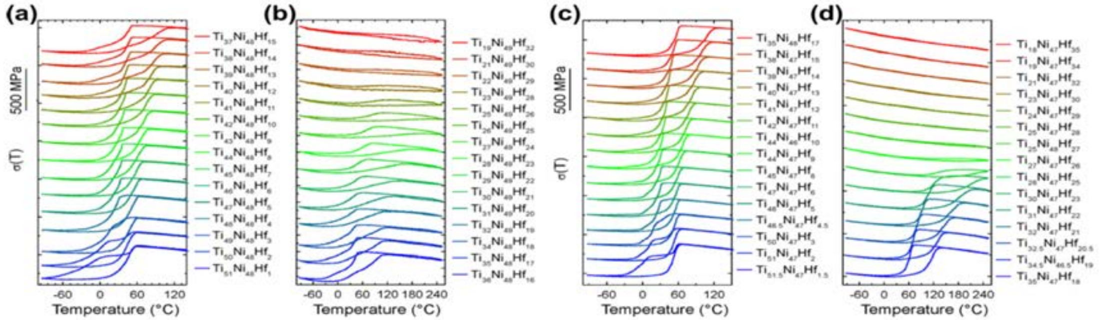
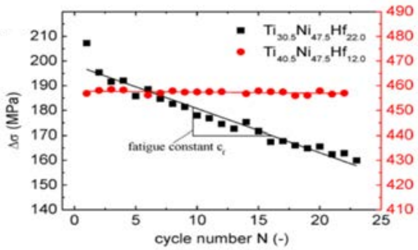
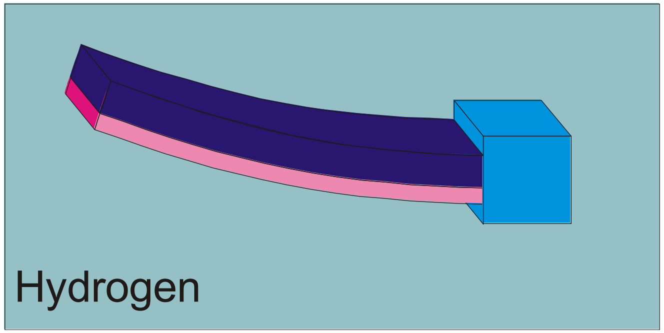
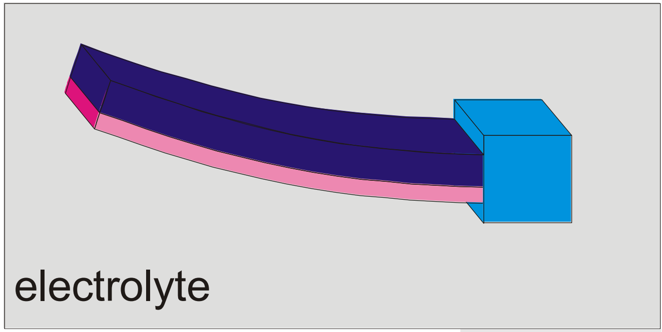


Fig. 6. $\sigma(T)$ curves of Ti–Ni–Hf thin films with nominal compositions of (a and b) $Ti_{51-x}Ni_{49}Hf_x$ and (c and d) $Ti_{52.5-x}Ni_{47.5}Hf_x$—first thermal cycle.



D. Koenig, A. Ludwig, et al.
Acta Mat 59 (2011) 3267-3275



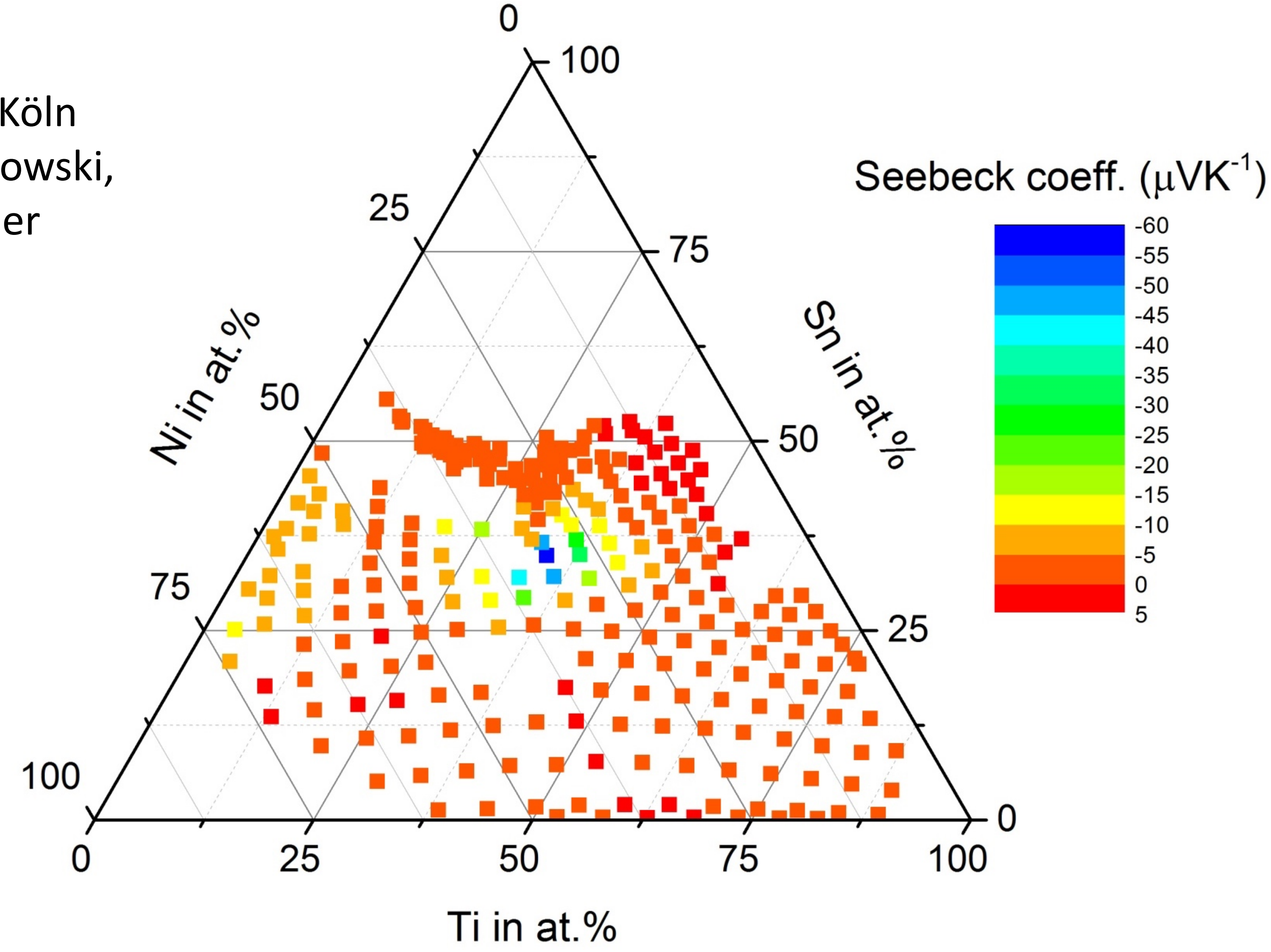


A. Ludwig, J. Cao, J. Brugger, I. Takeuchi (2005), Meas. Sci. Technol. 16, 111-118
S. Hamann, M. Ehmann, S. Thienhaus, A. Savan, A. Ludwig (2008), Sensors and Actuators A, 147, 57
R. Zarnetta, M. Ehmann, A. Savan, A. Ludwig (2010), Smart Materials and Structures 19, 065032

Thermoelectrics

High-throughput characterization of Seebeck coefficient

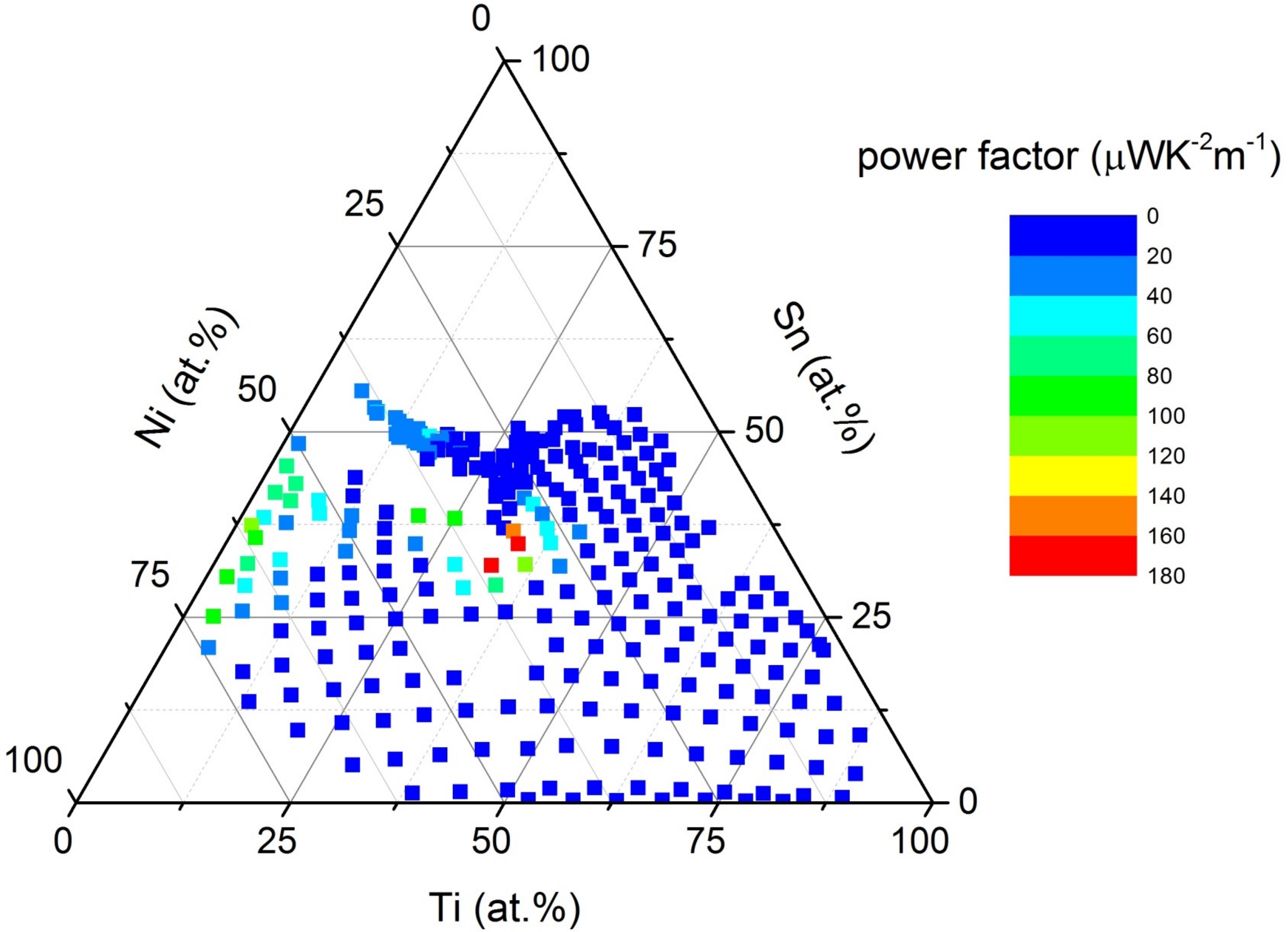
@DLR Köln
P. Ziolkowski,
E. Müller



M. Wambach, R. Stern, S. Bhattacharya, P. Ziolkowski, E. Müller, G.K.H. Madsen, A. Ludwig, Unraveling Self-Doping Effects in Thermoelectric TiNiSn Half-Heusler Alloys by combined Theory and High-Throughput Experiments, Adv Electronic Mat 2016

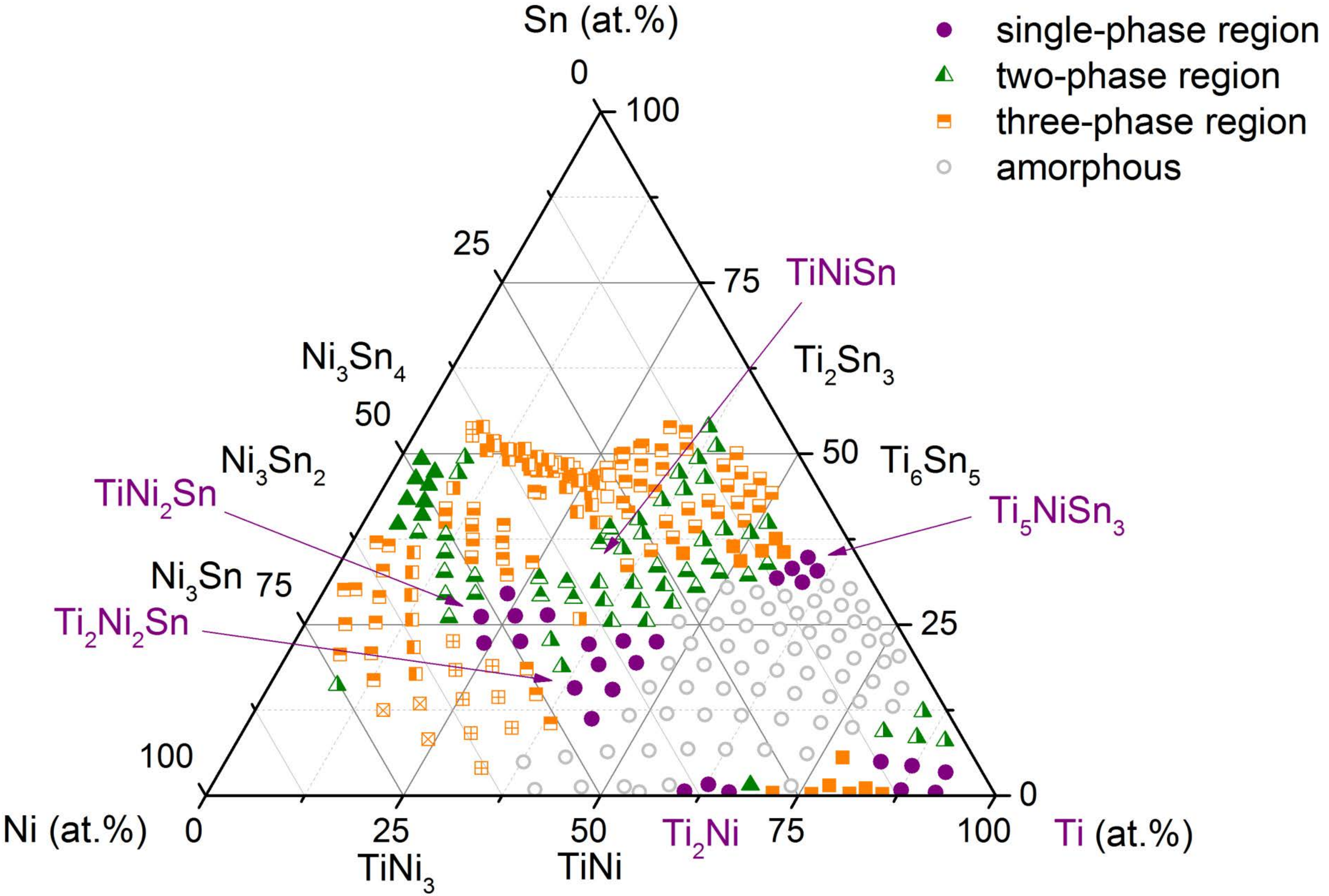
High-throughput characterization of thermoelectric power factor

$$P = \frac{\alpha^2}{\rho}$$



M. Wambach, R. Stern, S. Bhattacharya, P. Ziolkowski, E. Müller, G.K.H. Madsen, A. Ludwig, Unraveling Self-Doping Effects in Thermoelectric TiNiSn Half-Heusler Alloys by combined Theory and High-Throughput Experiments, Adv Electronic Mat 2016

Thin film phase diagram of Ti-Ni-Sn



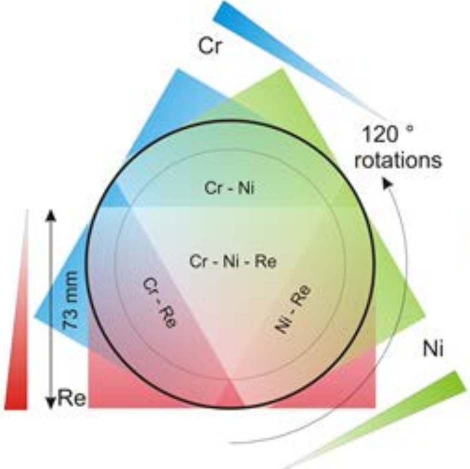
M. Wambach, R. Stern, S. Bhattacharya, P. Ziolkowski, E. Müller, G.K.H. Madsen, A. Ludwig, Unraveling Self-Doping Effects in Thermoelectric TiNiSn Half-Heusler Alloys by combined Theory and High-Throughput Experiments, Adv Electronic Mat 2016

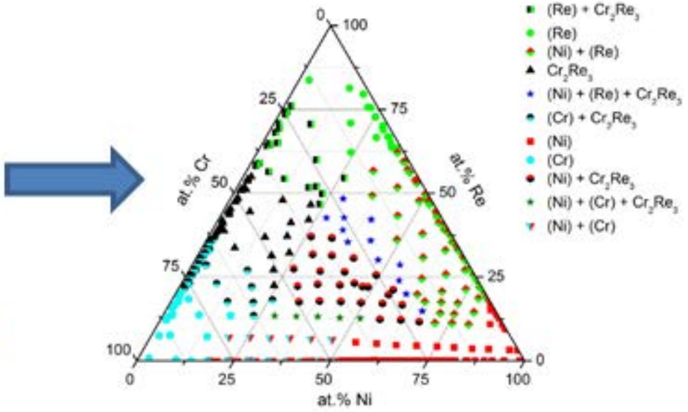
Superalloys

Understanding of the influence of alloying elements on phase stabilities in Ni- and Co-based superalloys in ternary model systems (TCP phases)

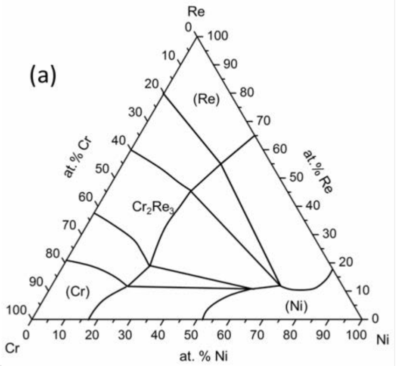
- high-temperature processing of materials libraries (> 1000°C)
- identification of compositions showing particular phases / or properties
- high-throughput oxidation studies

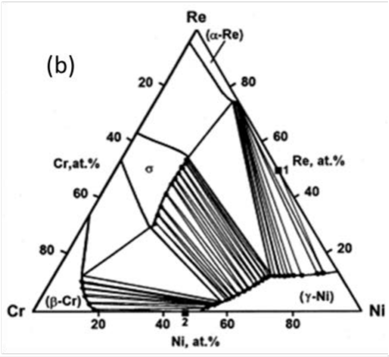
Cr-Ni-Re, Co-Ti-W, Ni-Al-Cr, Co-Al-W, …





Ar overpressure to lower sublimation of elements like Al, Mn at high temperatures

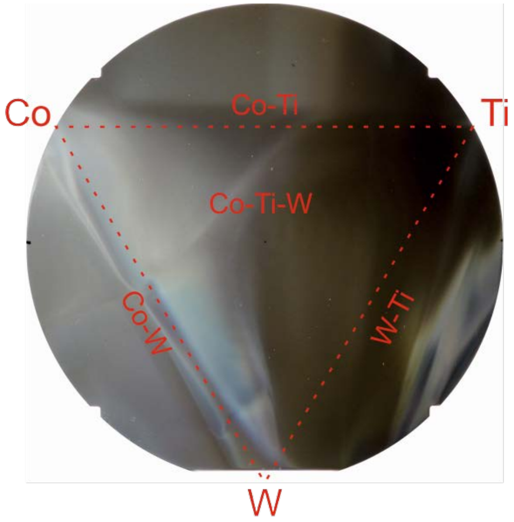


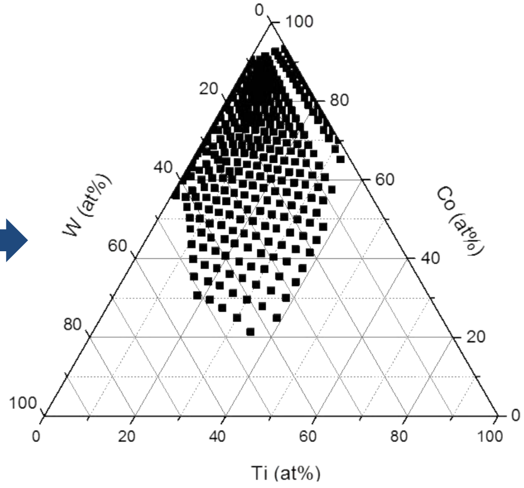


SFB/Transregio 103
SUPERALLOY SINGLE CRYSTALS

A. Janghorban, J. Pfetzing-Micklich, J. Frenzel, A. Ludwig (2014), *Investigation of the thin film system Cr-Ni-Re by high-throughput experimentation*, Advanced Engineering Materials, Vol. 16, 588-593

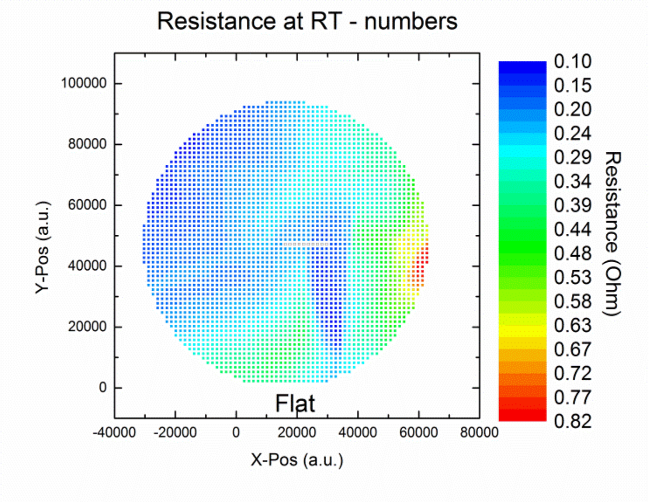
A new phase in Co-Ti-W?

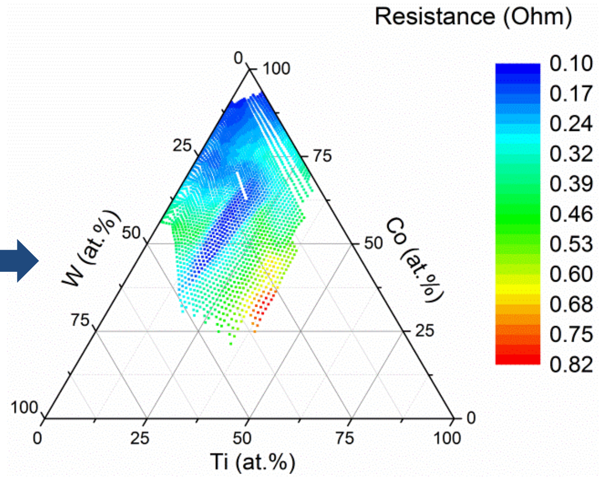




Substrate: Al_2O_3

Multilayer deposition at 300°C

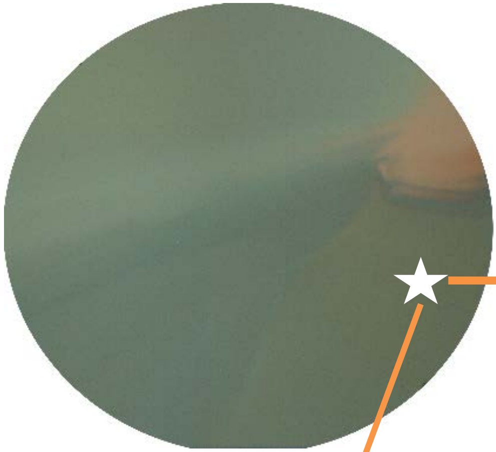


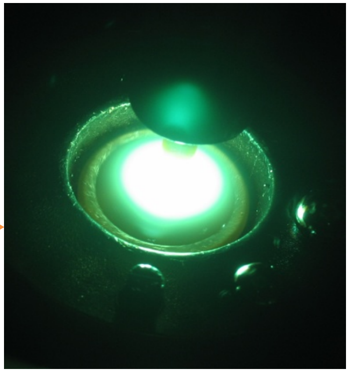


Heat treatment 950°C, 40h in vacuum

MATEC Web of Conferences **14**, 18002 (2014)
DOI: 10.1051/matecconf/20141418002

Upscaling of hits for thin film and bulk applications



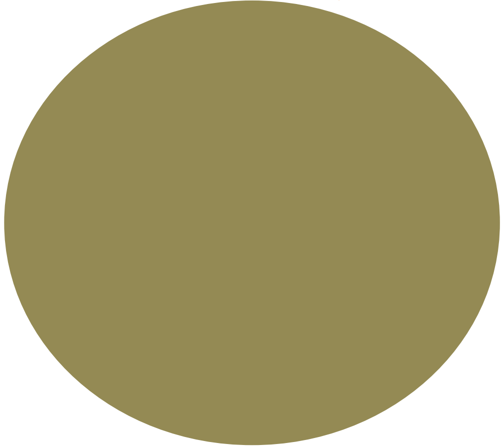


Fabrication of samples (< 70g)
in arc melter

heat treatment

Thermo-mechanical treatments

Device testing



Optimization of hit(s)
by combinatorial processing

Vacuum induction furnace (up to 5 kg)

New phase identified by cooperation between „combi“, bulk, DFT, Calphad and TEM groups

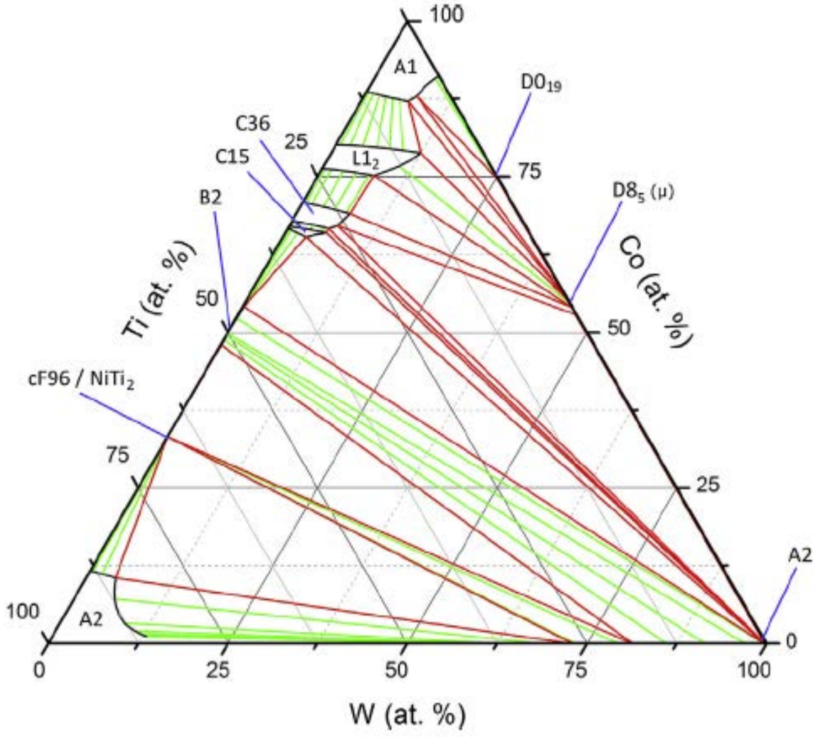


Fig. 2. Isothermal section through the ternary Co-Ti-W system at 1000 °C calculated by CALPHAD [9,12]. Green lines indicate two-phase fields, red lines enclose three-phase fields. The μ-phase (D8$_5$) appears only as a binary Co-W compound. (For interpretation of the references to colour in this figure, the reader is referred to the web version of this article.)

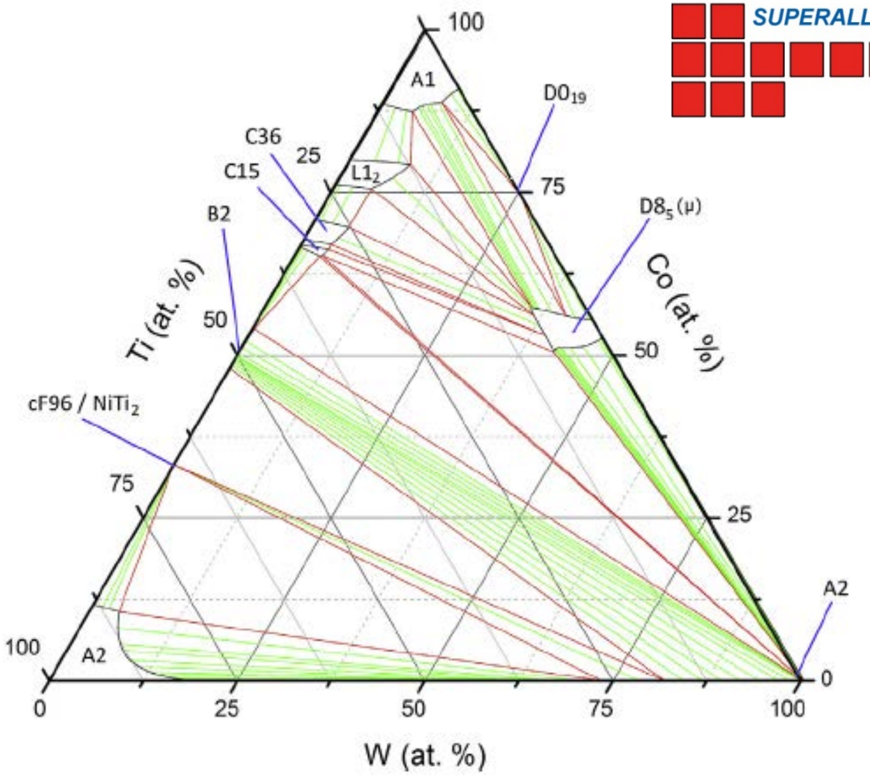
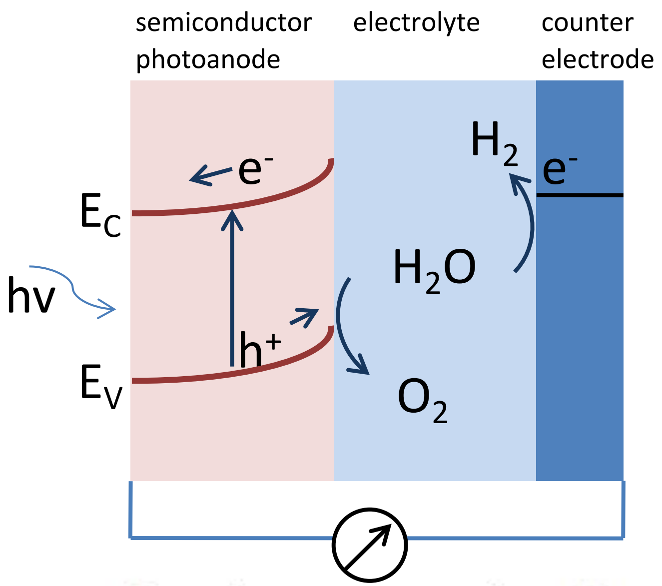


Fig. 10. Modified phase diagram at 1000 °C of the Co-Ti-W system obtained from CALPHAD calculations. The solubility of Ti in the μ-phase is taken into account and appears as ternary Co-Ti-W μ-phase (D8$_5$).

D. Naujoks, Y.M. Eggeler, P. Hallensleben, J. Frenzel, S.G. Fries, M. Palumbo, J. Koßmann, T. Hammerschmidt, J. Pfetzing-Micklich, G. Eggeler, E. Spiecker, R. Drautz, A. Ludwig (2017) *Identification of a ternary μ-phase in the Co-Ti-W system – An advanced correlative thin film-bulk combinatorial materials investigation*, Acta Materialia 138, 100-110

Materials for Solar Water Splitting

Concept of solar water splitting

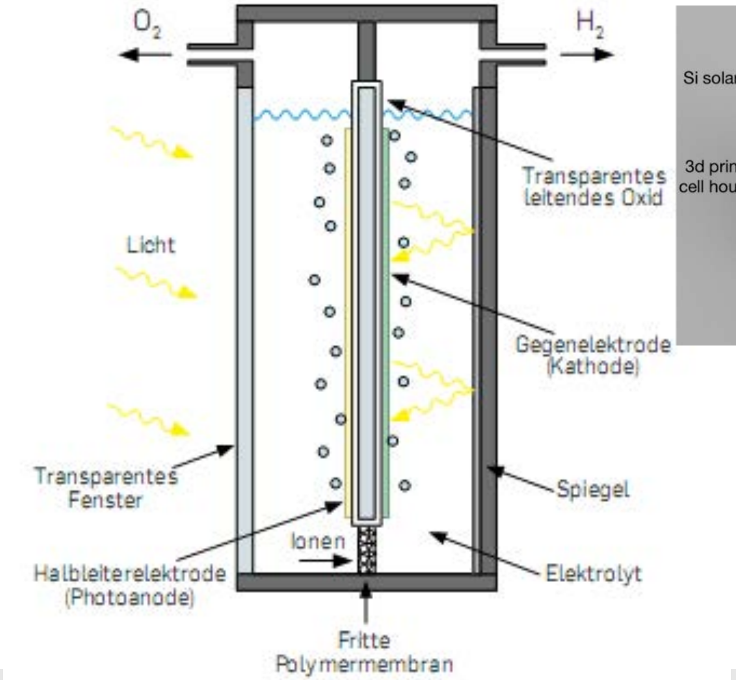


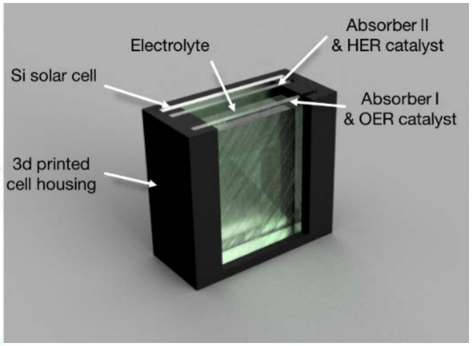
$4hv \rightarrow 4e^- + 4h^+$ (1)

$4h^+ + 2H_2O_{(liquid)} \rightarrow O_{2(g)} + 4H^+$ (2)

$4H^+ + 4e^- \rightarrow 2H_2(g)$ (3)

$4hv + 2H_2O_{(liquid)} \rightarrow O_{2(g)} + 2H_{2(g)}$ (4)

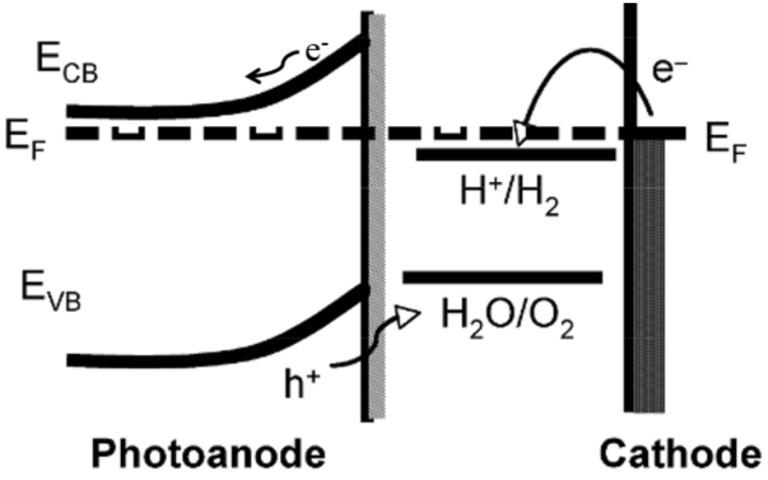




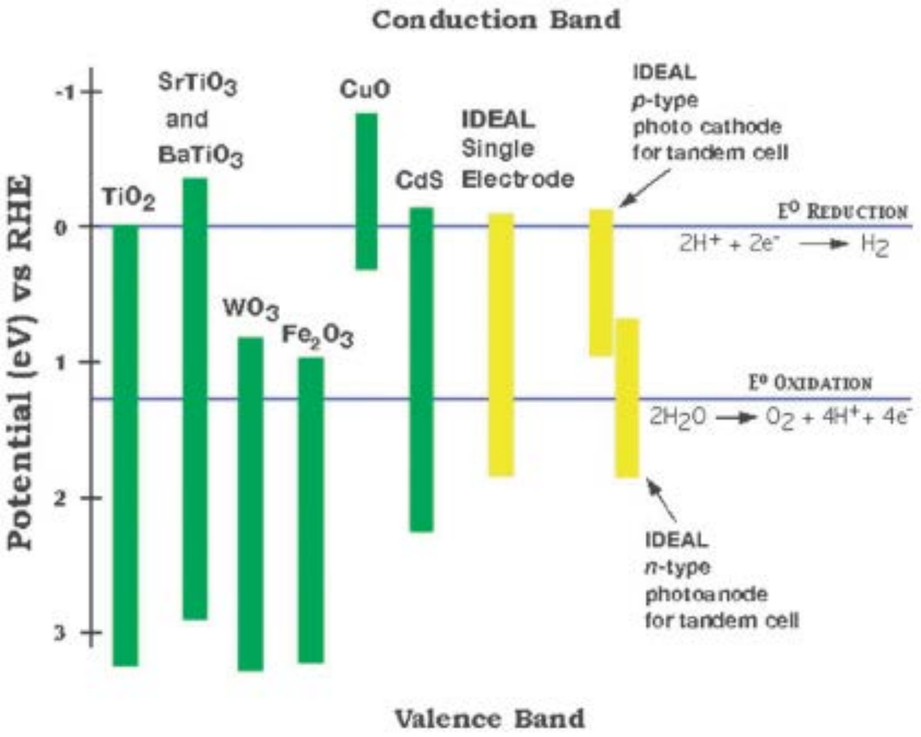
Important materials:
- **photoanodes**
- **photocathodes**
- **catalysts for HER and OER**
- **transparent conductive oxides (TCOs) tailored for photanode, photocathode materials**

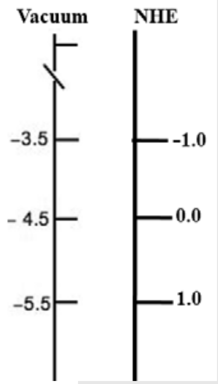
PEC: photo-electrochemical
HER: hydrogen-evolution reaction
OER: oxygen-evolution reaction

Semiconductors for solar water splitting



→ Semiconductor band edges straddle redox potential for water photoelectrolysis



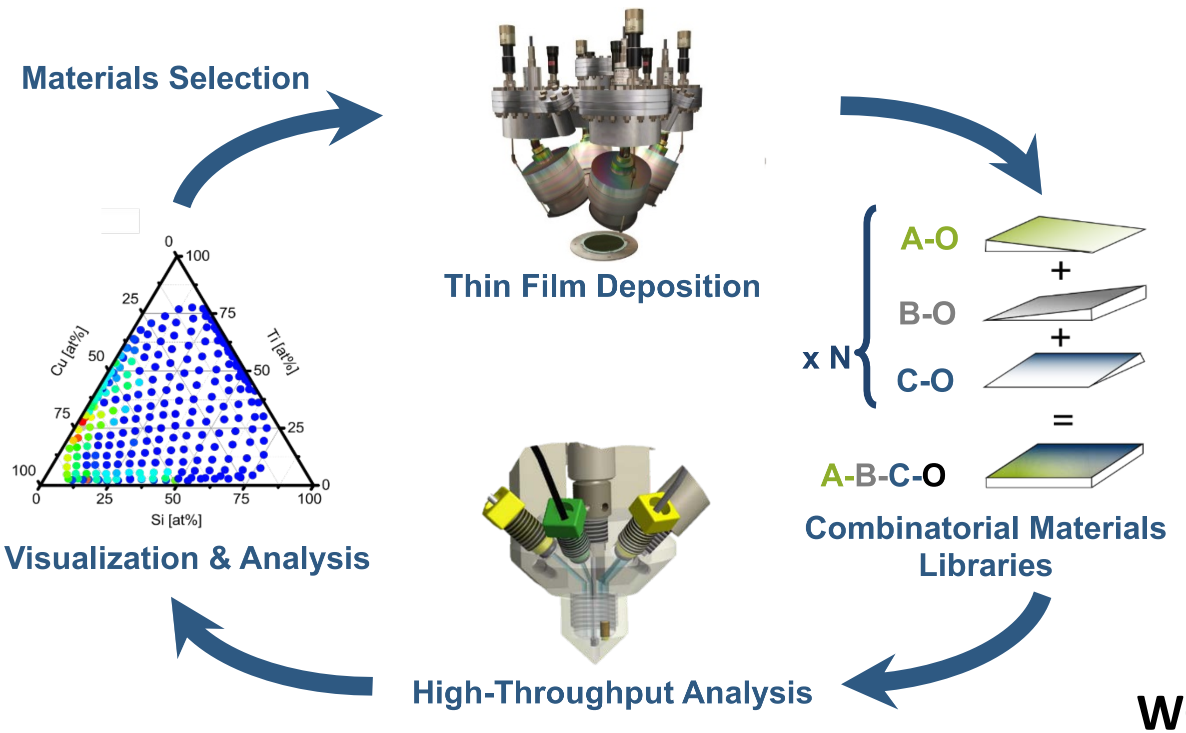


- semiconductors with bandgaps between 1.6 and 2 eV
- right energy levels with respect to redox potential of water
- n-type photoanodes
- p-type photocathodes
- nanostructured surfaces decorated with catalyst nanoparticles
- stable for years under illumination in electrolyte
- candidates: oxides, oxynitrides → cheap, earth-abundant, stable, …

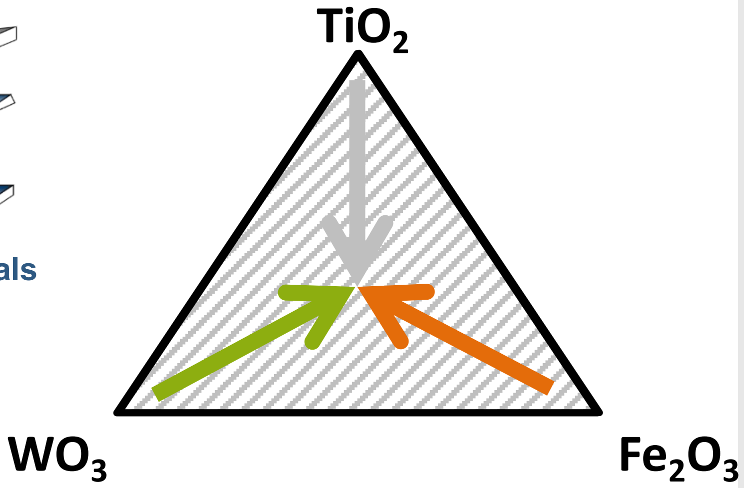
M. Woodhouse, B.A. Parkinson, Chem. Soc. Rev., 2009, 38, 197–210

Discovery and optimization of nanostructured functional materials

Combinatorial Materials Science for Solar Water Splitting



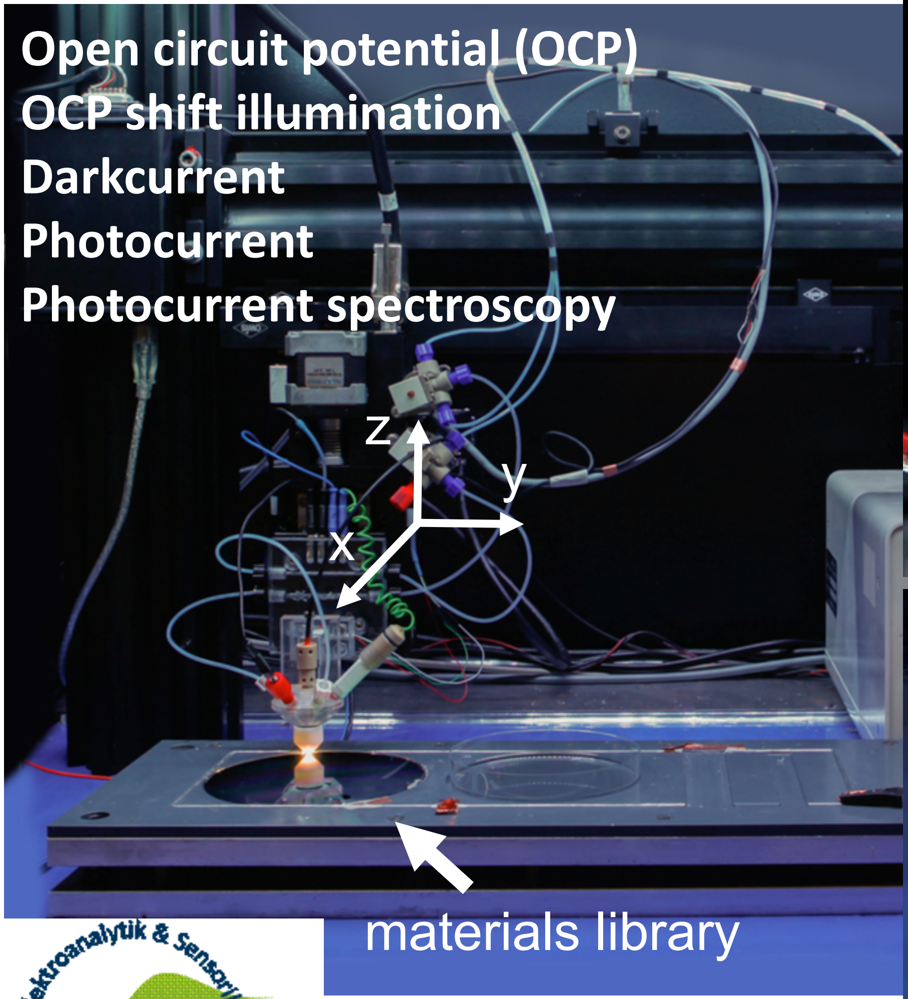
Well-explored binary, mostly unknown multinary oxides



- **proof-of-principle experiments (WO_3)**
- **from known binaries (WO_3, Fe_2O_3, TiO_2) to compositional complexity (W-Fe-Ti-O, Bi(V-Mo-X)O_4)**
- **from screening to in-depth characterization: Fe-Cr-Al-O**
- **stabilizing unstable materials: Cu-Si-Ti-O**
- **nanostructuring of solar water splitting materials**
- **towards systems**

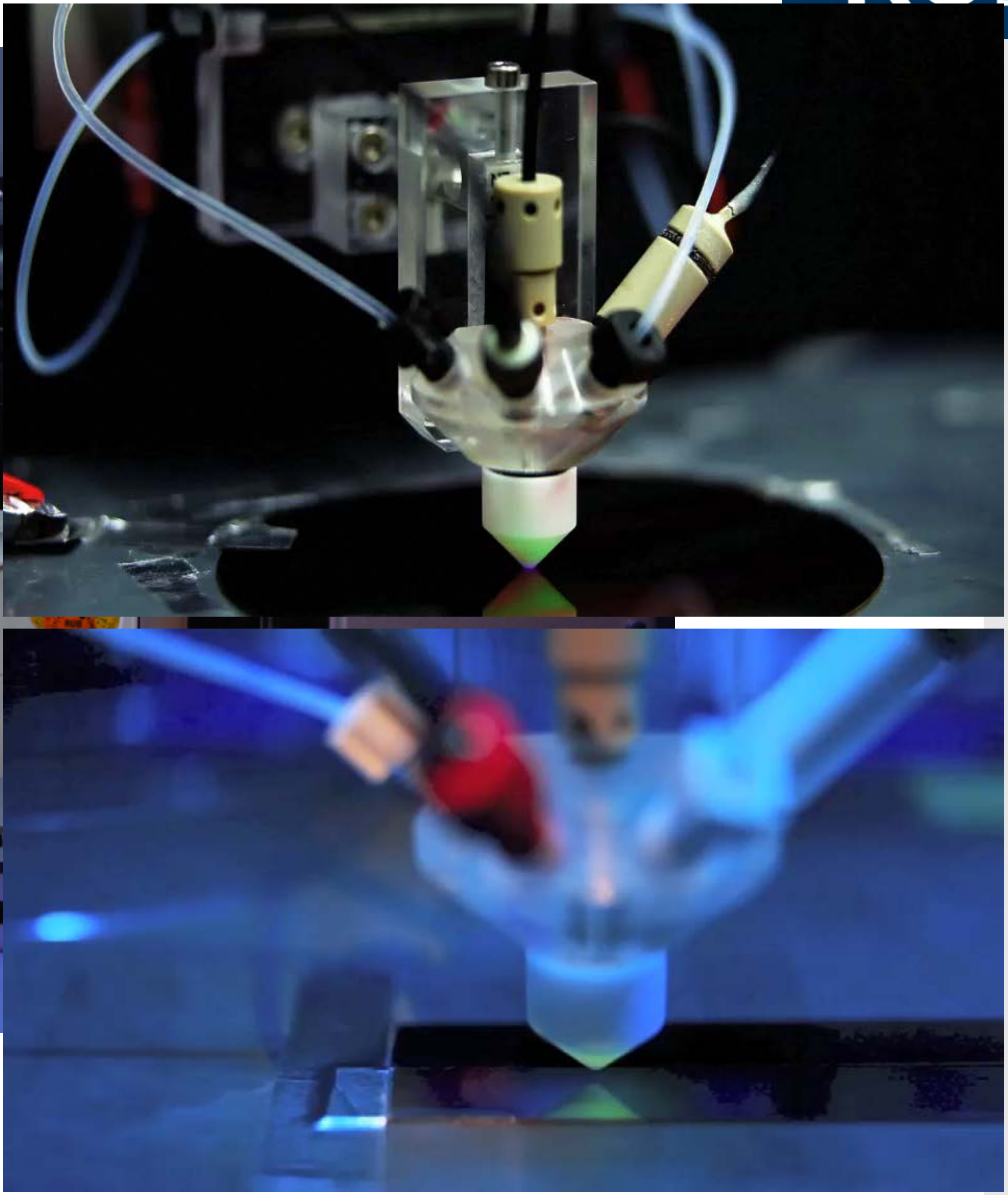
- n-type:
  - Ti-Fe-W-O
  - Bi-V-Mo-W-O
- p-type:
  - Cu-Si-Ti-O

Optical Scanning Droplet Cell



- Open circuit potential (OCP)
- OCP shift illumination
- Darkcurrent
- Photocurrent
- Photocurrent spectroscopy

materials library

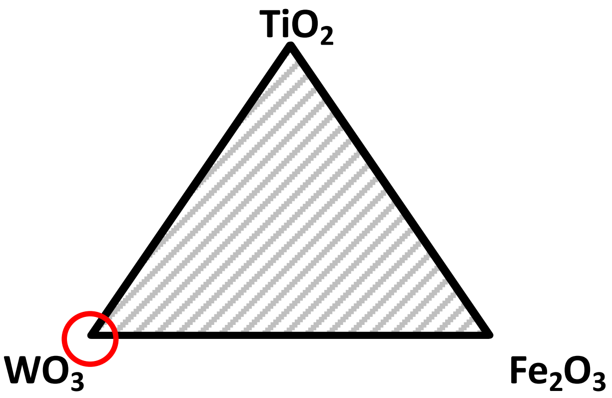


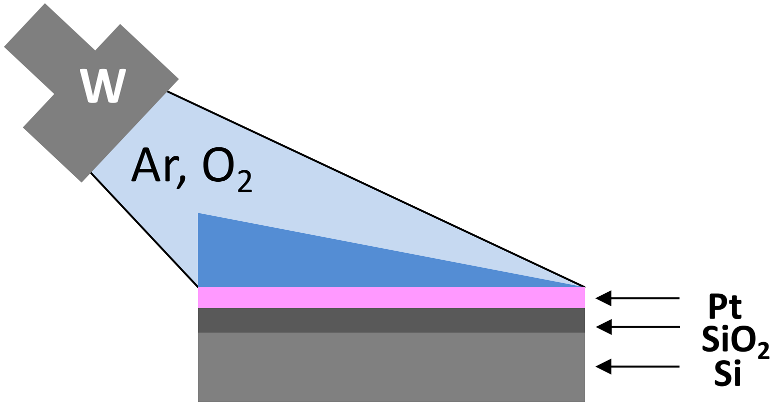
Prof. Dr. W. Schuhmann,
Dr. K. Sliozberg

K. Sliozberg, D. Schäfer, T. Erichsen, R. Meyer, C. Khare, A. Ludwig, and W. Schuhmann (2015) **High-throughput screening of thin film semiconductor materials libraries I: System development and a case study for Ti-W-O** ChemSusChem 8, 1270-1278

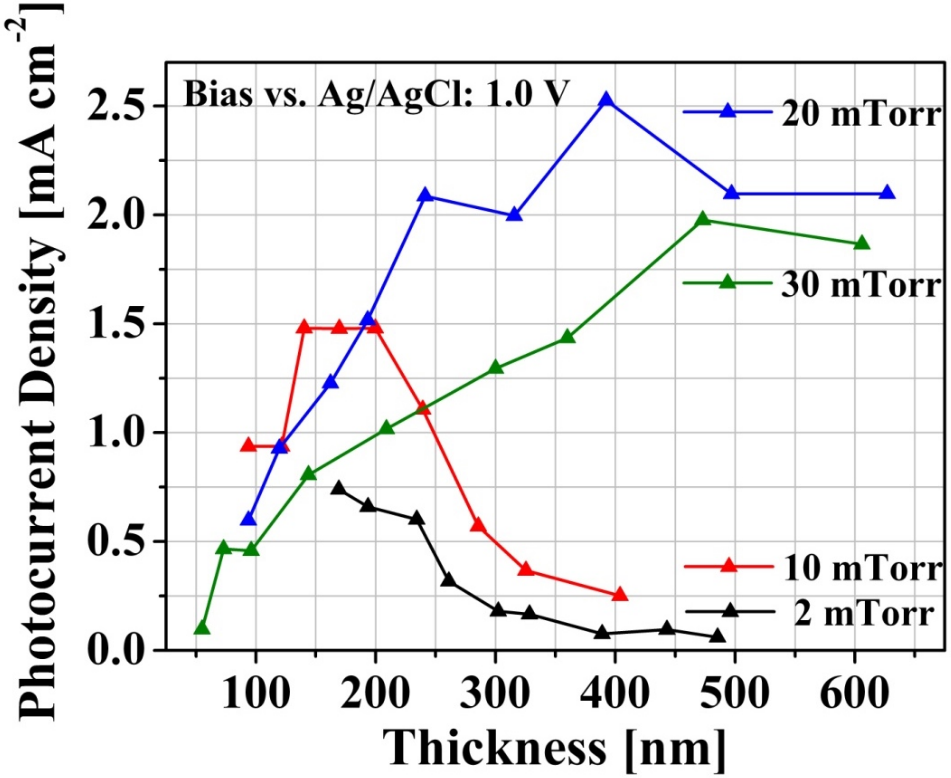
RUHR-UNIVERSITÄT BOCHUM

Thickness gradients of WO_{3-x}





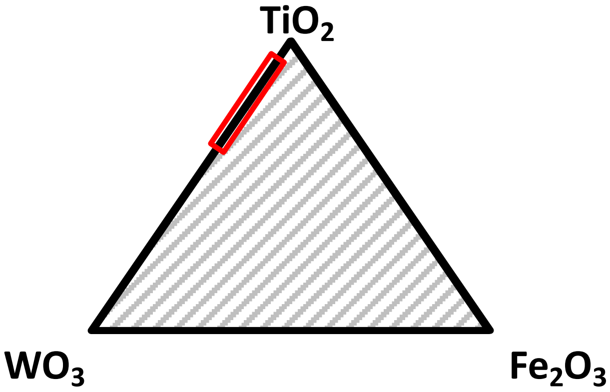
- Metal oxides by reactive magnetron sputtering
- Thickness gradient by sputtering with tilted cathode
- Strong dependence of the photocurrent on sputtering pressure and film thickness
- Composition effects have to be separated from thickness and morphology effects

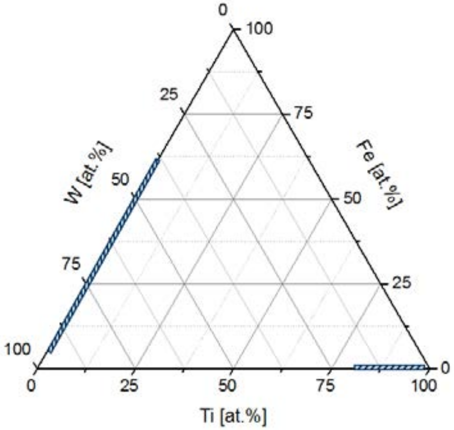


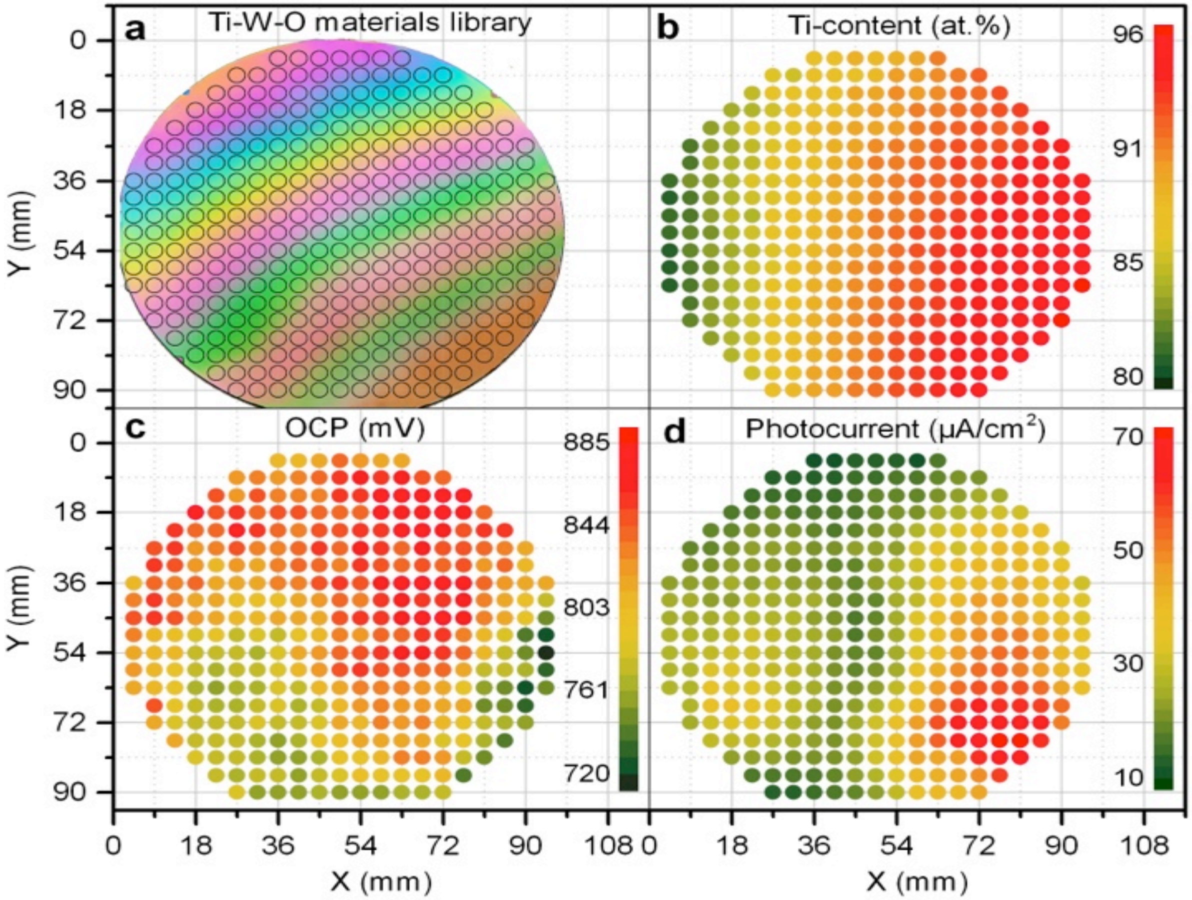
V.S. Vidyarthi, M. Hofmann, W. Schuhmann, A. Ludwig et al
Int. J. Hydrog. Energ. 36, 4724-4731, 2011

RUHR-UNIVERSITÄT BOCHUM

Results of high-throughput characterization of quasi-binary system Ti-W-O



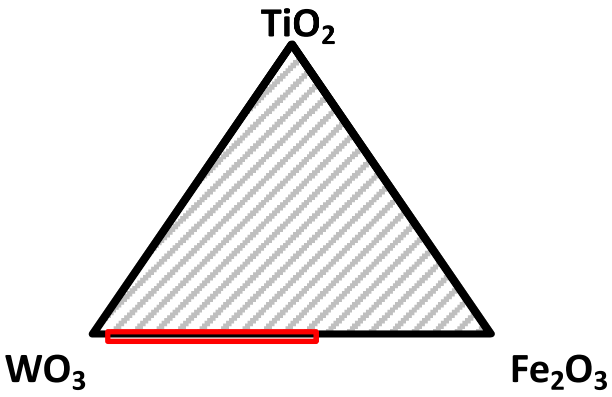


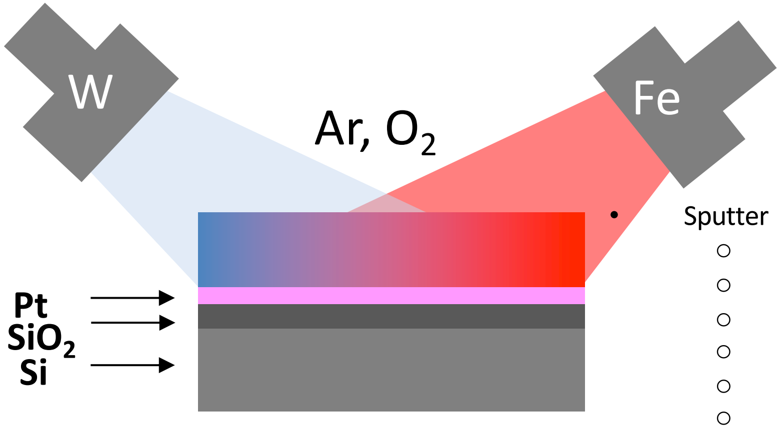


K. Sliozberg, D. Schäfer, T. Erichsen, C. Khare, R. Meyer, A. Ludwig, W. Schuhmann (2015)*High-throughput screening of thin-film semiconductor materials libraries I: System development and case study for Ti-W-O*, Chem. Sus. Chem., Vol. 8, Issue 7, 1270–1278

RUHR-UNIVERSITÄT BOCHUM

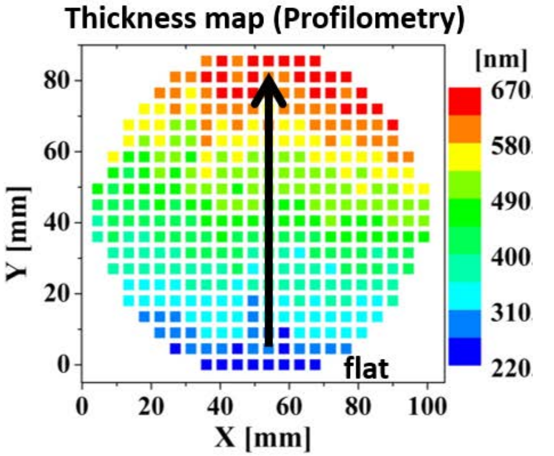
Results of high-throughput characterization of quasi-binary system Fe-W-O

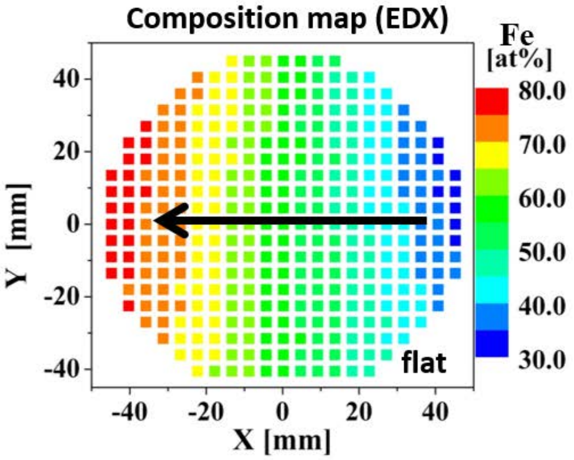


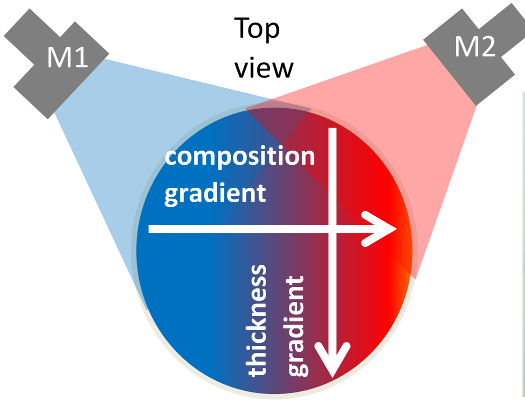


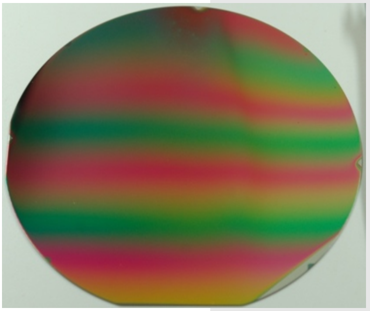
- Sputter Parameters:

○	Temperature	400°C
○	Pressure	10 mTorr
○	Ar flow	30 sccm
○	O_2 flow	90 sccm
○	Power	70 – 400 W
○	Targets	Fe, W


Thickness map (Profilometry)

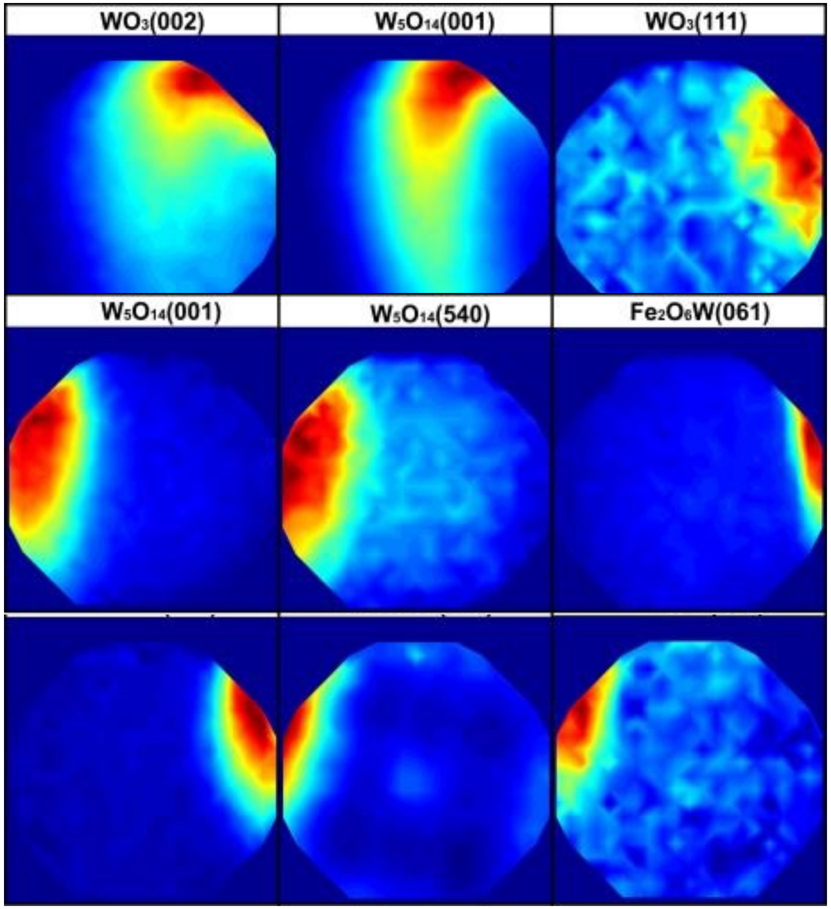

Composition map (EDX)



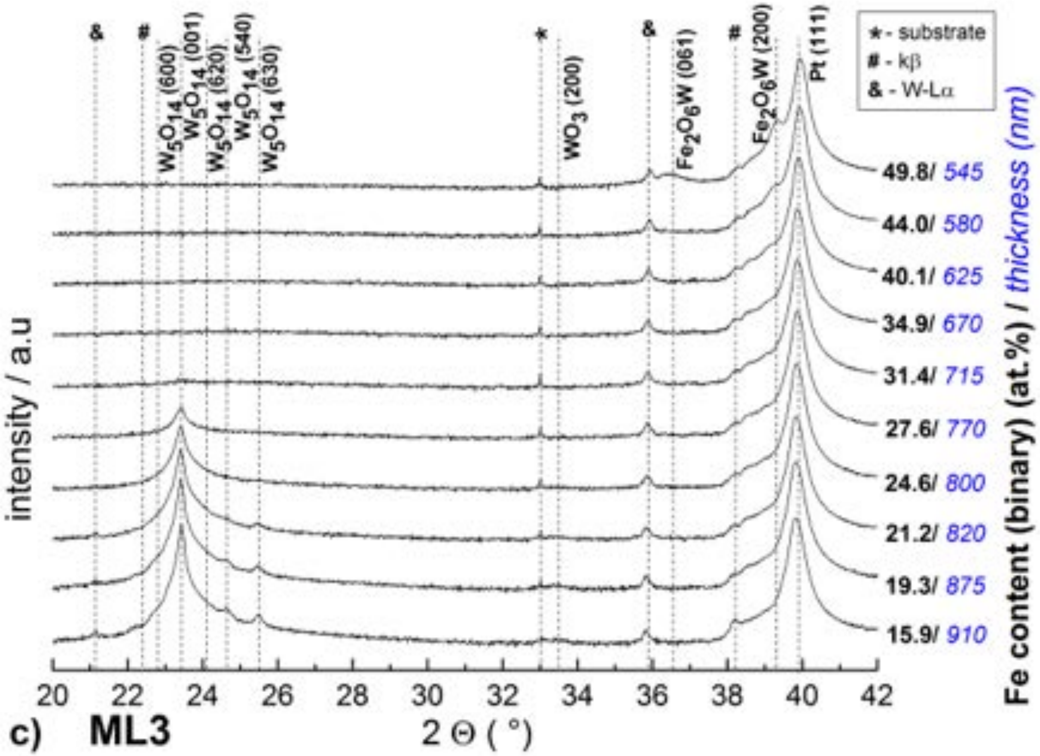


equal deposition rates result in perpendicular gradients

Crystal structure analysis of Fe-W-O



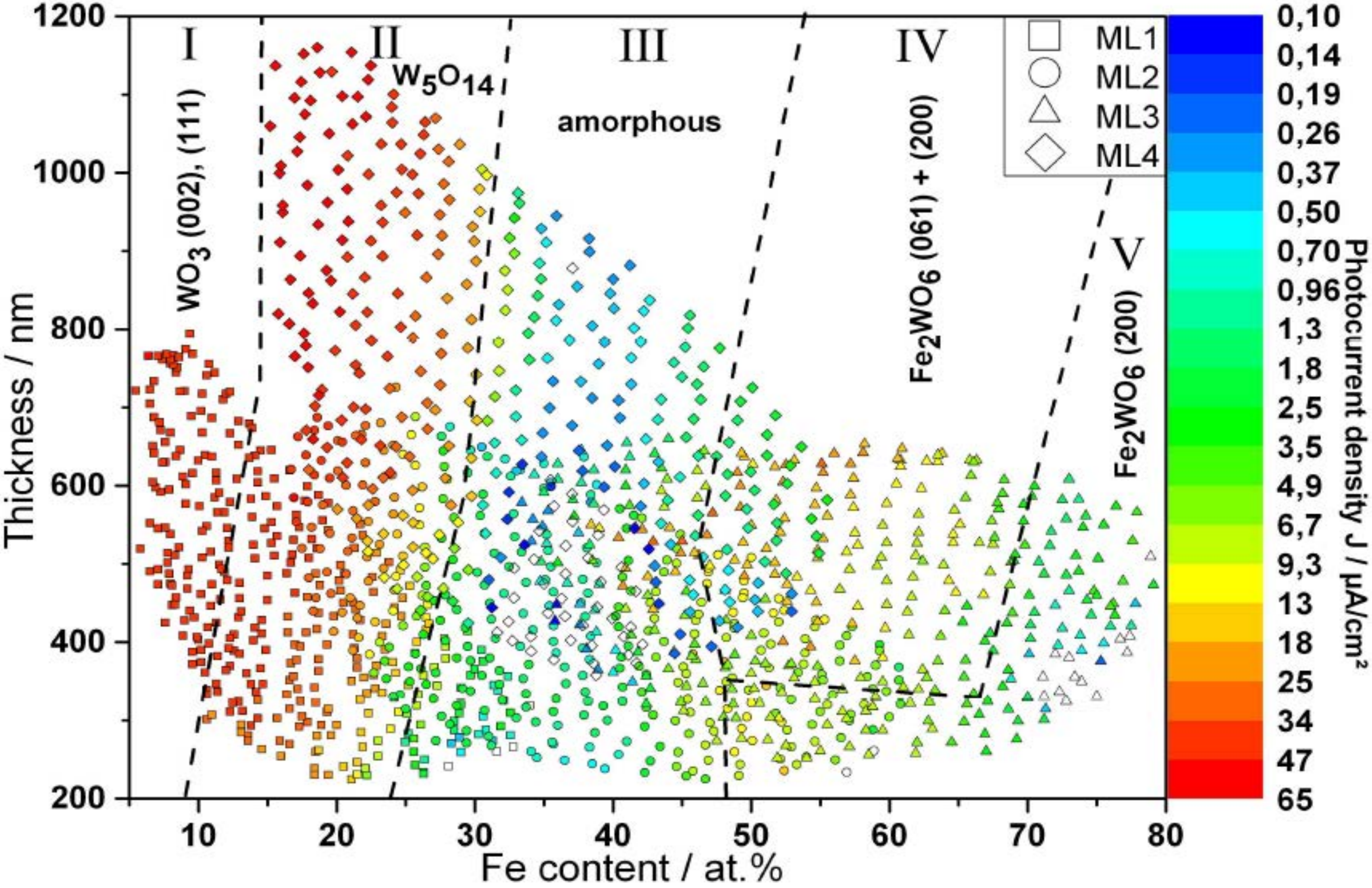
Selected XRD peak intensity plots over physical coordinates



XRD diffraction patterns for Fe-W-O materials library No. 3

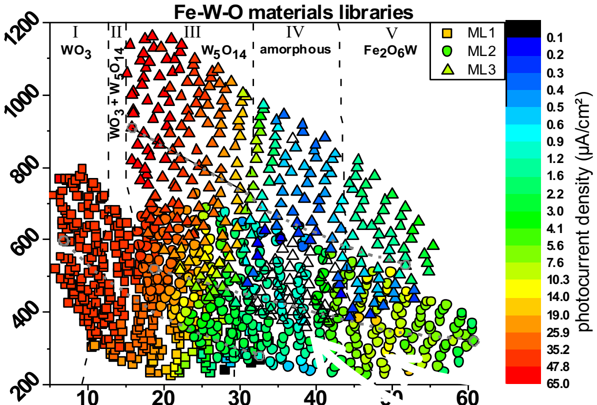
R. Meyer, K. Sliozberg, C. Khare, W. Schuhmann, A. Ludwig **High-Troughput screening of thin film semiconductor materials libraries II: Composition, crystallinity, morphology, thickness and photocurrent density of Fe-W-O libraries,** 2015 ChemSusChem 8, 1279–1285

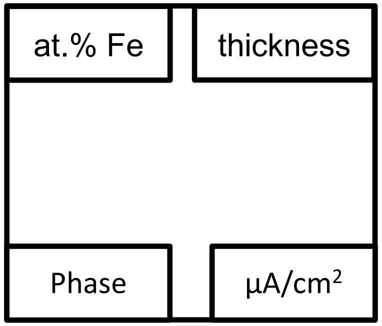
Photocurrent vs. thickness & composition in Fe-W-O materials libraries



R. Meyer, K. Sliozberg, C. Khare, W. Schuhmann, A. Ludwig (2015), *High-throughput screening of thin-film semiconductor materials libraries II: Characterization of Fe-W-O Libraries,* ChemSusChem 8, 1279 – 1285

Morphology of Fe-W-O materials libraries

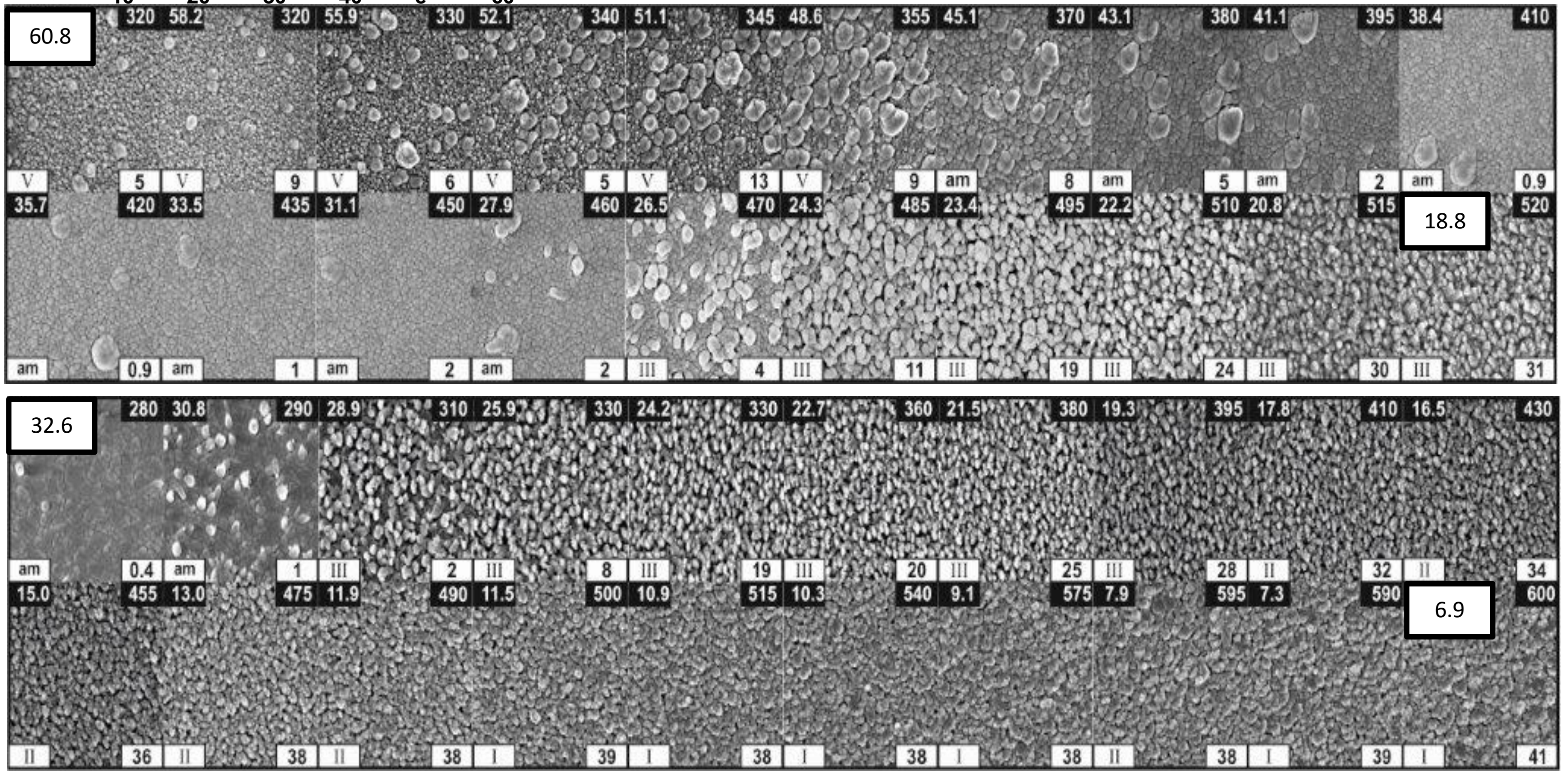



at.% Fe

thickness

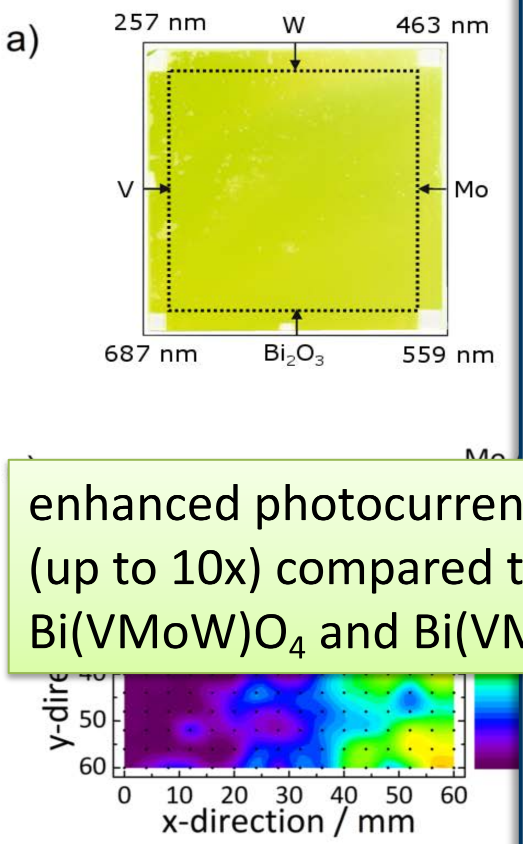
Phase

µA/cm²



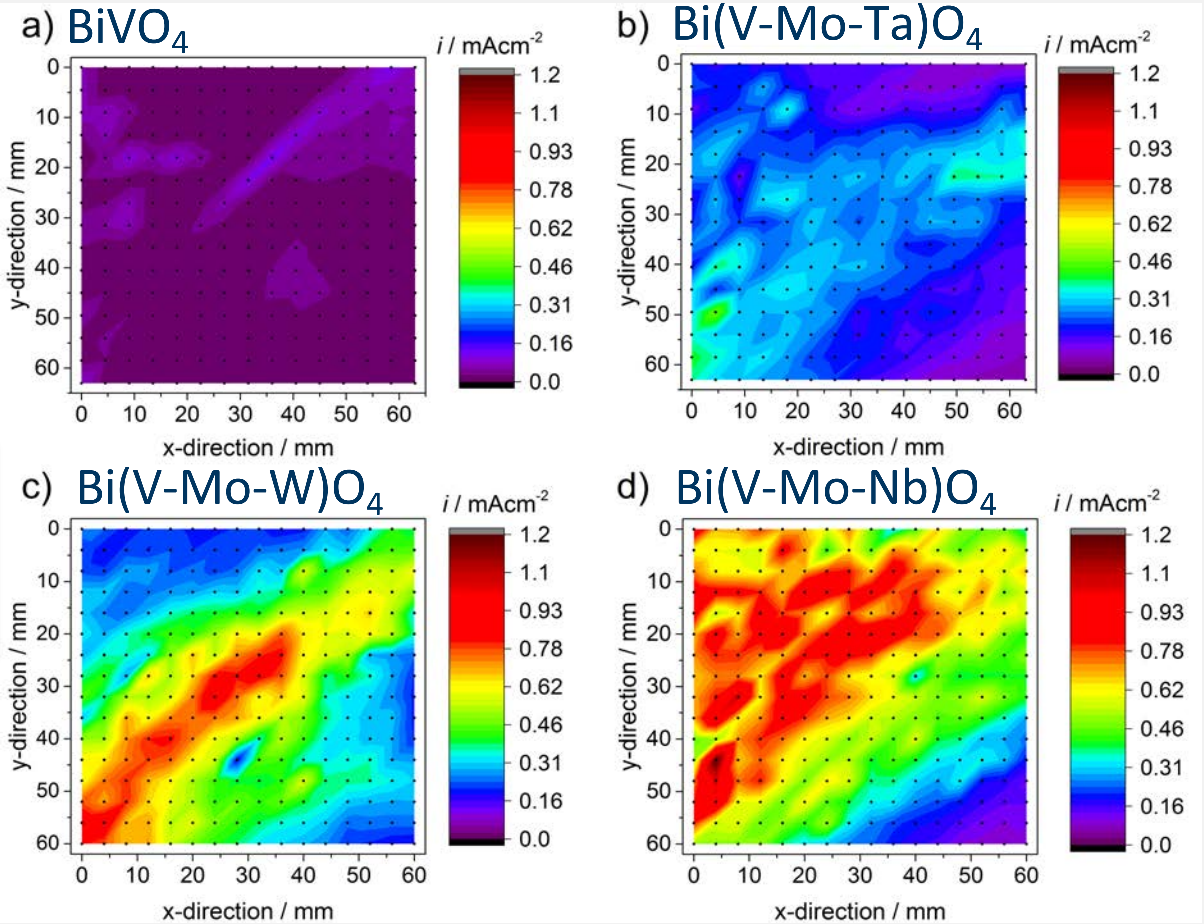
R. Meyer, K. Sliozberg, C. Khare, W. Schuhmann, A. Ludwig **High-Troughput screening of thin film semiconductor materials libraries II: Composition, crystallinity, morphology, thickness and photocurrent density of Fe-W-O libraries,** 2015 ChemSusChem 8, 1279–1285

Compositional effects on solar water splitting in Bi(V-Mo-X)O_4, X: Ta, W, Nb



Photoelectrochemistry

1.23 V vs. RHE (0.1 M borate buffer, pH = 9)

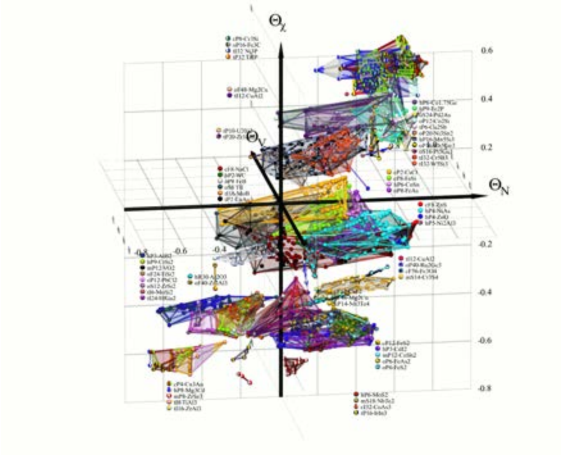


enhanced photocurrents
(up to 10x) compared to $BiVO_4$ in
Bi(VMoW)O_4 and Bi(VMoNb)O_4

R. Gutkowski, C. Khare, F. Conzuelo, Y.U. Kayran, A. Ludwig, W. Schuhmann (2017)
Unraveling compositional effects on the light-induced oxygen evolution in Bi(V-Mo-X)O_4 material libraries, accepted by **Energy & Environmental Science**

Computational Materials Science, Research Data Management and Materials Informatics

Materials discovery in a multidimensional search space: Necessities for data-guided discoveries



Reduction of search-space to feasible size → **ICAMS**

- High-throughput computational screening of search spaces
- Theoretical predictions

Efficient high-quality synthesis of large composition spread libraries

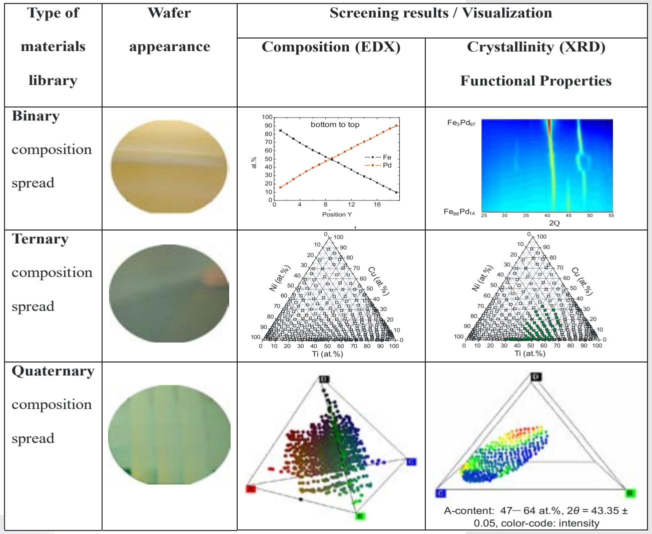
Combinatorial synthesis of thin-film materials libraries → **IW**

High-quality high-throughput characterization tools

Composition, structure, properties

Materials informatics for data-guided experimentation, visualization and analysis

Efficient in-depth characterization of discoveries → **ZGH**



Type of materials library	Wafer appearance	Screening results / Visualization	
		Composition (EDX)	Crystallinity (XRD) Functional Properties
Binary composition spread			
Ternary composition spread			
Quaternary composition spread			A-content: 47— 64 at.%, 2θ = 43.35 ± 0.05, color-code: intensity

Zentrum für
Grenzflächendominierte
Höchstleistungswerkstoffe

Cooperation between computational and experimental high-throughput experimentation

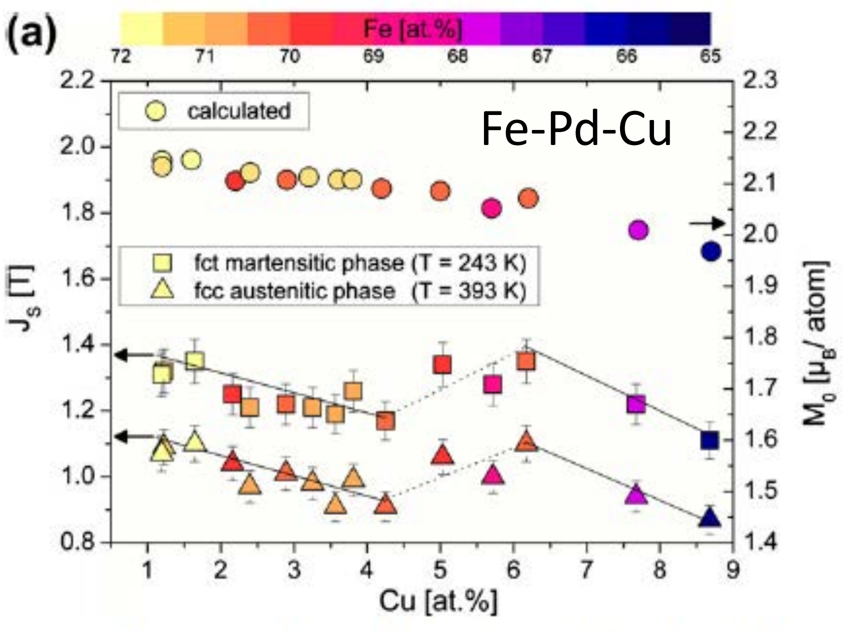
Theory/Simulation/Modelling

Suggestions
Predicitions
Calculate reference data

Experiments

Suggestions

Measure reference data
Validation/Assessment of data



S. Hamann et al. / Acta Materialia 58 (2010) 5949–5961

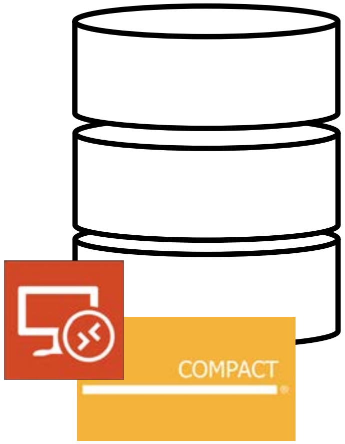
Materials Informatics

Databases
Visualization
Data Mining

Data management in combinatorial and high-throughput experiments

- **Compositional data of multinary systems**
  (materials libraries, typically 342 measurement areas)
  in different processing states (e.g. annealing temperatures)
- **Data from crystallographic phase analysis using XRD**
- **Data on mechanical properties**
  (Young‘s modulus, hardness, stress)
- **Data on functional properties**
  (electrical, magnetic, optical, catalytic, …)
- **Data on multifunctional properties**
  (shape memory effect, magnetic shape memory, …)
- **Processing data**
- **Data on materials behavior in systems**
  (e.g. electrode in thin film battery)

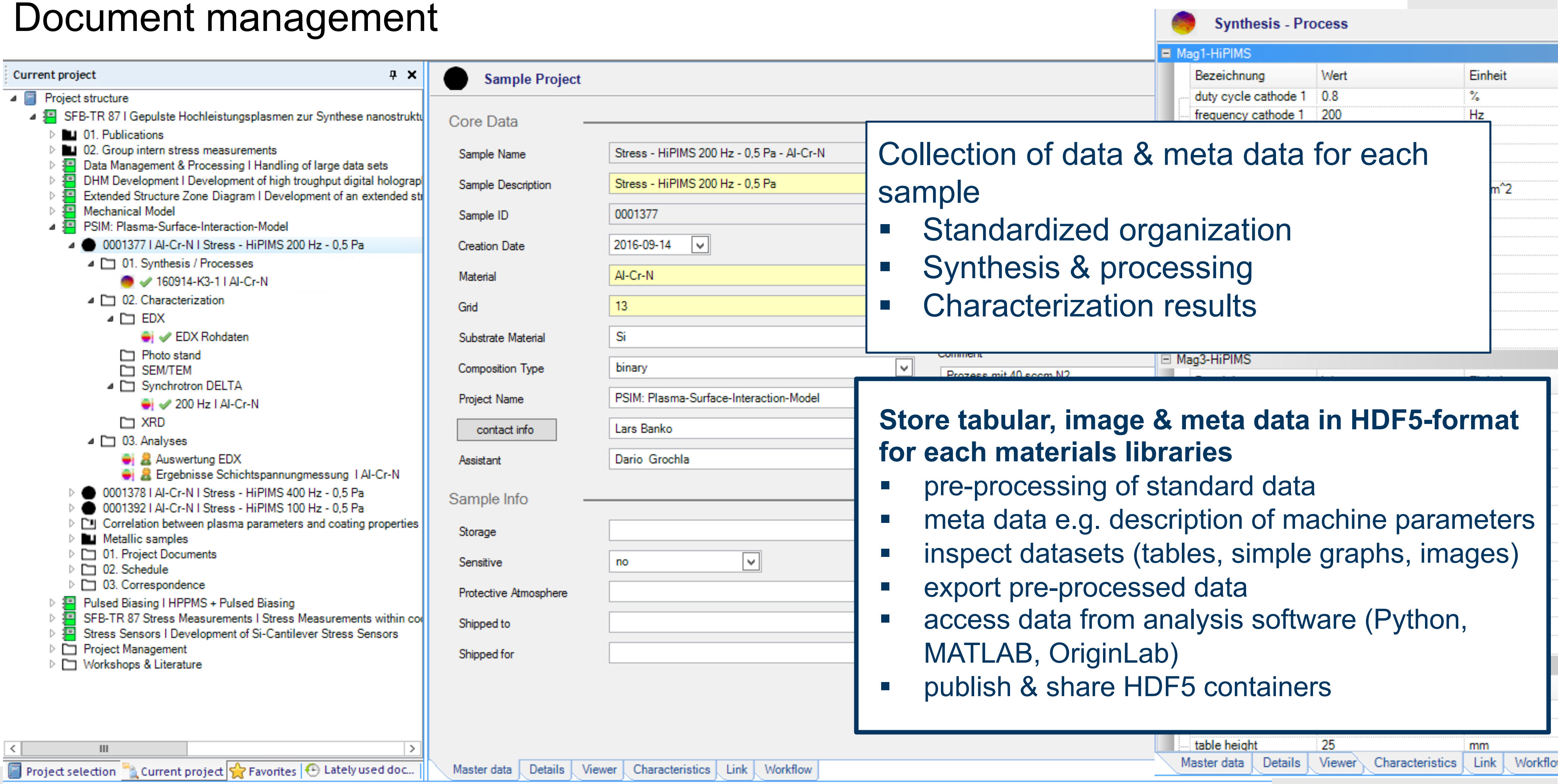
Research data management system



Research data management system

Sample lifecycle management („digital twins“)
Project management
Digital lab-book
Document management

Adapted commercial software
(Compact DMS, ISAP AG, Herne)



Current project

- Project structure
  - SFB-TR 87 I Gepulste Hochleistungsplasmen zur Synthese nanostrukt
    - 01. Publications
    - 02. Group intern stress measurements
    - Data Management & Processing I Handling of large data sets
    - DHM Development I Development of high troughput digital holograp
    - Extended Structure Zone Diagram I Development of an extended st
    - Mechanical Model
    - PSIM: Plasma-Surface-Interaction-Model
      - 0001377 I Al-Cr-N I Stress - HiPIMS 200 Hz - 0,5 Pa
        - 01. Synthesis / Processes
          - ✓ 160914-K3-1 I Al-Cr-N
        - 02. Characterization
          - EDX
            - ✓ EDX Rohdaten
          - Photo stand
          - SEM/TEM
          - Synchrotron DELTA
            - ✓ 200 Hz I Al-Cr-N
          - XRD
        - 03. Analyses
          - Auswertung EDX
          - Ergebnisse Schichtspannungmessung I Al-Cr-N
      - 0001378 I Al-Cr-N I Stress - HiPIMS 400 Hz - 0,5 Pa
      - 0001392 I Al-Cr-N I Stress - HiPIMS 100 Hz - 0,5 Pa
      - Correlation between plasma parameters and coating properties
      - Metallic samples
      - 01. Project Documents
      - 02. Schedule
      - 03. Correspondence
    - Pulsed Biasing I HPPMS + Pulsed Biasing
    - SFB-TR 87 Stress Measurements I Stress Measurements within co
    - Stress Sensors I Development of Si-Cantilever Stress Sensors
    - Project Management
    - Workshops & Literature

Sample Project

Core Data

Sample Name	Stress - HiPIMS 200 Hz - 0,5 Pa - Al-Cr-N
Sample Description	Stress - HiPIMS 200 Hz - 0,5 Pa
Sample ID	0001377
Creation Date	2016-09-14
Material	Al-Cr-N
Grid	13
Substrate Material	Si
Composition Type	binary
Project Name	PSIM: Plasma-Surface-Interaction-Model
contact info	Lars Banko
Assistant	Dario Grochla

Sample Info

Storage	
Sensitive	no
Protective Atmosphere	
Shipped to	
Shipped for	

Synthesis - Process

Mag1-HiPIMS

Bezeichnung	Wert	Einheit
duty cycle cathode 1	0.8	%
frequency cathode 1	200	Hz

Mag3-HiPIMS

Bezeichnung	Wert	Einheit
table height	25	mm

Collection of data & meta data for each sample
- Standardized organization
- Synthesis & processing
- Characterization results

Store tabular, image & meta data in HDF5-format for each materials libraries
- pre-processing of standard data
- meta data e.g. description of machine parameters
- inspect datasets (tables, simple graphs, images)
- export pre-processed data
- access data from analysis software (Python, MATLAB, OriginLab)
- publish & share HDF5 containers

Expediting Combinatorial Dataset Analysis by Combining Human and Algorithmic Analysis

Modular software for expedited analysis of ”combi-datasets”

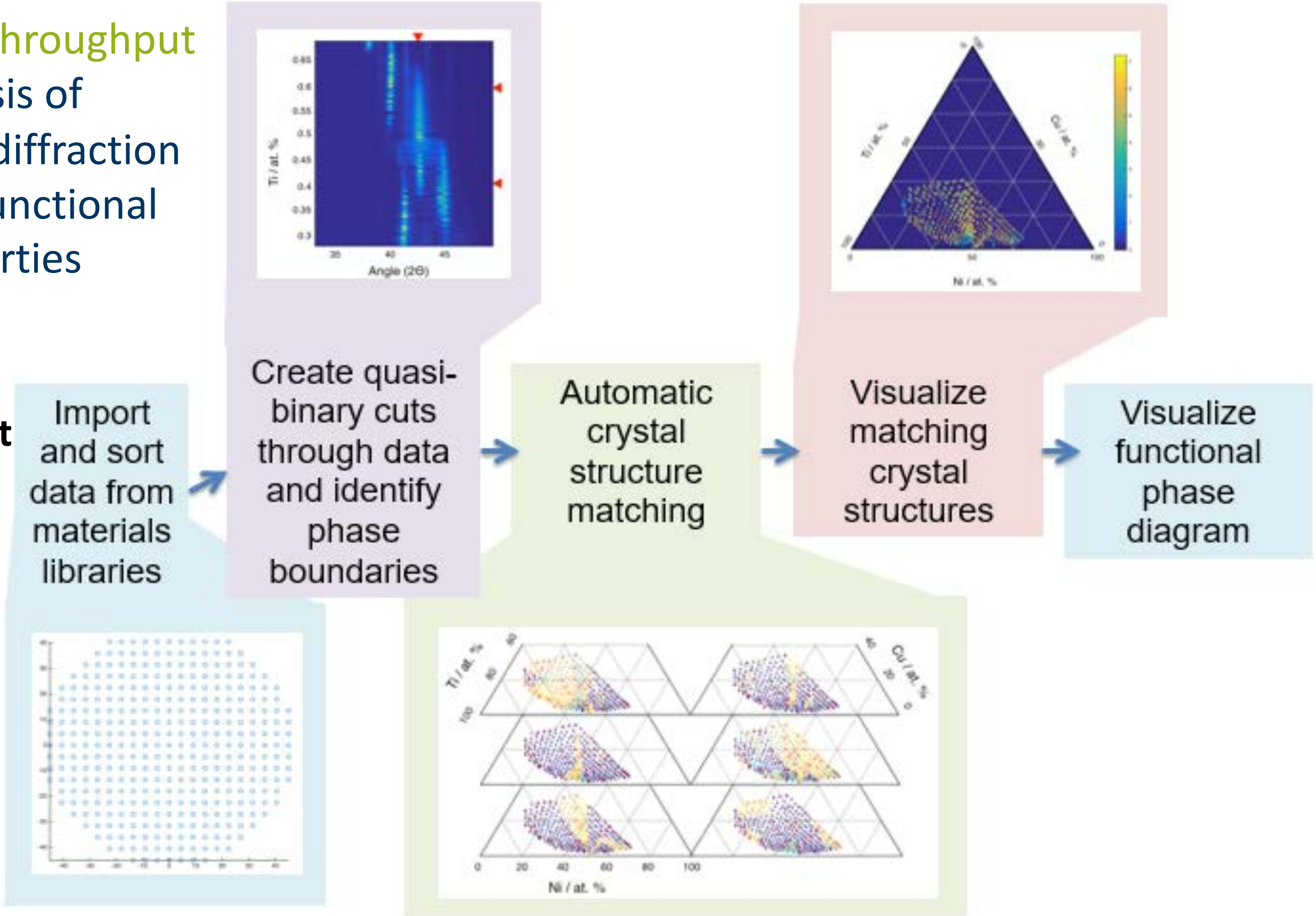
htAx

high-throughput
analysis of
x-ray diffraction
and functional
properties

+ new adapted data management system

Database

COMPACT

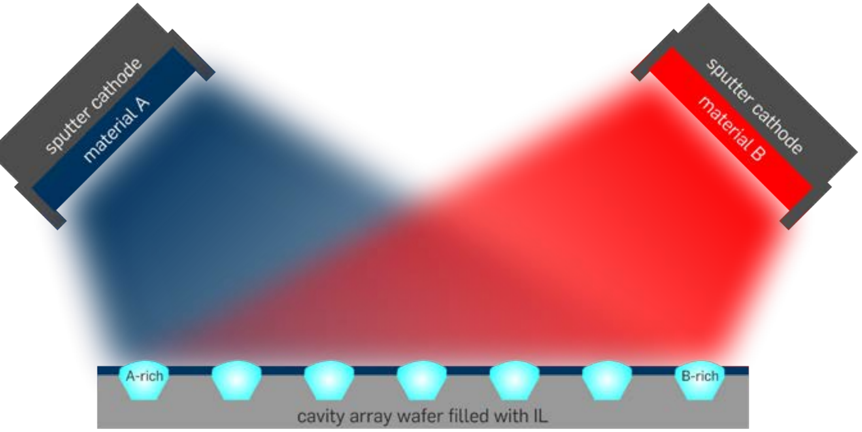


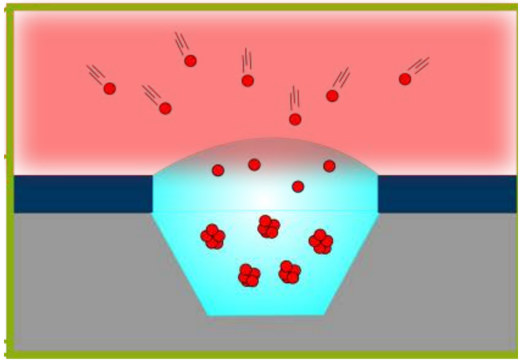
Import and sort data from materials libraries →
Create quasi-binary cuts through data and identify phase boundaries →
Automatic crystal structure matching →
Visualize matching crystal structures →
Visualize functional phase diagram

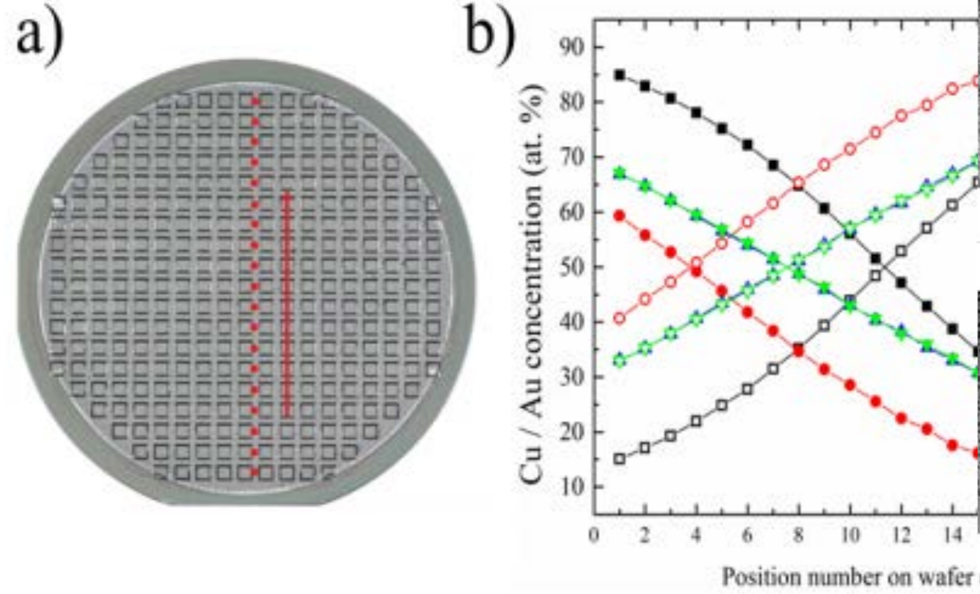
H. S. Stein, S. Jiao, A. Ludwig (2017) ACS Combinatorial Science, 19, 1-8

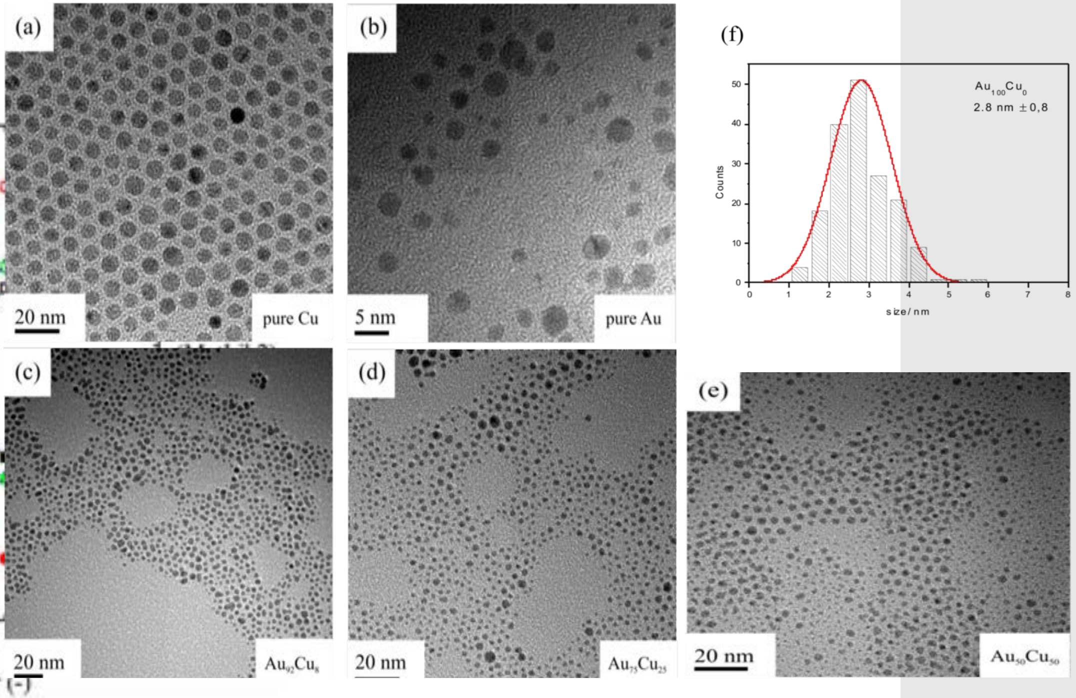
www.github.com/WDM-RUB/htAx

Nanoparticle libraries by combinatorial sputtering in ionic liquids (ILs) : Au-Cu



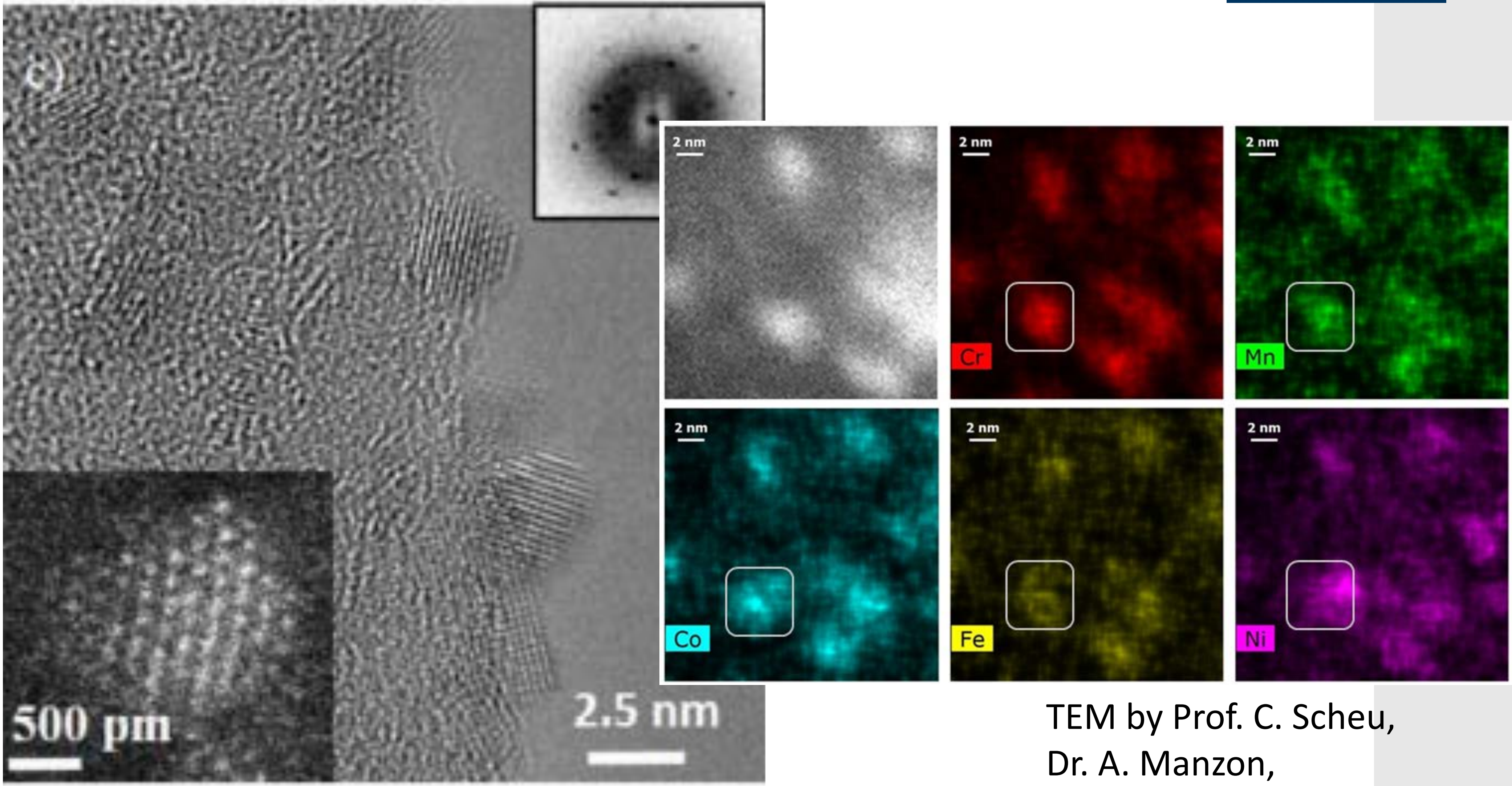






D. König, K. Richter, A. Siegel, A.-V. Mudring, A. Ludwig (2014), High-throughput Fabrication of Au-Cu Nanoparticle Libraries by Combinatorial Sputtering in Ionic Liquids, **Advanced Functional Materials** Vol. 24, Iss. 14, 2049-2056

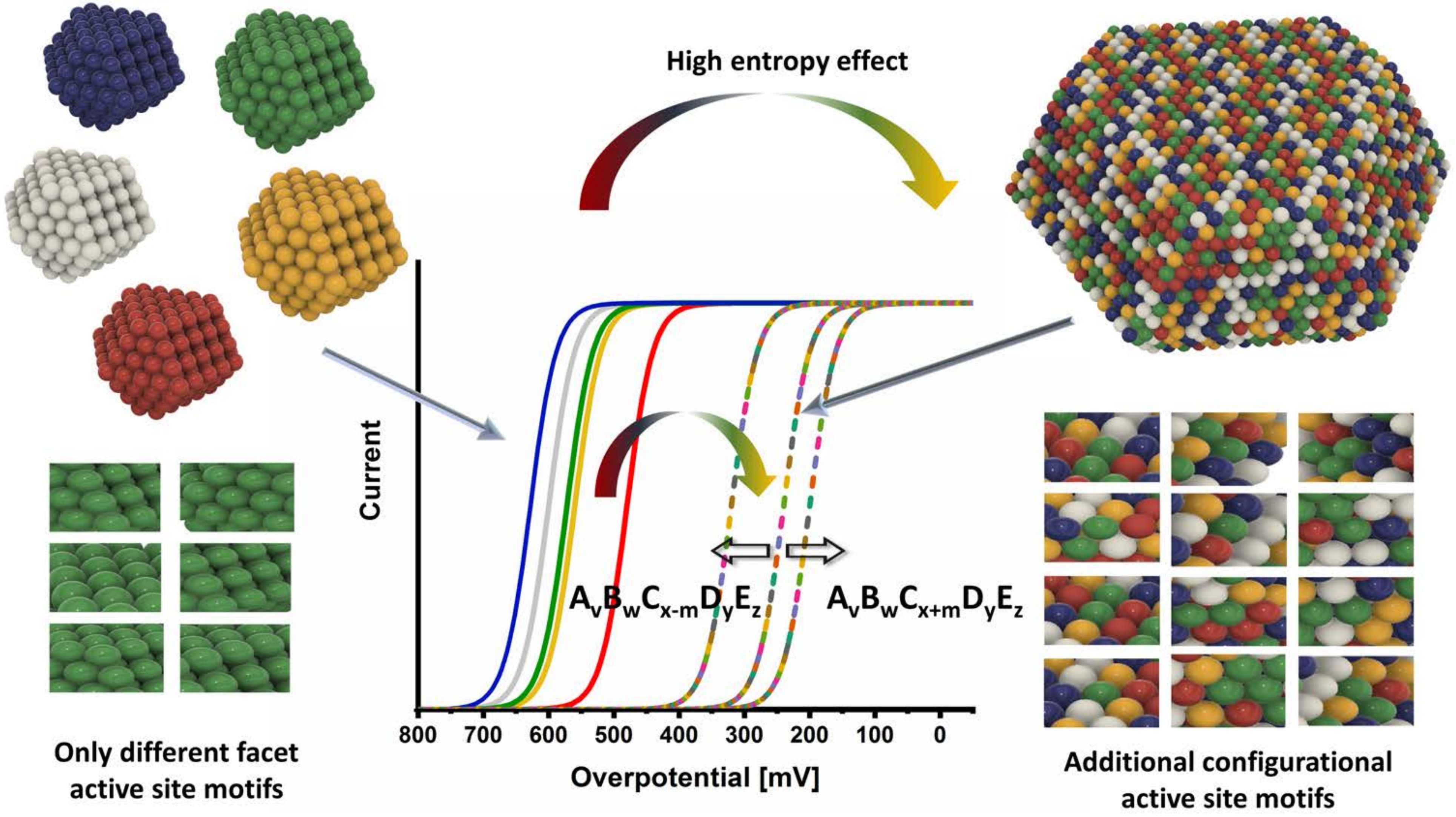
„High entropy“ alloy nanoparticle libraries: Cr-Mn-Fe-Co-Ni



TEM by Prof. C. Scheu,
Dr. A. Manzon,
MPIE Düsseldorf

A. Garzón-Manjón, H. Meyer, D. Grochla, T. Löffler, W. Schuhmann, A. Ludwig, C. Scheu (2018)
Controlling amorphous and crystalline state of multinary alloy nanoparticles in an ionic liquid, Nanomaterials 2018, 8, 903

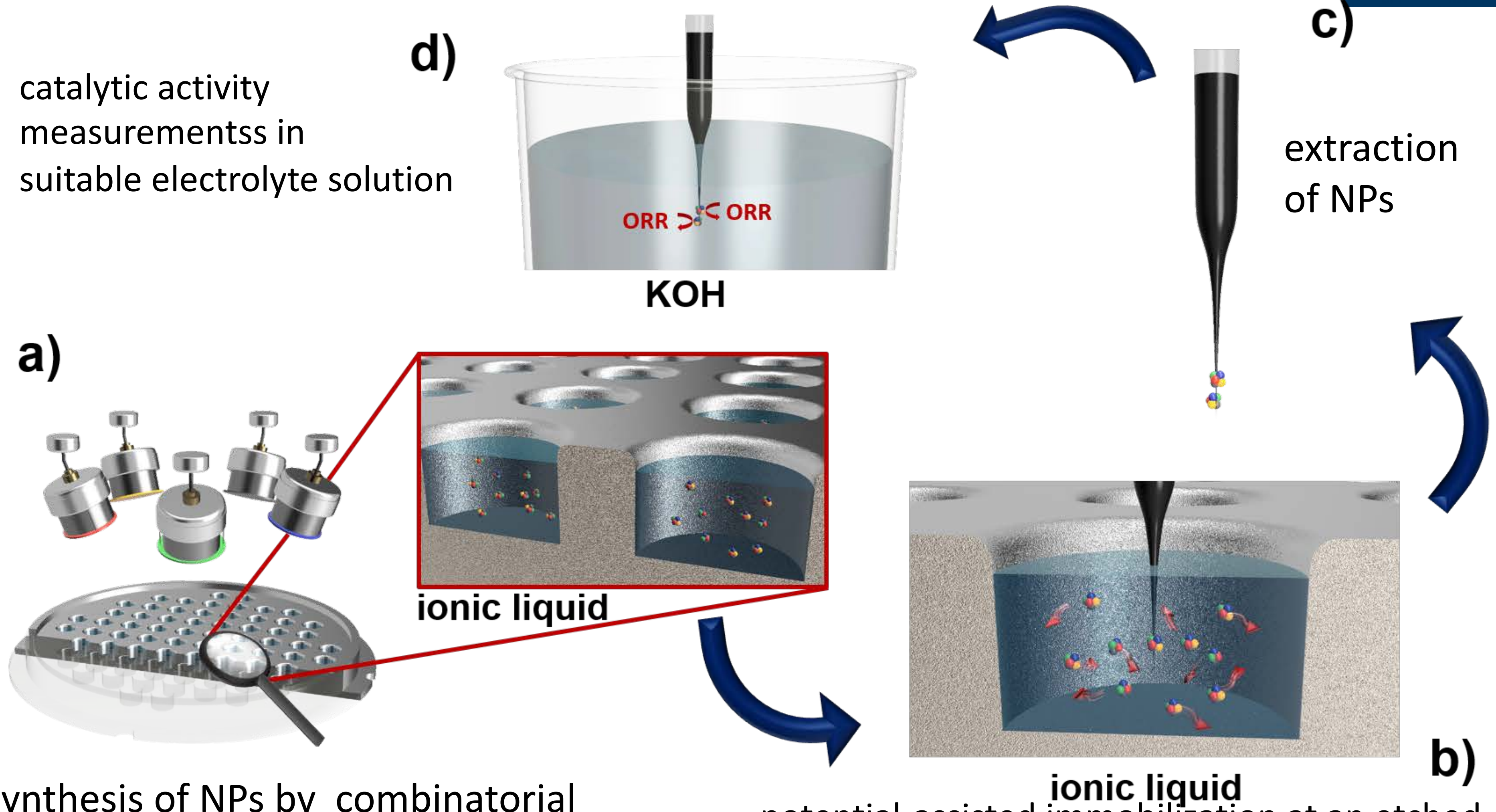
Cr-Mn-Fe-Co-Ni nanoparticle libraries: ORR catalysts



T. Löffler, H. Meyer, A. Savan, P. Wilde, A. Garzón Manjón, Y.-T. Chen, E. Ventosa, C. Scheu, A. Ludwig, W. Schuhmann (2018) Discovery of a Multinary Noble Metal Free Oxygen Reduction Catalyst, Advanced Energy Materials1 802269

Patent application 10 2017 128 058.8

Discovery of a multinary noble metal free oxygen reduction catalyst: Strategy for evaluation of intrinsic activity of multinary alloy NPs



catalytic activity
measurementss in
suitable electrolyte solution

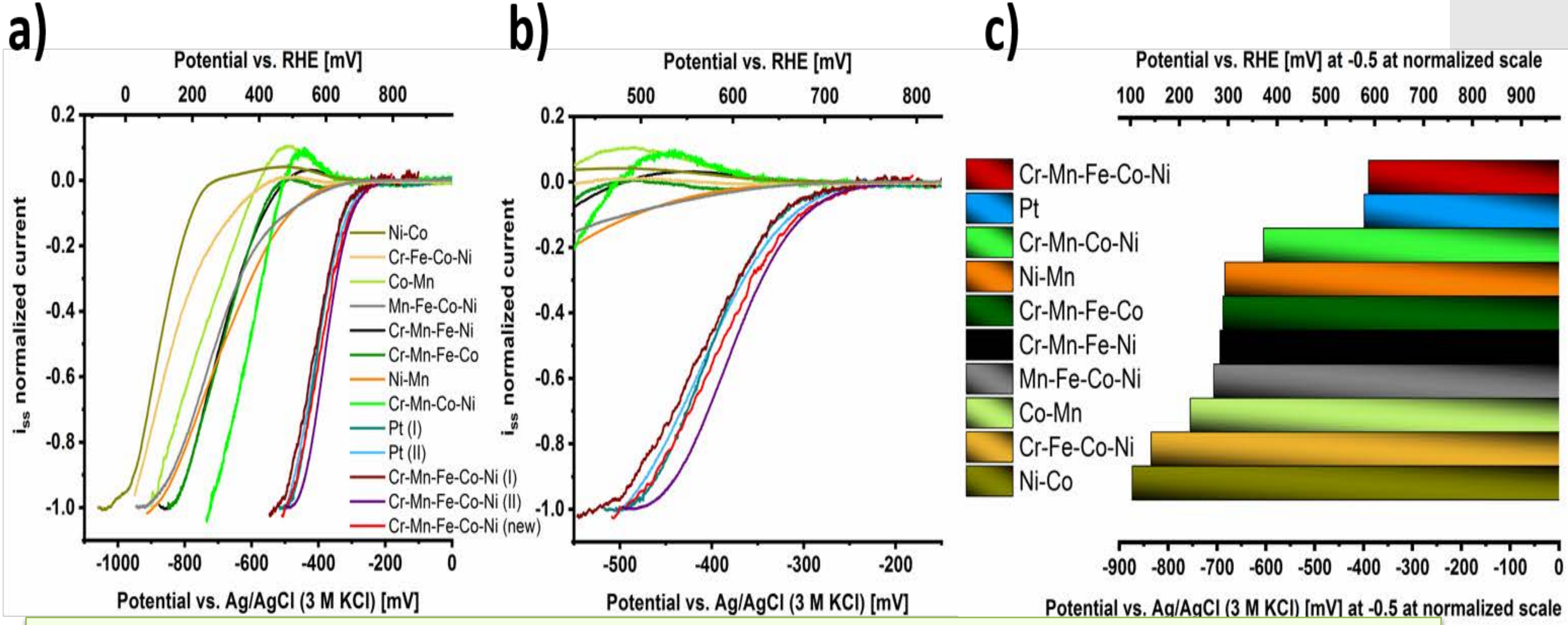
extraction
of NPs

synthesis of NPs by combinatorial
co-sputtering into an ionic liquid
[Bmim][Tf2N]

potential-assisted immobilization at an etched
carbon nanoelectrode utilizing nanoimpacts

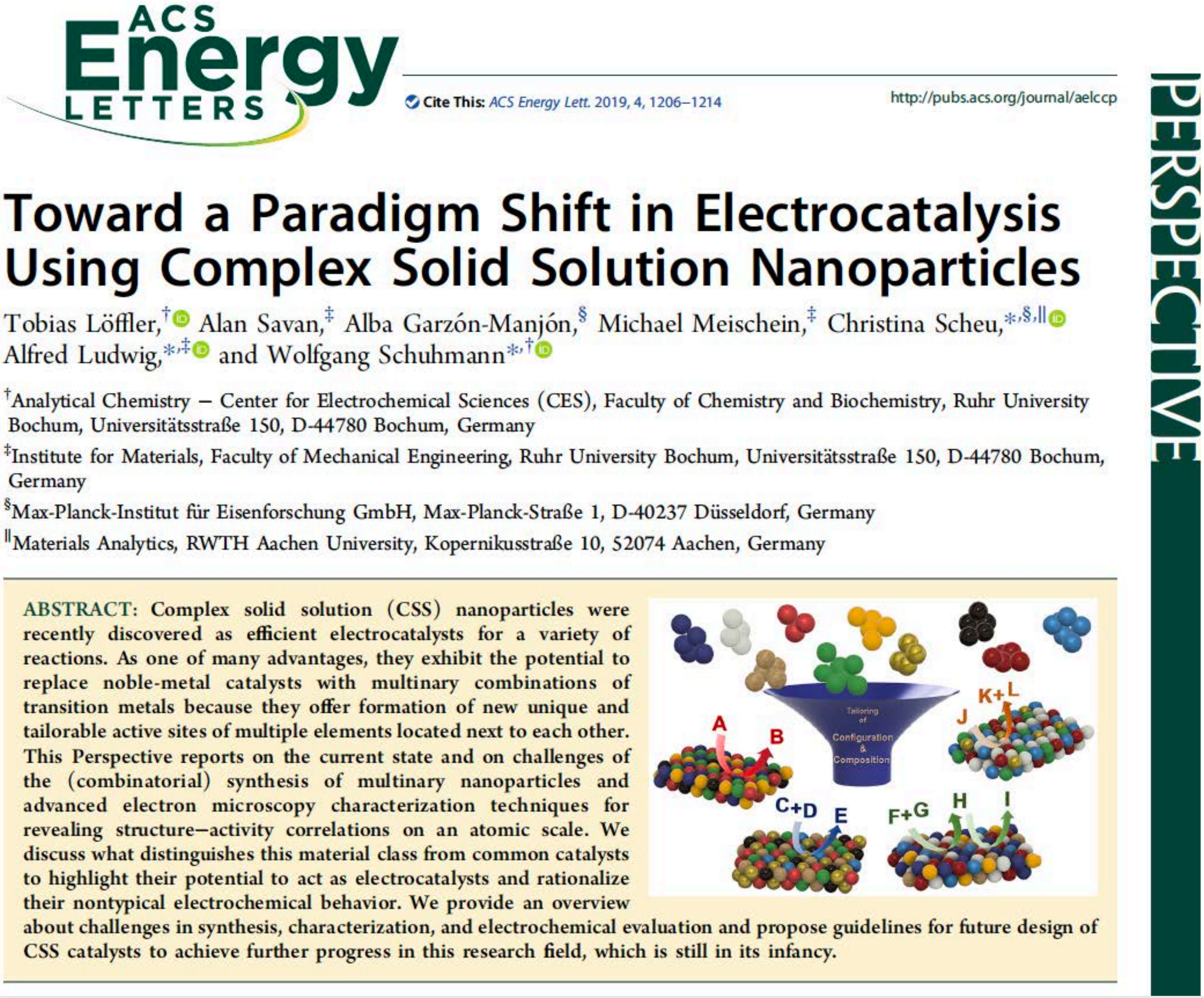
T. Löffler, H. Meyer, A. Savan, P. Wilde, A. Garzón Manjón, Y.-T. Chen, E. Ventosa, C. Scheu, A. Ludwig, W. Schuhmann (2018) Discovery of a Multinary Noble Metal Free Oxygen Reduction Catalyst, Advanced Energy Materials1 802269

„High entropy“ alloy nanoparticle libraries: Cr-Mn-Fe-Co-Ni



Systematic removal of each element from the quinary system yields a significant drop in activity for all quaternary alloys, indicating the **importance of the synergistic combination of all 5 elements**, likely due to formation of a **single solid solution** phase with altered properties which enables overcoming limitations of single elements

T. Löffler, H. Meyer, A. Savan, P. Wilde, A. Garzón Manjón, Y.-T. Chen, E. Ventosa, C. Scheu, A. Ludwig, W. Schuhmann (2018) Discovery of a Multinary Noble Metal Free Oxygen Reduction Catalyst, Advanced Energy Materials1 802269



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http://pubs.acs.org/journal/aelccp

PERSPECTIVE

Toward a Paradigm Shift in Electrocatalysis Using Complex Solid Solution Nanoparticles

Tobias Löffler,[†] Alan Savan,[‡] Alba Garzón-Manjón,[§] Michael Meischein,[‡] Christina Scheu,[*,§,∥] Alfred Ludwig,[*,‡] and Wolfgang Schuhmann[*,†]

[†]Analytical Chemistry − Center for Electrochemical Sciences (CES), Faculty of Chemistry and Biochemistry, Ruhr University Bochum, Universitätsstraße 150, D-44780 Bochum, Germany

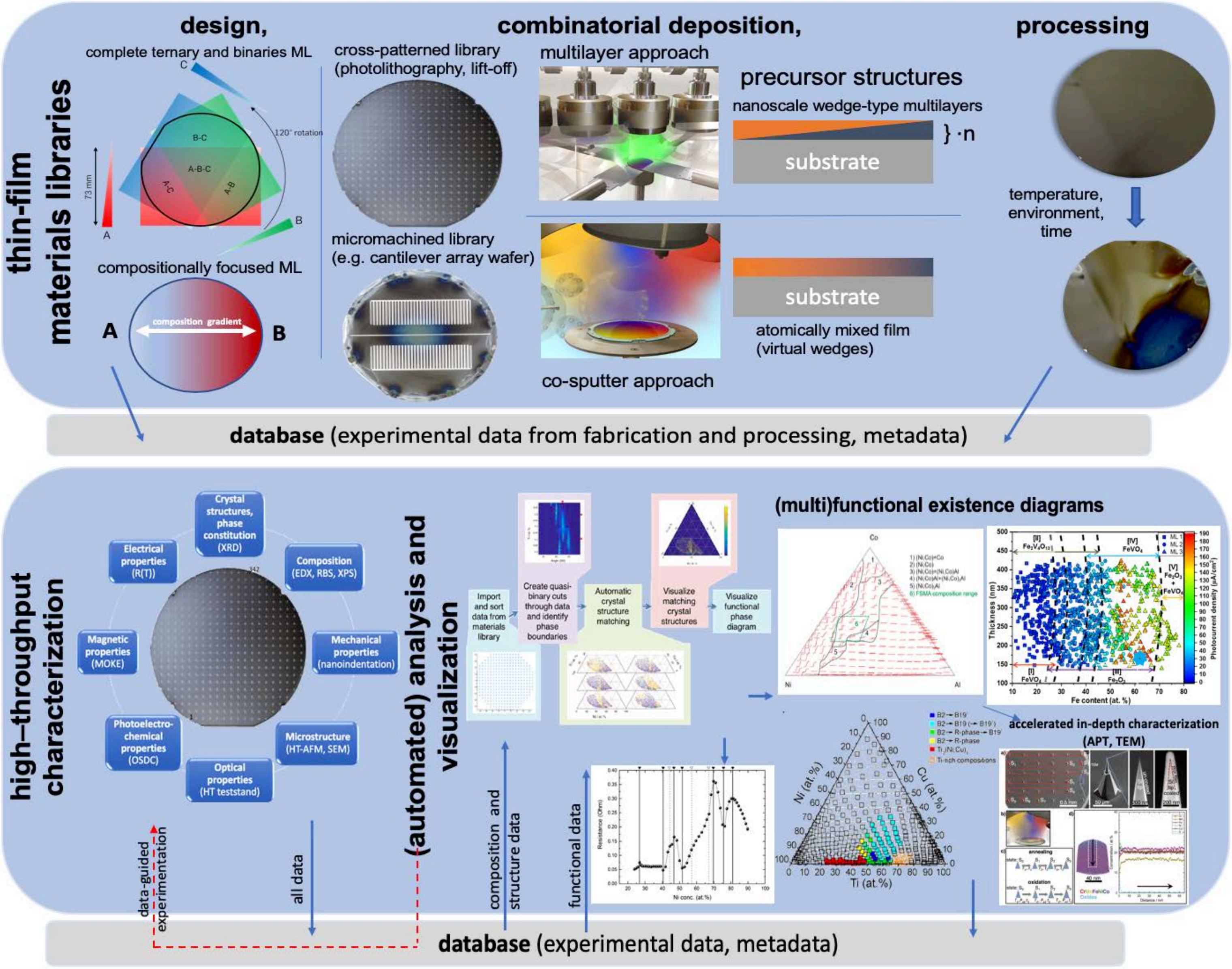
[‡]Institute for Materials, Faculty of Mechanical Engineering, Ruhr University Bochum, Universitätsstraße 150, D-44780 Bochum, Germany

[§]Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, D-40237 Düsseldorf, Germany

[∥]Materials Analytics, RWTH Aachen University, Kopernikusstraße 10, 52074 Aachen, Germany

ABSTRACT: Complex solid solution (CSS) nanoparticles were recently discovered as efficient electrocatalysts for a variety of reactions. As one of many advantages, they exhibit the potential to replace noble-metal catalysts with multinary combinations of transition metals because they offer formation of new unique and tailorable active sites of multiple elements located next to each other. This Perspective reports on the current state and on challenges of the (combinatorial) synthesis of multinary nanoparticles and advanced electron microscopy characterization techniques for revealing structure−activity correlations on an atomic scale. We discuss what distinguishes this material class from common catalysts to highlight their potential to act as electrocatalysts and rationalize their nontypical electrochemical behavior. We provide an overview about challenges in synthesis, characterization, and electrochemical evaluation and propose guidelines for future design of CSS catalysts to achieve further progress in this research field, which is still in its infancy.

Summary and Outlook



Materials discovery and optimization

Consistent and complete multidimensional data-sets on multinary material systems: (multi)functional existence diagrams

Materials data management + informatics

A. Ludwig (2019) *Discovery of new materials using combinatorial synthesis and high-throughput characterization of thin-film materials libraries combined with computational methods*, npj computational materials 5, 70

Review papers on combinatorial and high-throughput methods

H. Koinuma, I. Takeuchi (2004), *Combinatorial solid-state chemistry of inorganic materials*, Nature Materials, 3, 429-438

W. F. Maier, K. Stöwe, S. Sieg (2007), *Combinatorial and High-Throughput Materials Science*, Angew. Chem. Int. Ed., 46, 6016 – 6067

R.A. Potyrailo, V.M. Mirsky (2008), *Combinatorial and High-Throughput Development of Sensing Materials: The first 10 years*, Chem. Rev., 108, 770-813

Eric J. Amis, Xiao-Dong Xiang, Ji-Cheng Zhao (2002), *Combinatorial Materials Science: What's New Since Edison?*, MRS Bulletin, 27(04), 295-300

R.A. Potyrailo, K. Rajan, K. Stöwe, I. Takeuchi, B. Chisholm, H. Lam (2011), *Combinatorial and High-Throughput Screening of Materials Libraries: Review of State of the Art*, ACS Comb. Sci., 13 (6), 579–633

K. Rajan (2008), *Combinatorial Materials Sciences: Experimental Strategies for Accelerated Knowledge Discovery*, Annu. Rev. Mater. Res., 38, 299-322

Martin L. Green, Ichiro Takeuchi, J.R. Hattrick-Simpers, *Applications of high throughput (combinatorial) methodologies to electronic, magnetic, optical, and energy-related materials*, J. Appl. Phys., 113, 231101

Further lectures (Master)

Thin films and high-throughput methods in materials science (winter term)

MEMS and Nanotechnology (summer term)

Questions

(1) What is the aim of combinatorial materials science?

(2) Name and explain the four typical work steps of combinatorial materials science

(3) What is a materials library? Explain the fabrication process.

(4) Explain the high-throughput characterization of materials libraries with respect to chemical composition and phases being present in the library?

(5) Give two examples for functional materials screening parameters.

(6) Which screening method is suitable for the high-throughput characterization of reversible phase transformations?

(7) What is the idea of a composition-processing-structure-property correlation map?

(8) How can nanoparticle libraries be produced?