Sekcja Metod Badań Materiałów Komitetu Nauki o Materiałach PAN
oraz
Instytut Metalurgii i Inżynierii Materiałowej PAN

Wykorzystanie zaawansowanych technik mikroskopii transmisyjnej w badaniach nano-materiałów

Jerzy Morgiel

TEM LAB

Kraków – 29. 02. 2008

TECNAI G2 F20 S-TWIN

HREM

Point res.	0.24 nm
Inf. Limit	0.15 nm

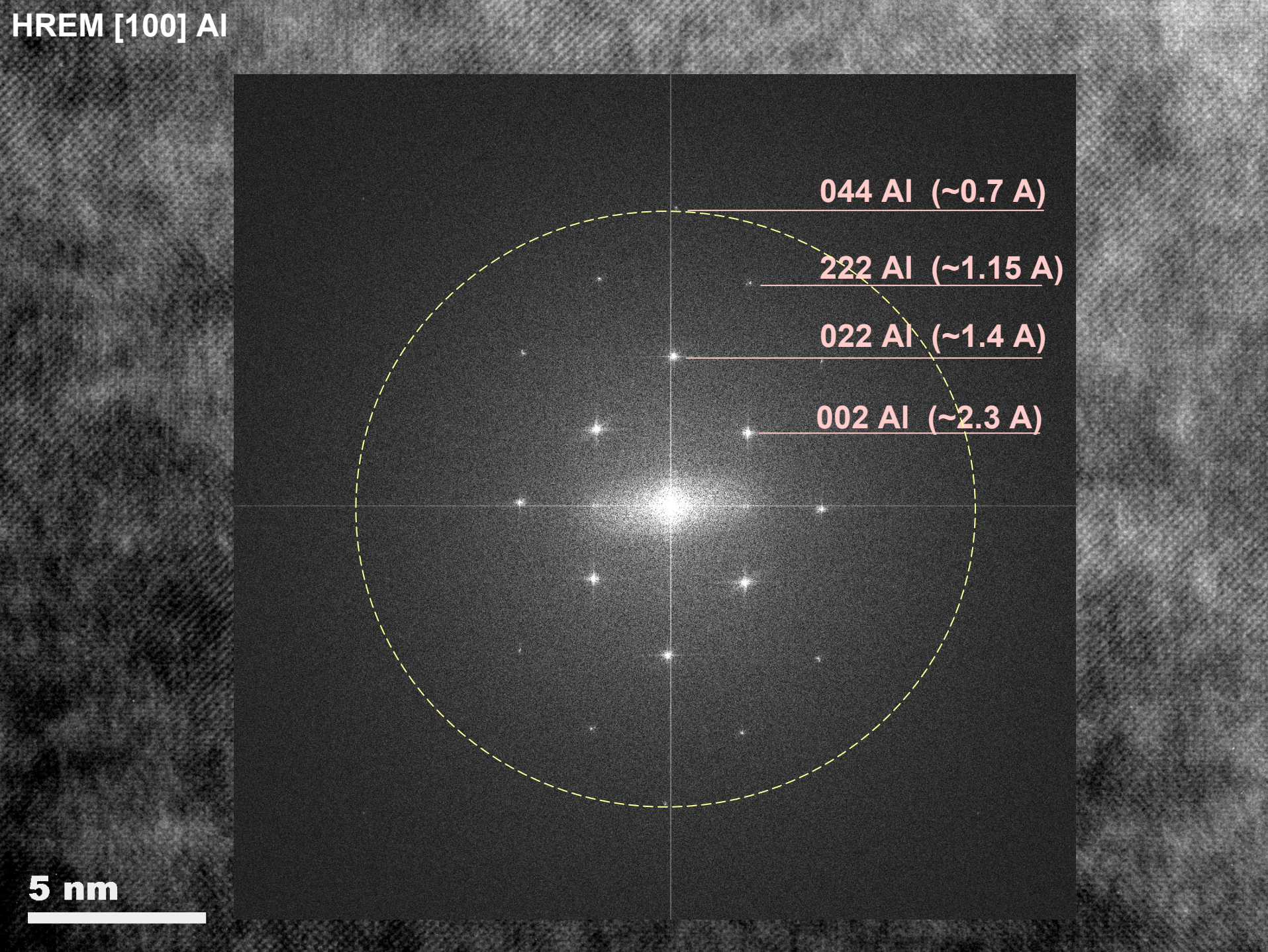
STEM (HAADF)

Point res.	0.2 nm

EDS

Probe	0.3 nm/ 0.5nA
UTW Si(Li+)	133eV

IMIM PAN Kraków - 2005


HREM [100] Al
044 Al (~0.7 A)
222 Al (~1.15 A)
022 Al (~1.4 A)
002 Al (~2.3 A)
5 nm

DigitalMicrograph

File Edit Object Process Analysis Window Camera Microscope MSCcheckout HREM Help

Standard Tools

ROI Tools

Histogram

Image Status

Image Q
Type: Real 4
Size: 360
Pos: 4.733 nm
Value: 1218.27

Target

Page
Q: Image

Control

Line Plot Tools

Masking Tools

Display Control

Acquisition Status

Profile Line Plot

Slice

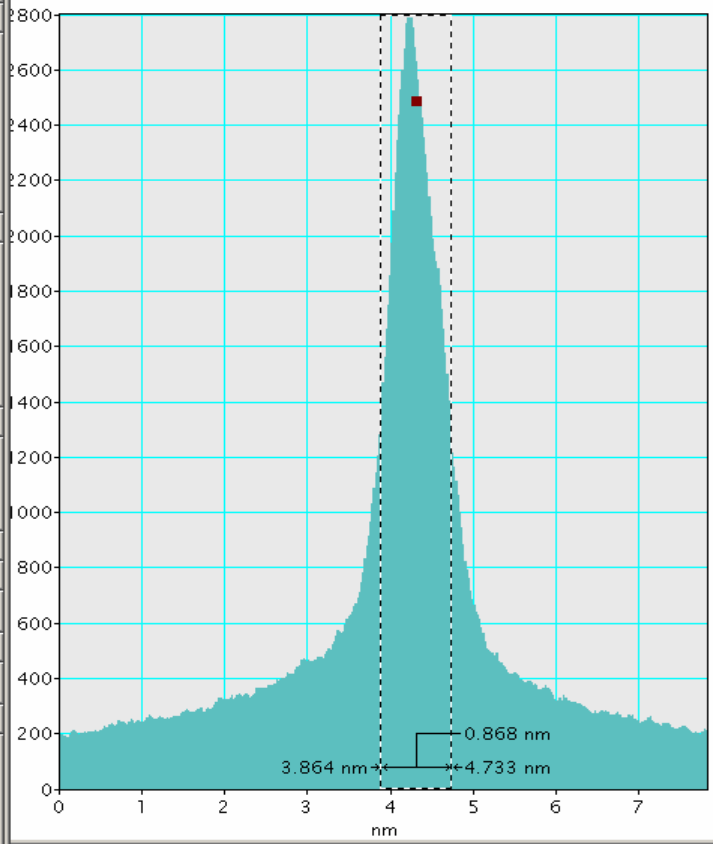
Camera

Progress

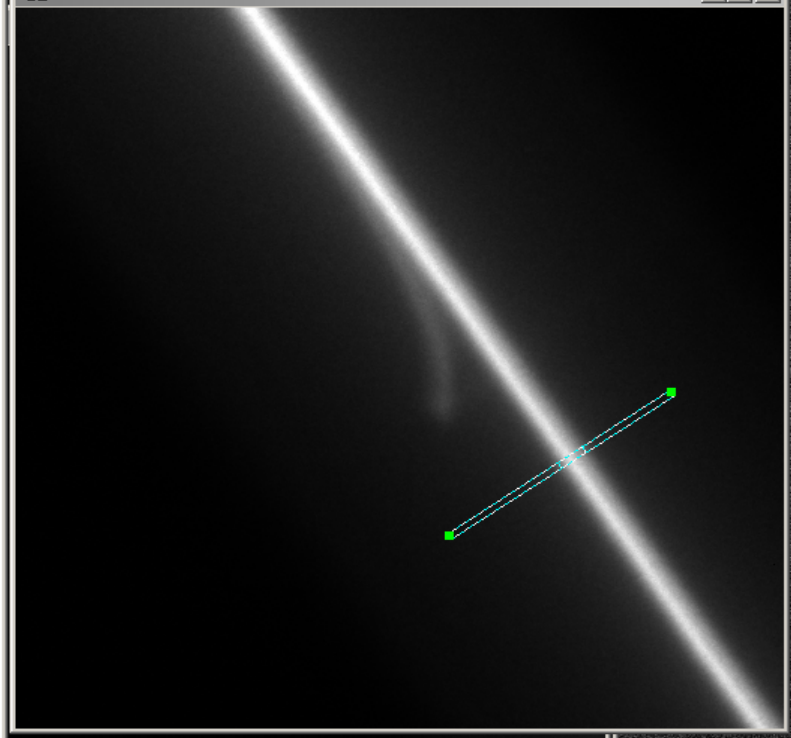
J: FFT infoL3best

N: Frame

Q: Profile Of Frame



P: Frame



Results

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Microscope Control Initialization Succeeded.
Dynamic camera registered.
Welcome to DigitalMicrograph.  9/5/2005, 9:29:08 PM
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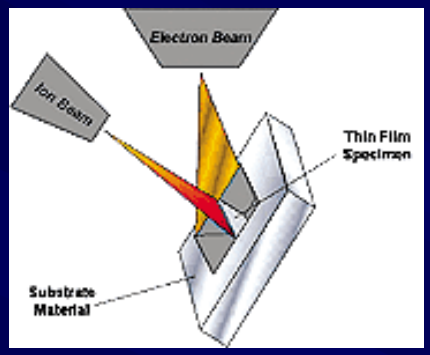
Start | DigitalMi... | FEI Com... | Microsco... | Tecnai Im... | FEI Com... | Acrobat ... | Temspy -... | 9:08 PM



FIB

Dual Beam:

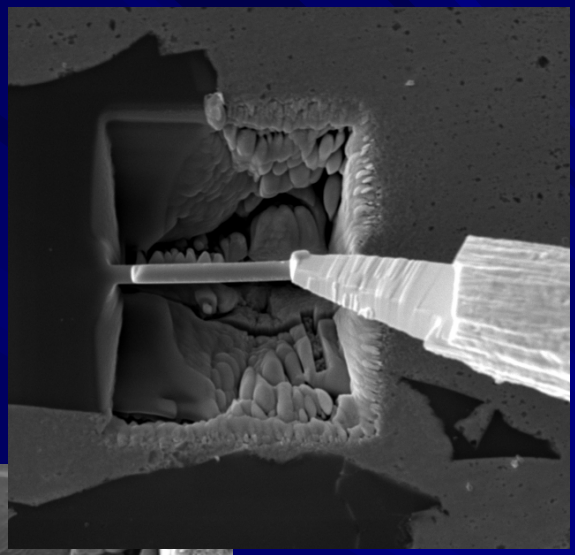
- e^-
- Ga^+

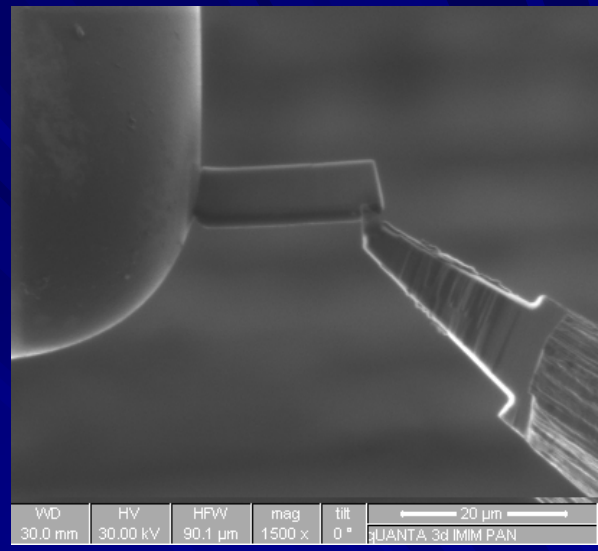
Plus:

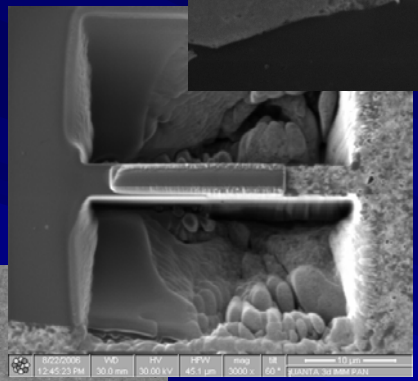
- Pt gun (shadowing)
- W gun
- („welding”)

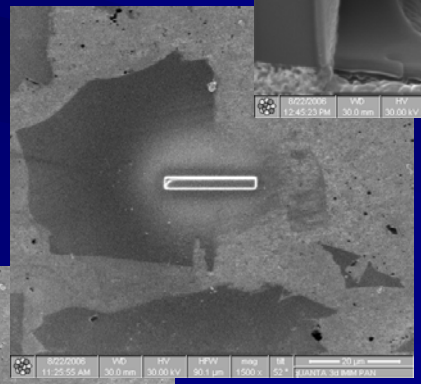
IMIM PAN Kraków - 2005

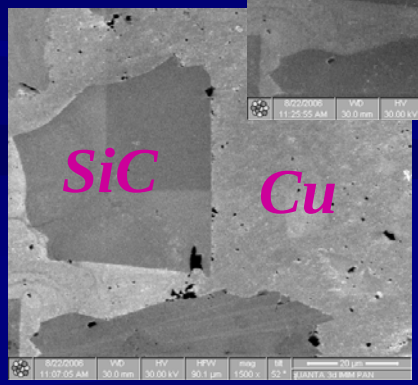
FIB – *in situ* pick up

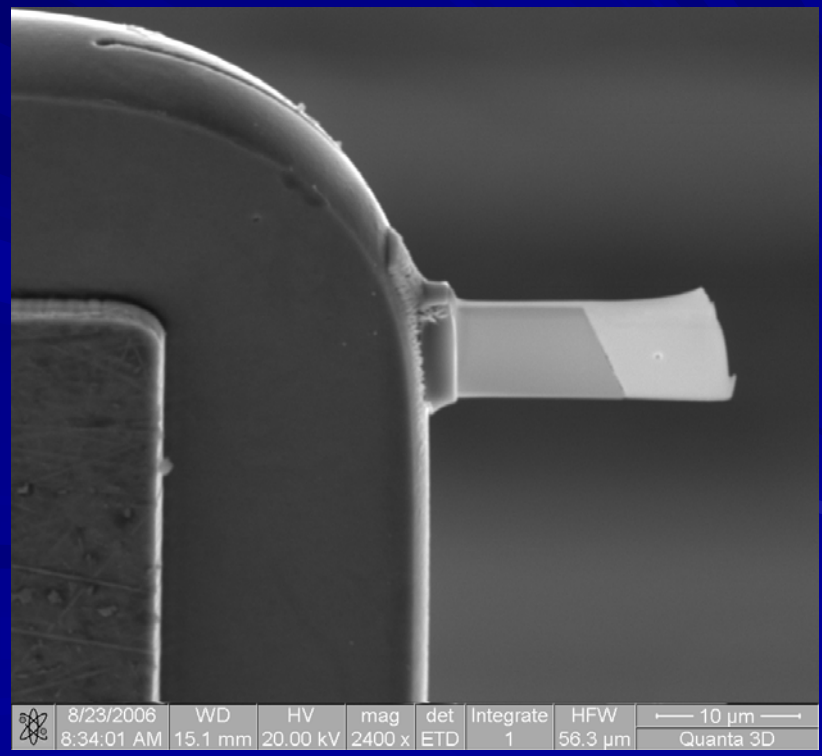












Network of Excellence
Knowledge-based Multicomponent Materials for Durable and Safe Performance

WPI „Intermetalics”
(J. Dutkiewicz)

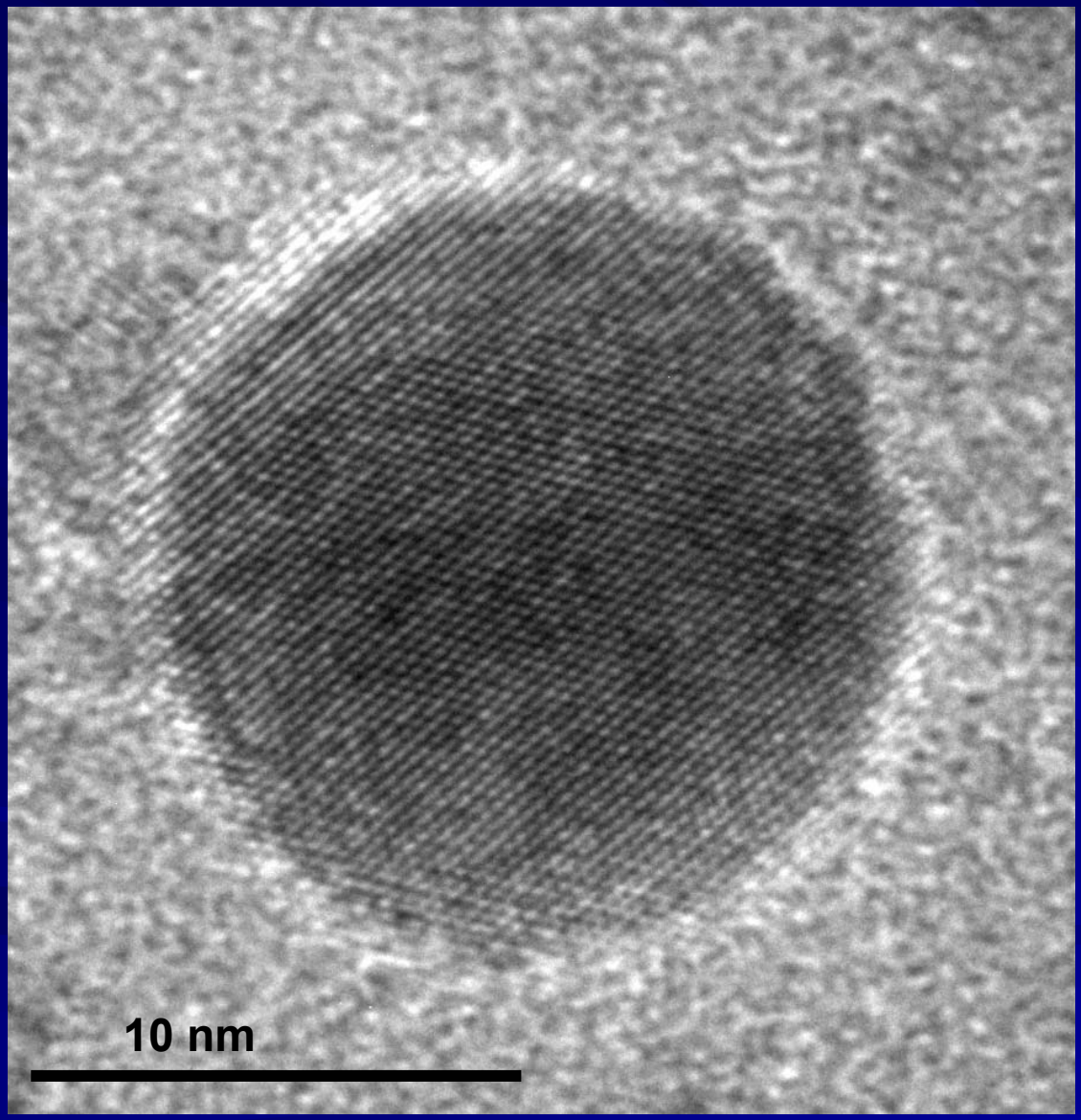
WPII „Composites”
(J. Morgiel)

WPIII „Coatings + FGM”
(B. Major)

Ł. Major, J. Grzonka, M. Pomorska, A.M. Janus, Ł. Rogal

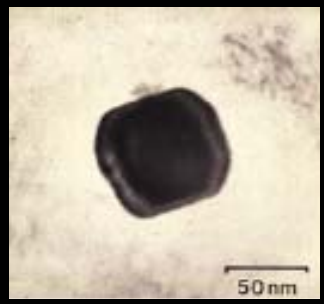
- IPPT - Institute Fundamental Technological Research, Polish Academy of Sciences
- TUD - Technische Universität Darmstadt
- FHG - Fraunhofer-Gesellschaft zur Föerderung der angewandten Forschung e.V.
- TUV - Vienna University of Technology
- ONERA - Office National d'Etudes et de Recherches Aérospatiales
- UM - Université de Metz
- POLIMI - Politecnico di Milano
- UNIPAD - Università degli Studi di Padova
- UWC - University of Wales Cardiff
- IMBAS - Institute of Mechanics, Bulgarian Academy of Sciences
- AGH - AGH University of Science and Technology
- IMIM - Institute of Metallurgy and Materials Science, Polish Academy of Science
- NETCOM - NetComposites
- ITC - Instituto de Tecnología Cerámica - AICE
- IMPER - Imperial College
- UH - University of Hertfordshire
- LMT - Ecole Normale Supérieure de Cachan
- POLITO - Politecnico di Torino
- UNIVPM - Università Politecnica delle Marche
- CIDETEC - Fundacion CIDETEC
- ICASAS - Institute of Construction and Architecture, Slovak Academy of Sciences
- IMRSAS - Institute of Materials Research of Slovak Academy of Sciences
- CUT - Cracow University of Technology
- WUT - Warsaw University of Technology
- IPSUA - Institute for Problems of Strength, National Academy of Sciences
- MCL - Werkstoff-Kompetenzzentrum- (Materials Centre Leoben)
- INASMET - Fundación Inasmet
- MERL - Materials Engineering Research Laboratory Ltd
- ATECA - ATECA
- IFM - Institute for Ferrous Metallurgy
- PZL - Wytwornia Sprzetu Komunikacyjnego 'PZL-Swidnik' S.A.
- EADSG - EADS Deutschland GmbH - Corporate Research Center Germany
- EADSF - EADS CCR
- SNECMA - Snecma Moteurs
- FIAT - Centro Ricerche Fiat S.C.p.A.
- ALENIA - Alenia Aeronautica S.P.A

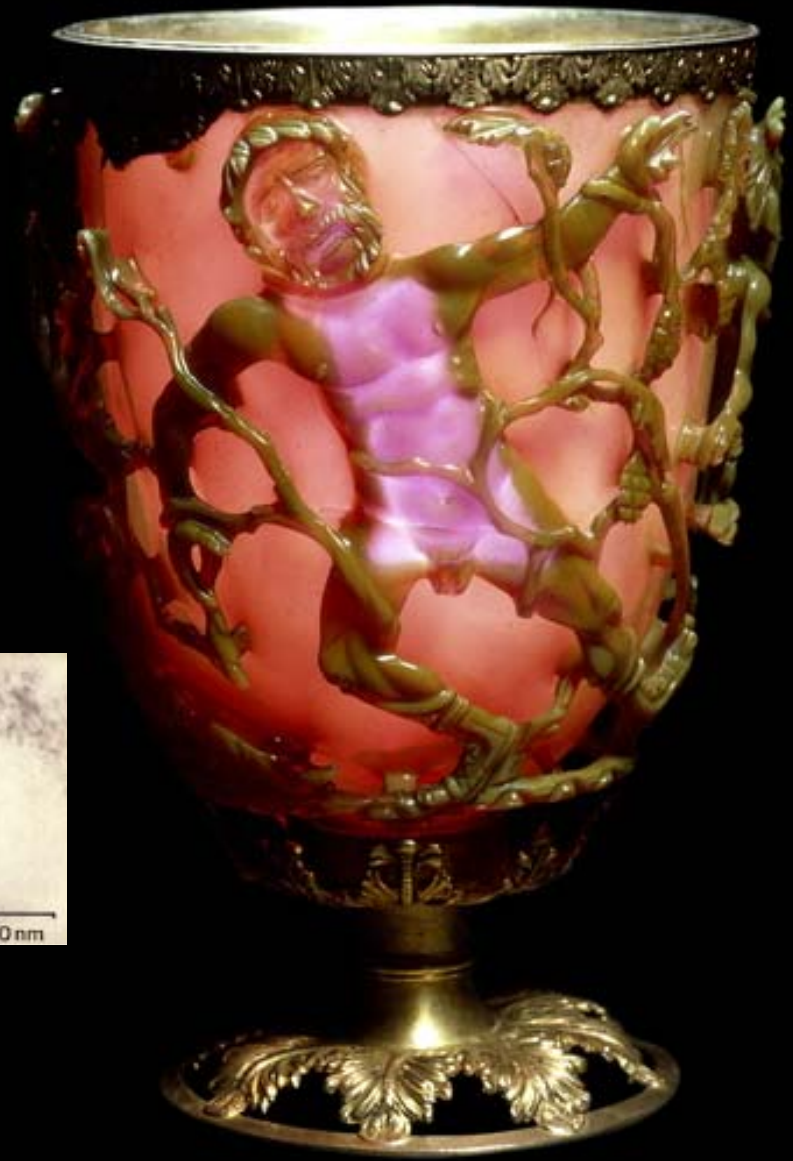
Cz. I. Nanokrystality metaliczne (Au, Ag, Cu) w amorficznej osnowie SiO_2



we współpracy
z zespołem Moniki
Ferraris
z Poitechniki w Turynie
(POLITO)

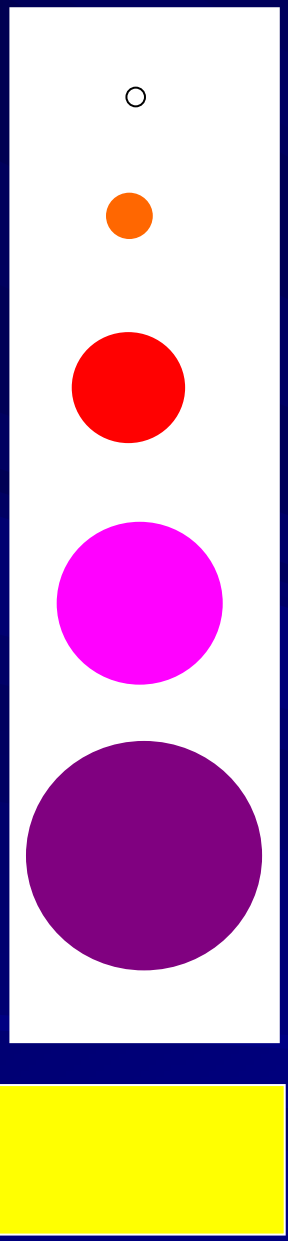
British
Museum
IV th Cent.
A.D.





Lycurgus Cup is the only complete example of a dichroic type of glass, which changes colour when held up to the light. The opaque green cup turns to a glowing translucent red when light is shone through it. The glass contains tiny amounts of colloidal gold and silver

Paul Mulvaney, MRS Bulletin, Dec. 2001, p.1009



Au Atom: ~0,1 nm (1A), colorless

Au clasters: < 1nm, nonmetalic, orange

Au nanocrystallites: 3 - 30 nm, metalic, transparent / red

Au particles: 30 - 500 nm, metalic, transparent / turbid

crimson -> blue

M. Faraday, Philos. Trans. R. Soc. London, 147 (1857) 145-181

Gold leaf can be beaten to thicknesses of 1/278000 of an inch (around 90 nm). Such films are continuous and green in transmission. Further thinning with KCN gives ruby red films.

Chemical means to finely divided gold. Also deflagration of gold wires to produce ruby red particles. Chemically indistinguishable from gold.

Au bulk: golden color!

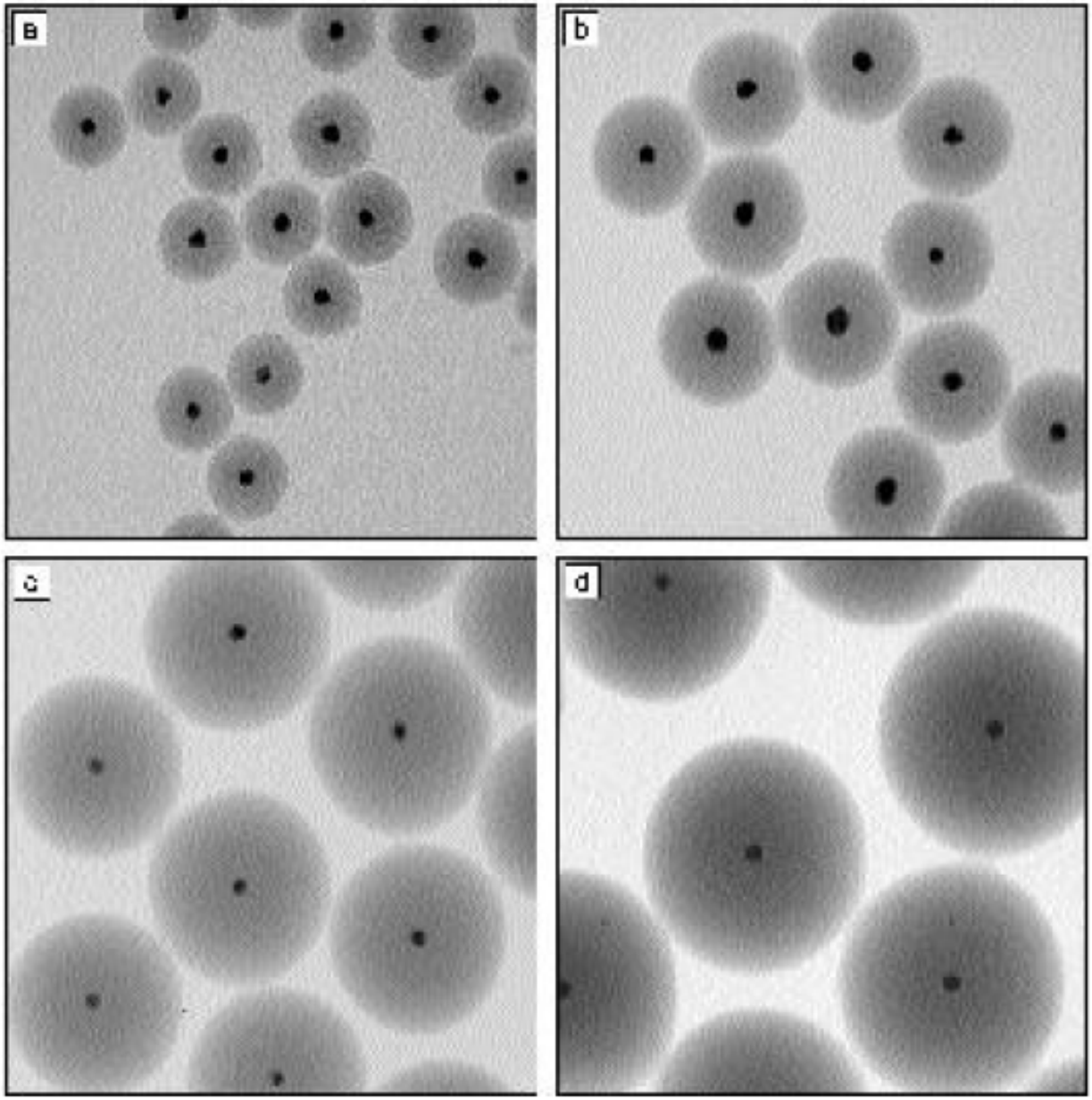
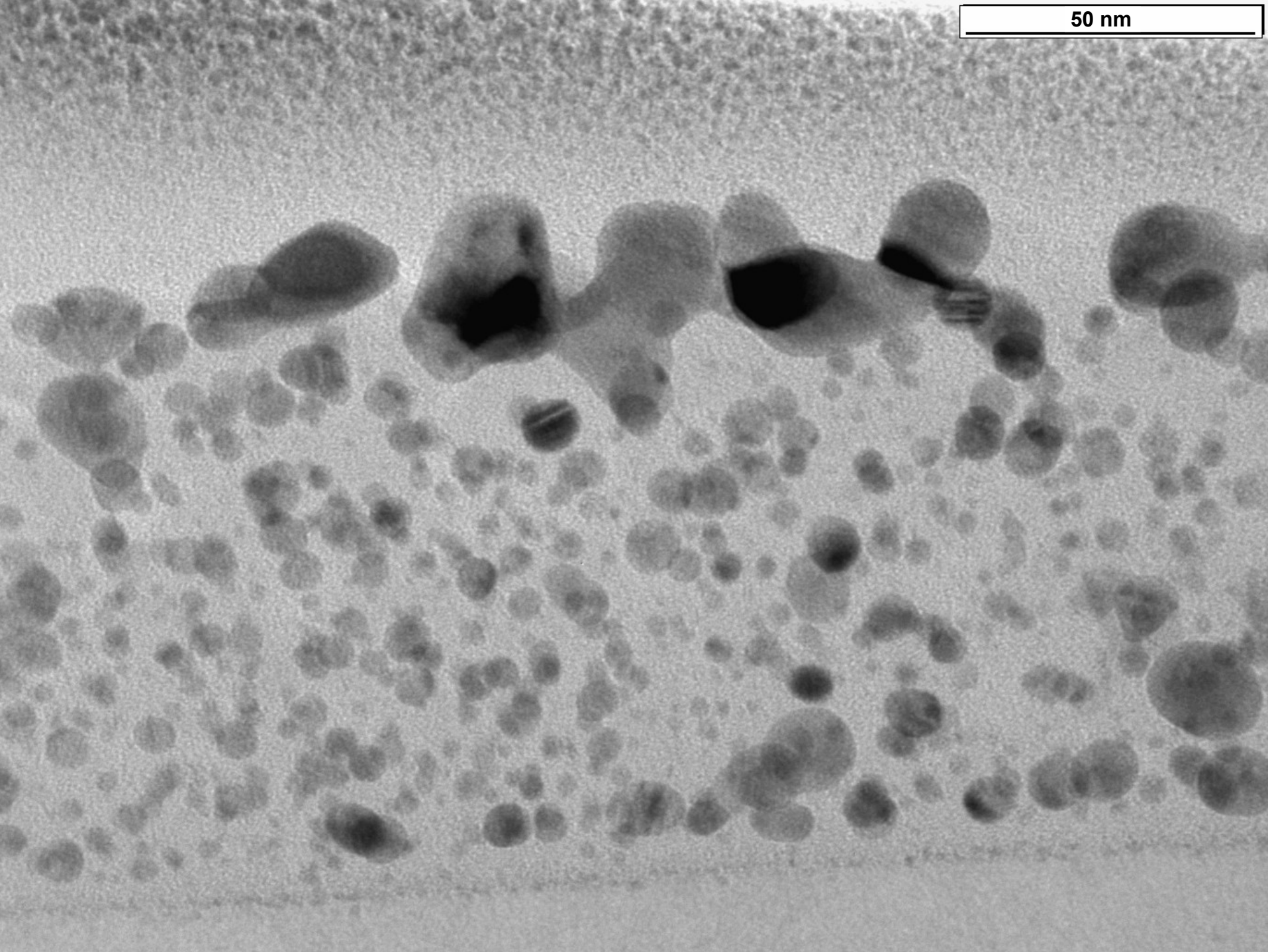
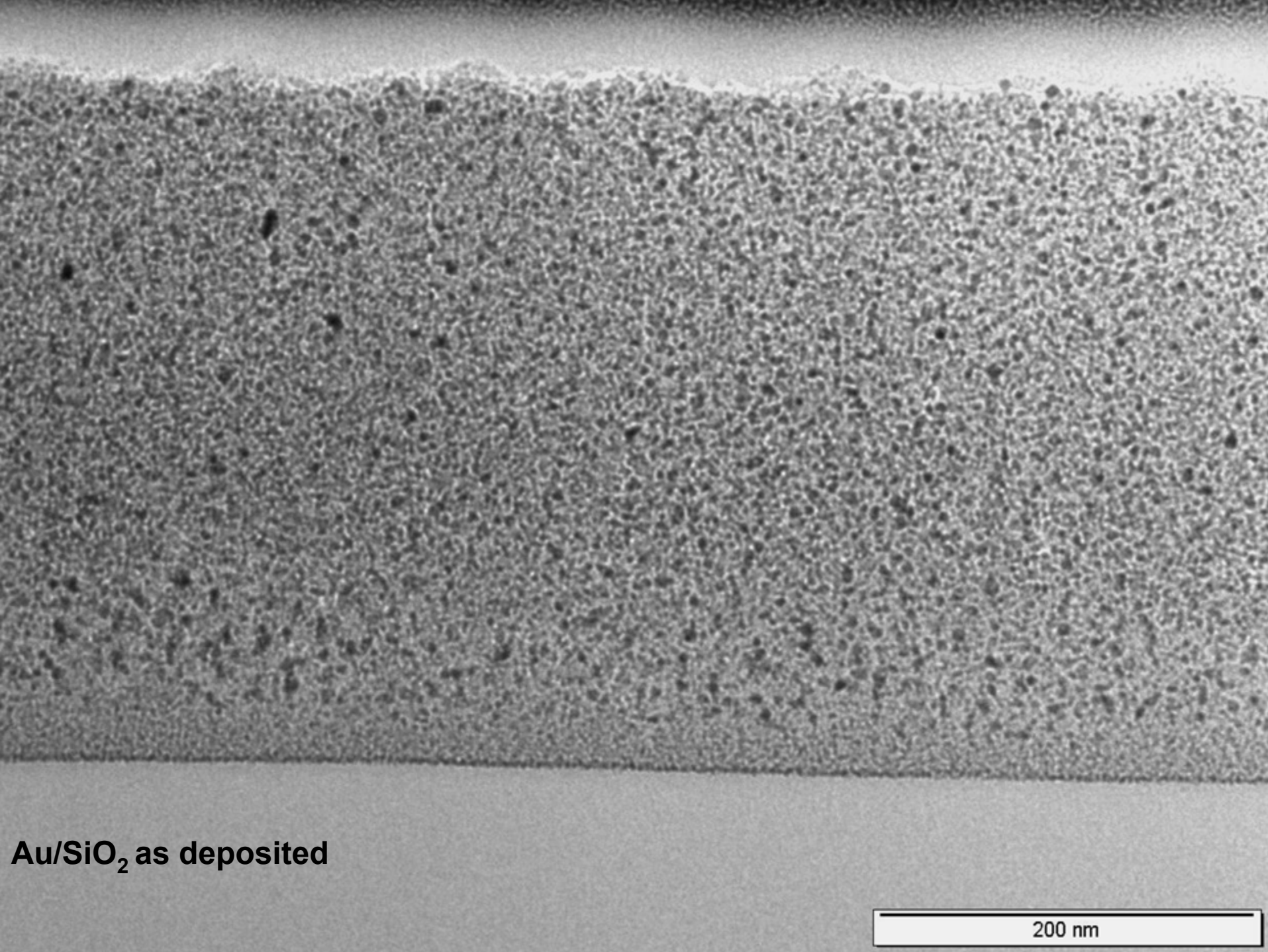


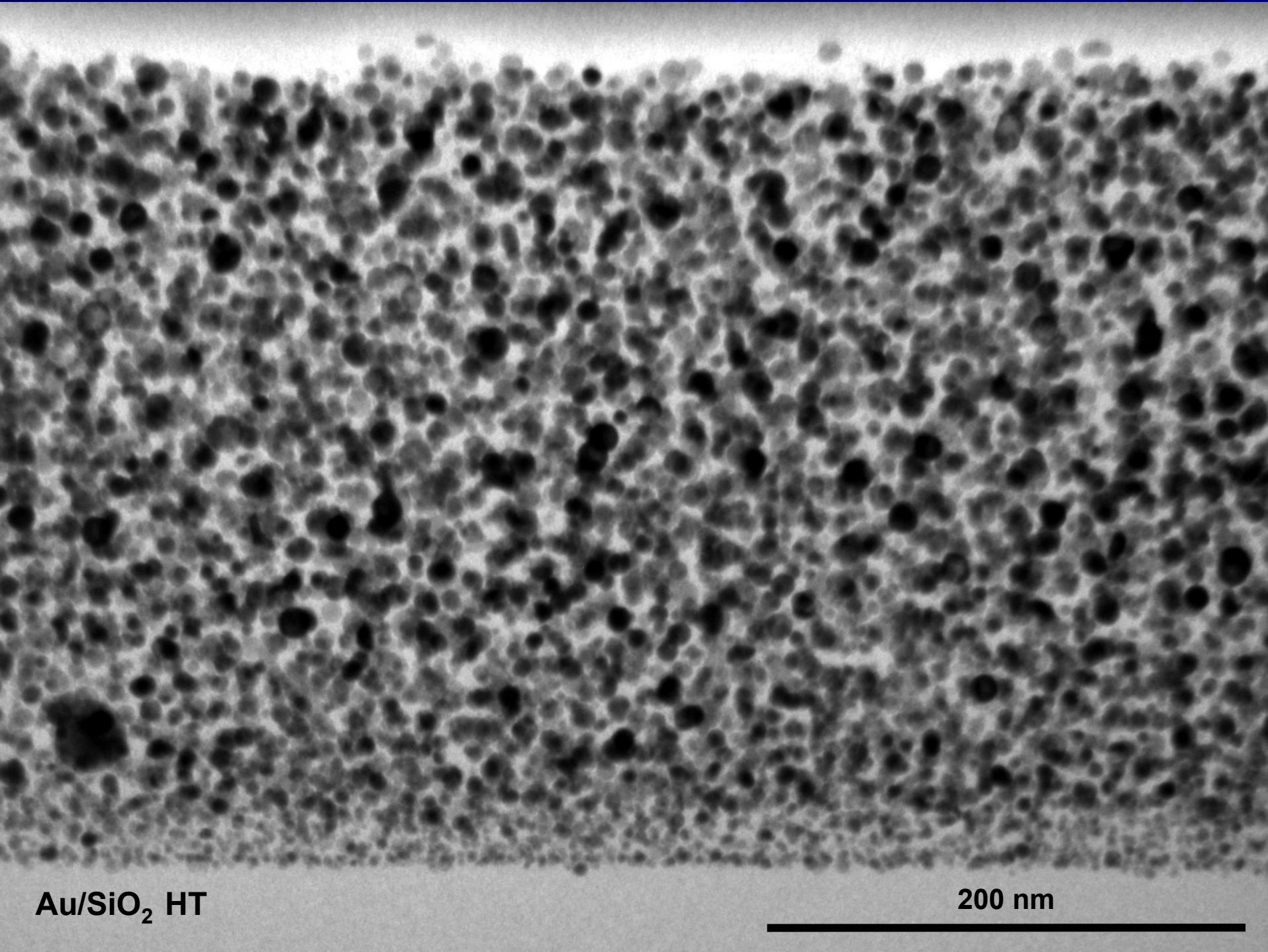
Figure4.(a)–(d) Electron micrographs of silica-coated 15-nm gold particles with various shell thicknesses.

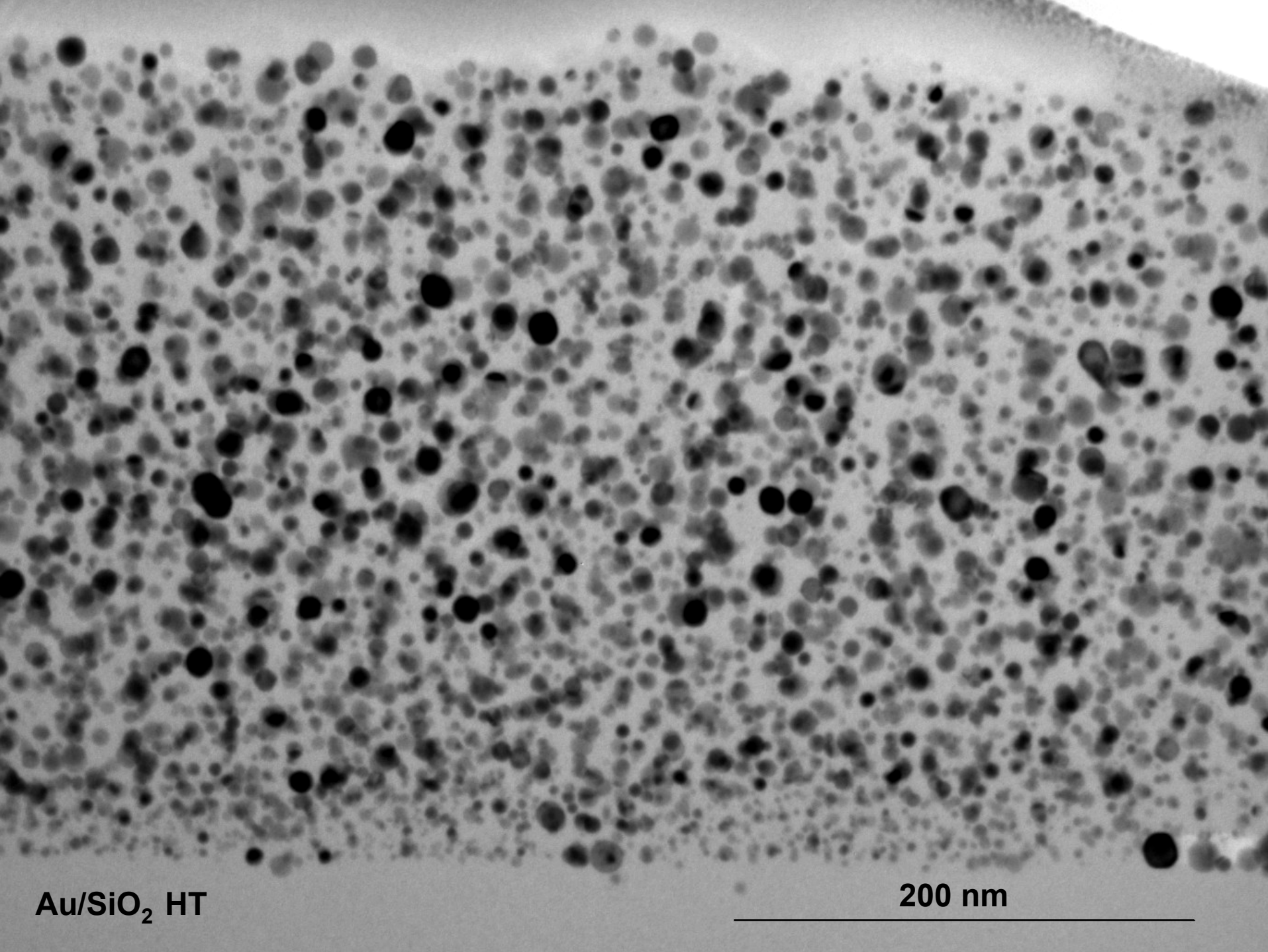
Paul Mulvaney, MRS Bulletin, Dec. 2001, p.1009

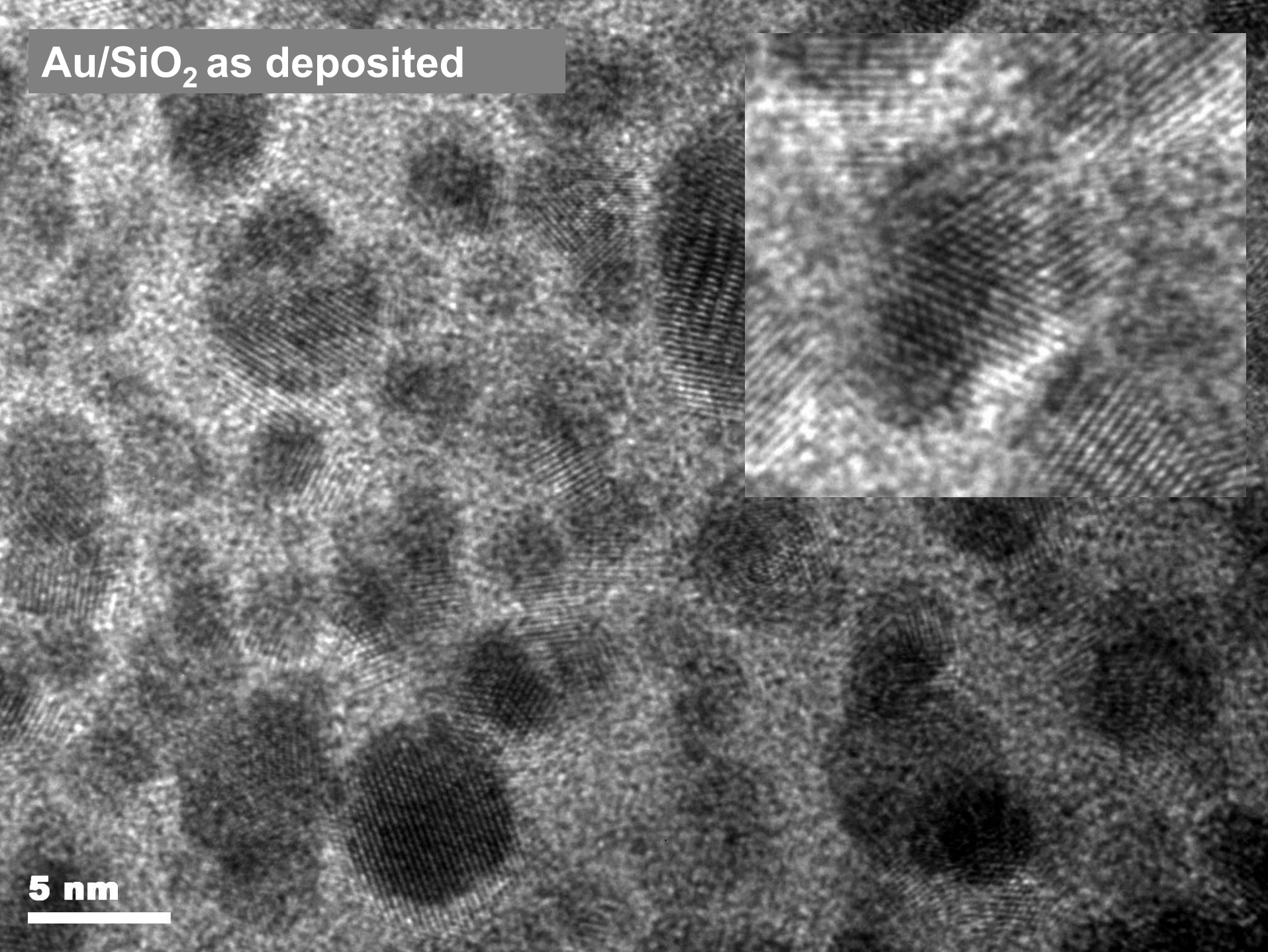
in the limit of very small spacings and a gold volume fraction 50%, the film spectrum is almost identical to that of the bulk gold thin film

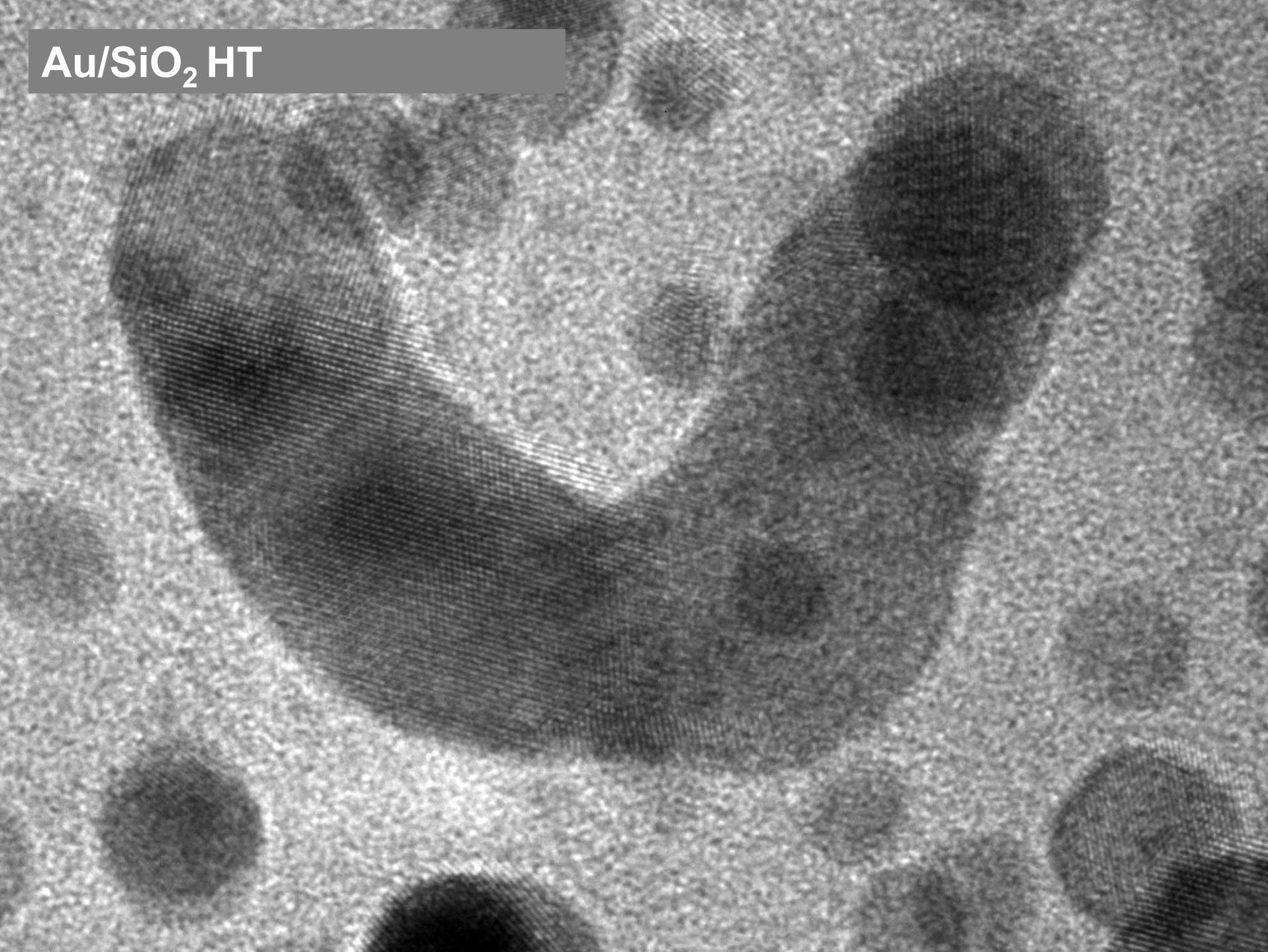

50 nm

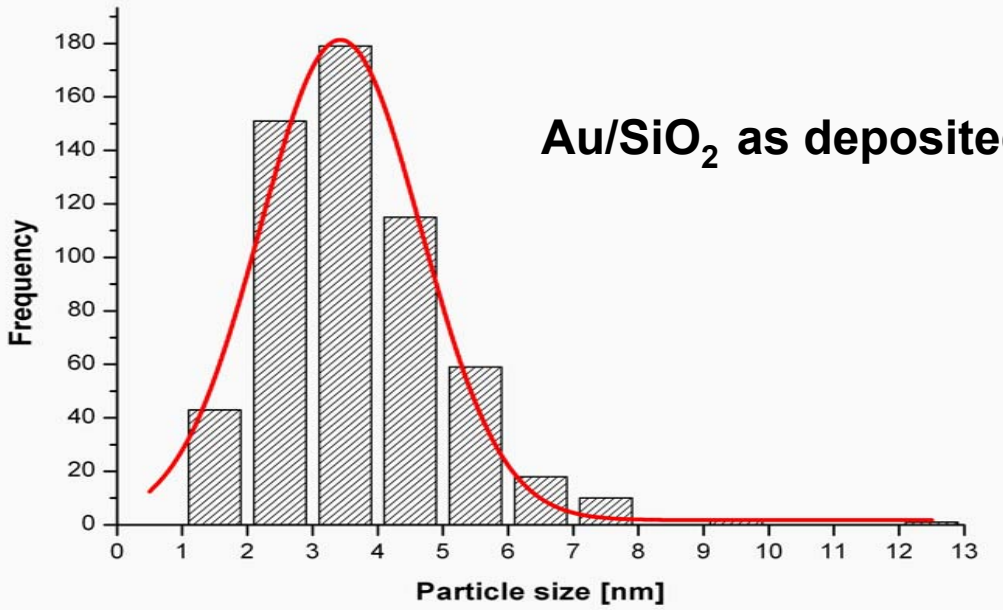

Au/SiO2 as deposited
200 nm


Au/SiO2 HT
200 nm


Au/SiO2 HT
200 nm


Au/SiO2 as deposited
5 nm


Au/SiO2 HT


Au/SiO2 as deposited
Frequency
Particle size [nm]
0
20
40
60
80
100
120
140
160
180
0
1
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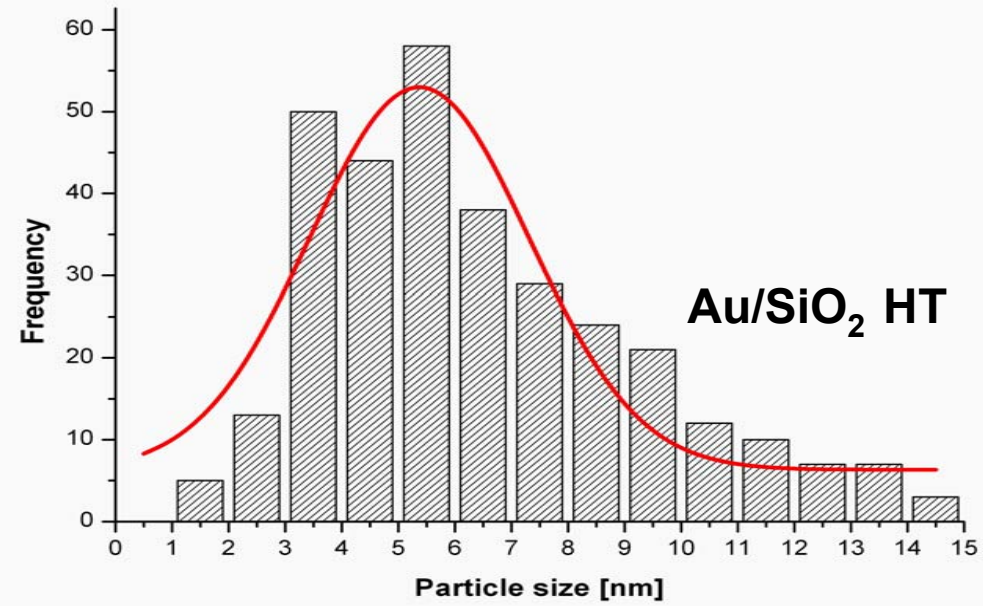
4
5
6
7
8
9
10
11
12
13


Au/SiO2 HT
Frequency
Particle size [nm]
0
10
20
30
40
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60
0
1
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3
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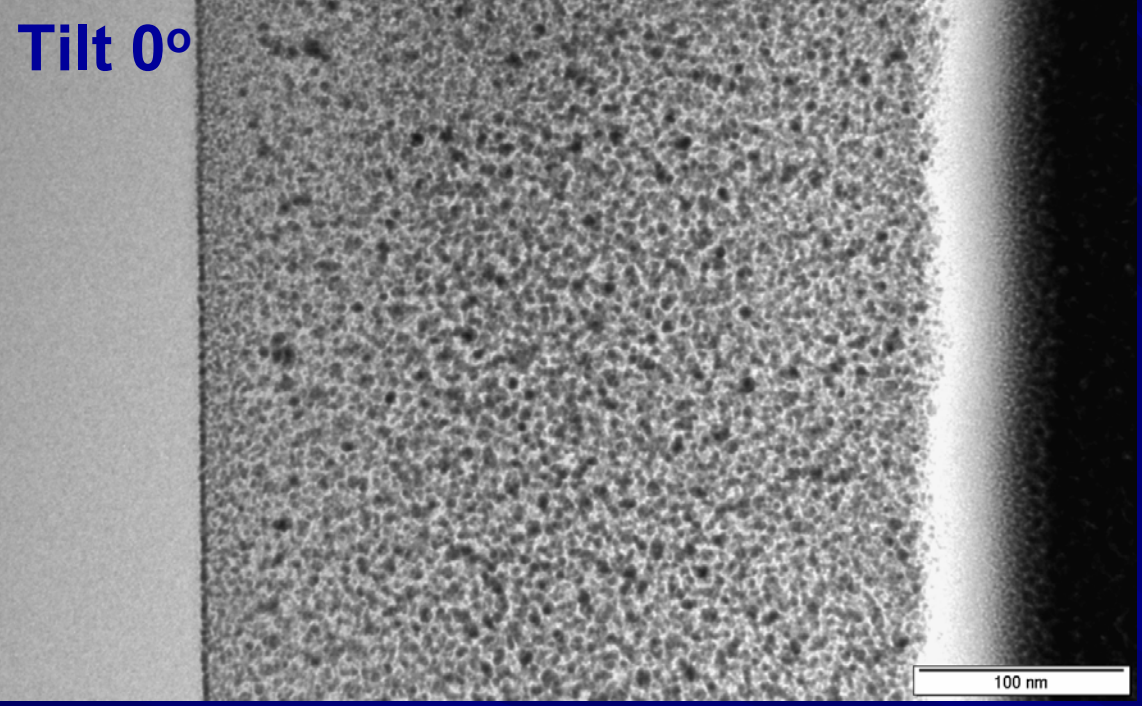
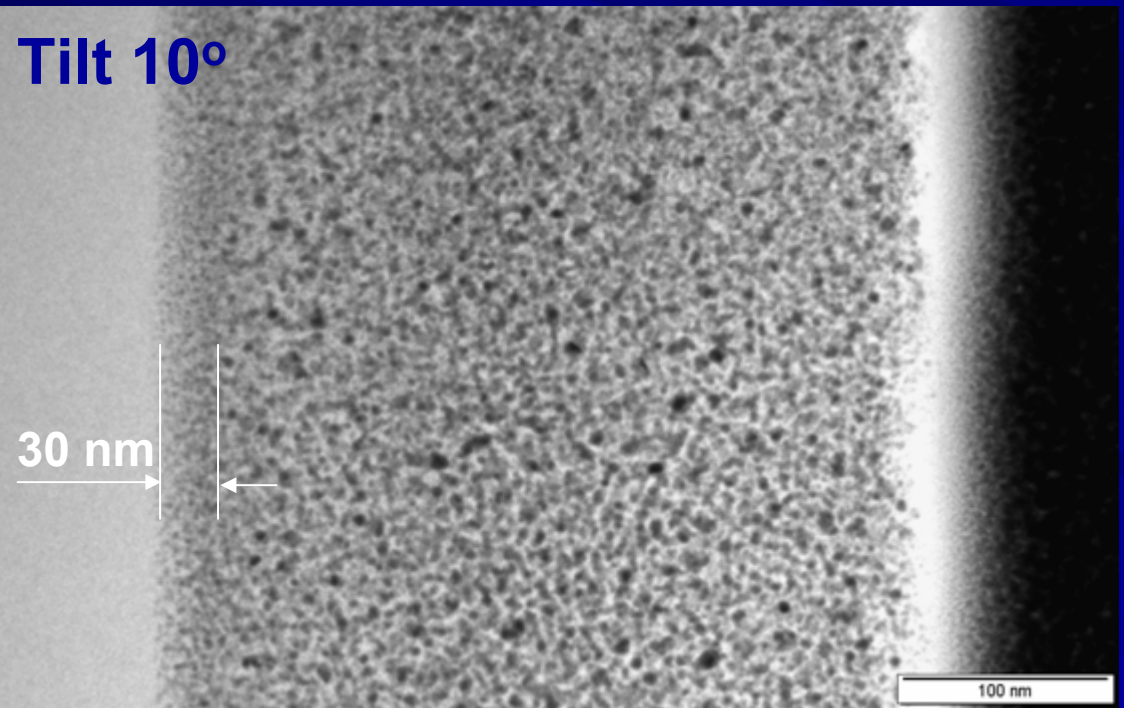
7
8
9
10
11
12
13
14
15





thin foil thickness ~170 nm

Cz. I. Nanokrystality Au - podsumowanie

Problemy rozwiązane:

- **Opisano (jakościowo) mikrostrukturę nanokrystalitów Au w stanie po osadzaniu oraz po dodatkowej obróbce termicznej.**
- **Wykazano (ilościowo), że rozkład wielkości nanokrystalitów ma charakter normalny oraz, że średnia wielkość nanokrystalitów wzrasta od 3 do 5,5 nm**

Problemy do podjęcia:

- **Określenie udziału nanokrystalitów**
- **Określenie minimalnej wielkości nanokrystaltów**
- **Określenie minimalnej wielkości zdefektowanych nanokrystalitów**

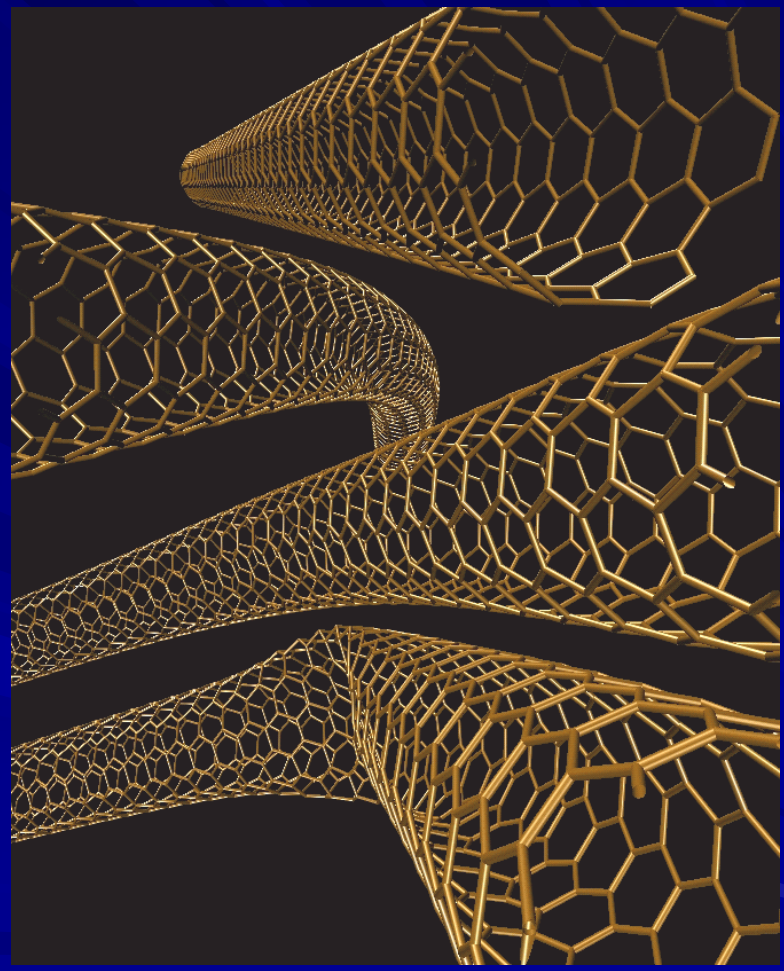
NANO-MAGIC

NANOstructured materials with tailored MAGneto- optICal properties for novel sensor systems

Cz. II. Nanokompozyty ceramika + CNT

Podniesienie przewodności:
(CNT~1GA/cm², Cu ~1MA/cm²)

- **ZrO_2 + CNT**
  (Jan Dusza IMR SAS, Koszyce)



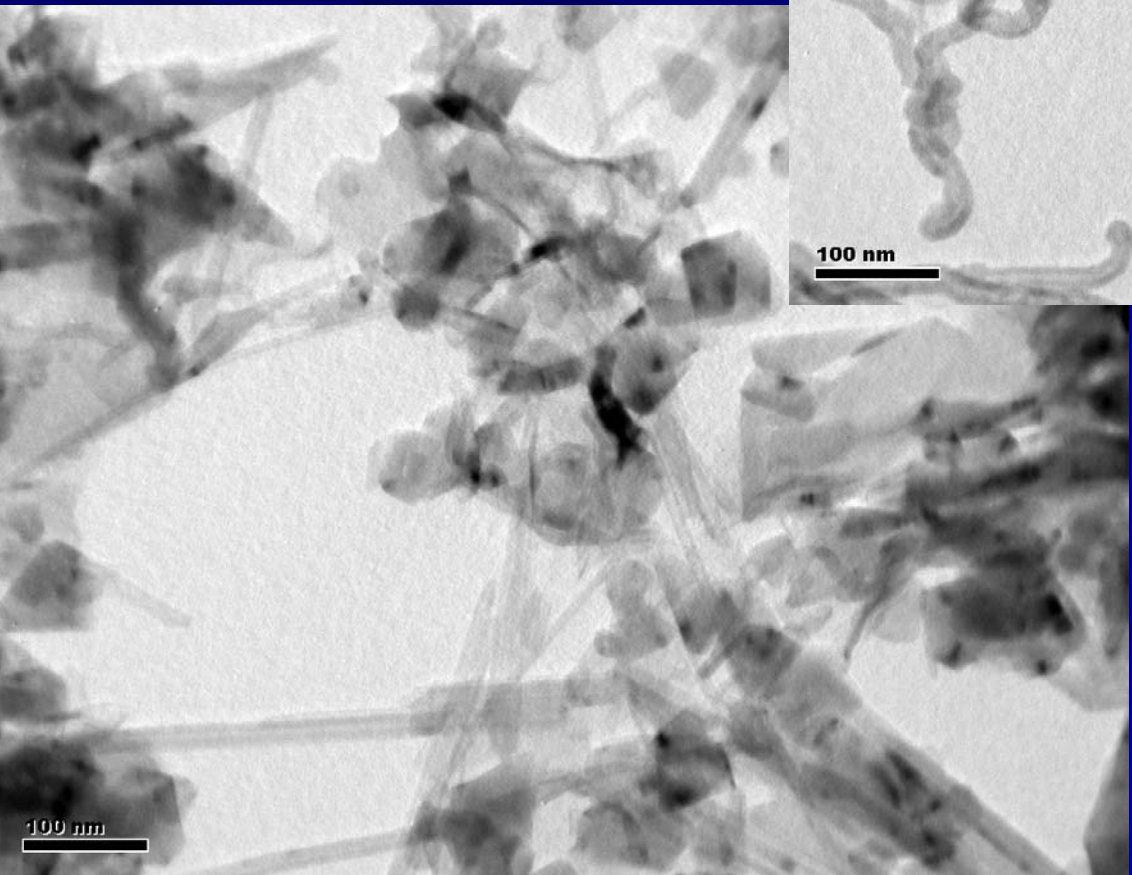
Podniesienie wytrzymałości:
(CNT ~45GPa, stal <2GPa)

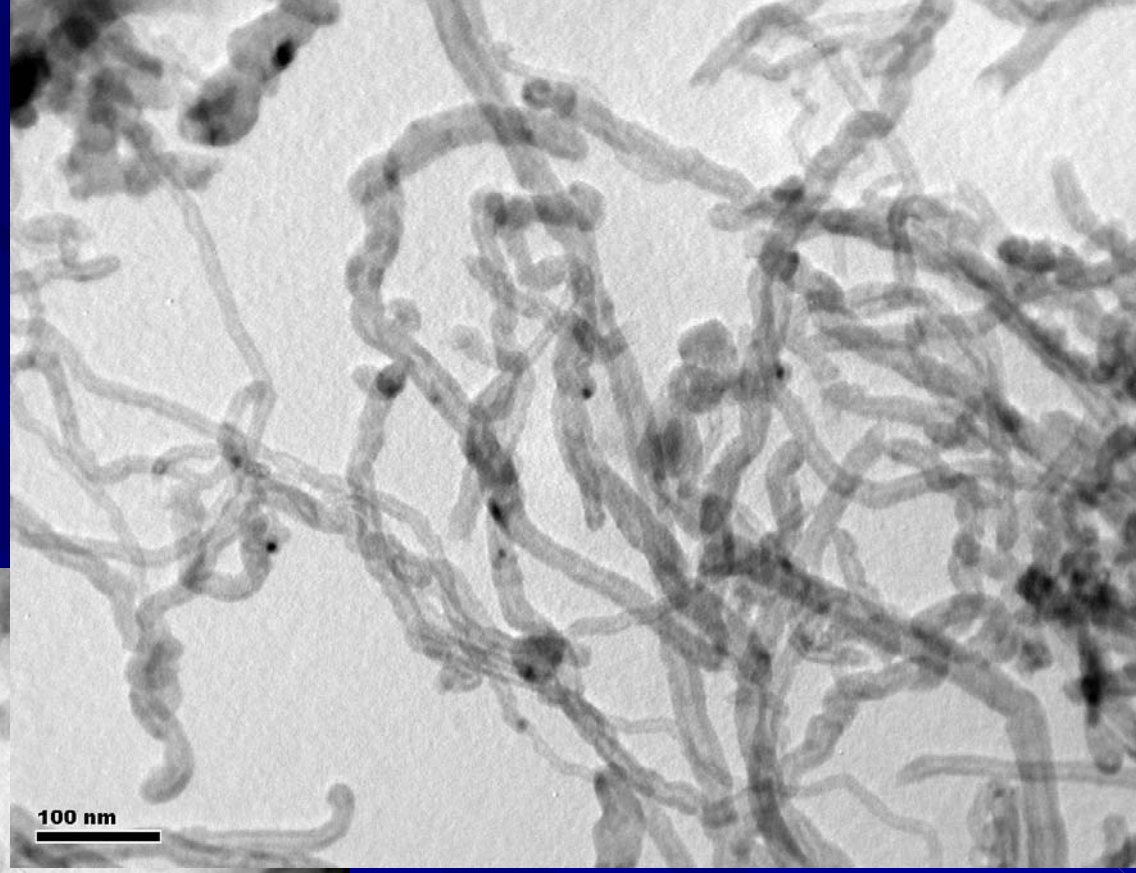
$(Zr,Ti)O_2$ + CNT
(Waldemar Pyda, AGH)

- **Bioszkło + CNT**
  (Aldo Boccaccini/ Imperial College London)

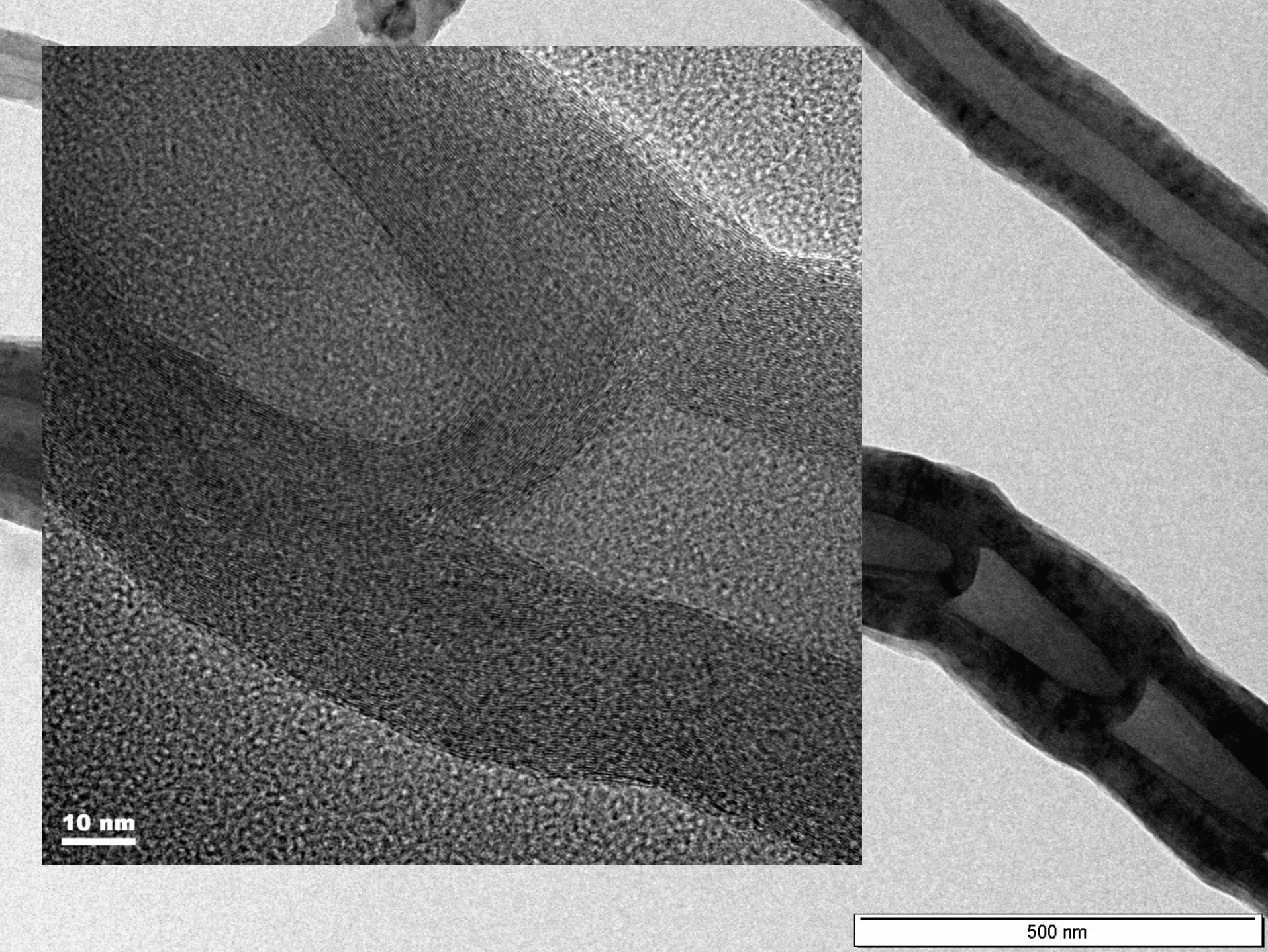
CNT

Prof.. Stanisław Błażewicz,
Katedra Biomateriałów AGH

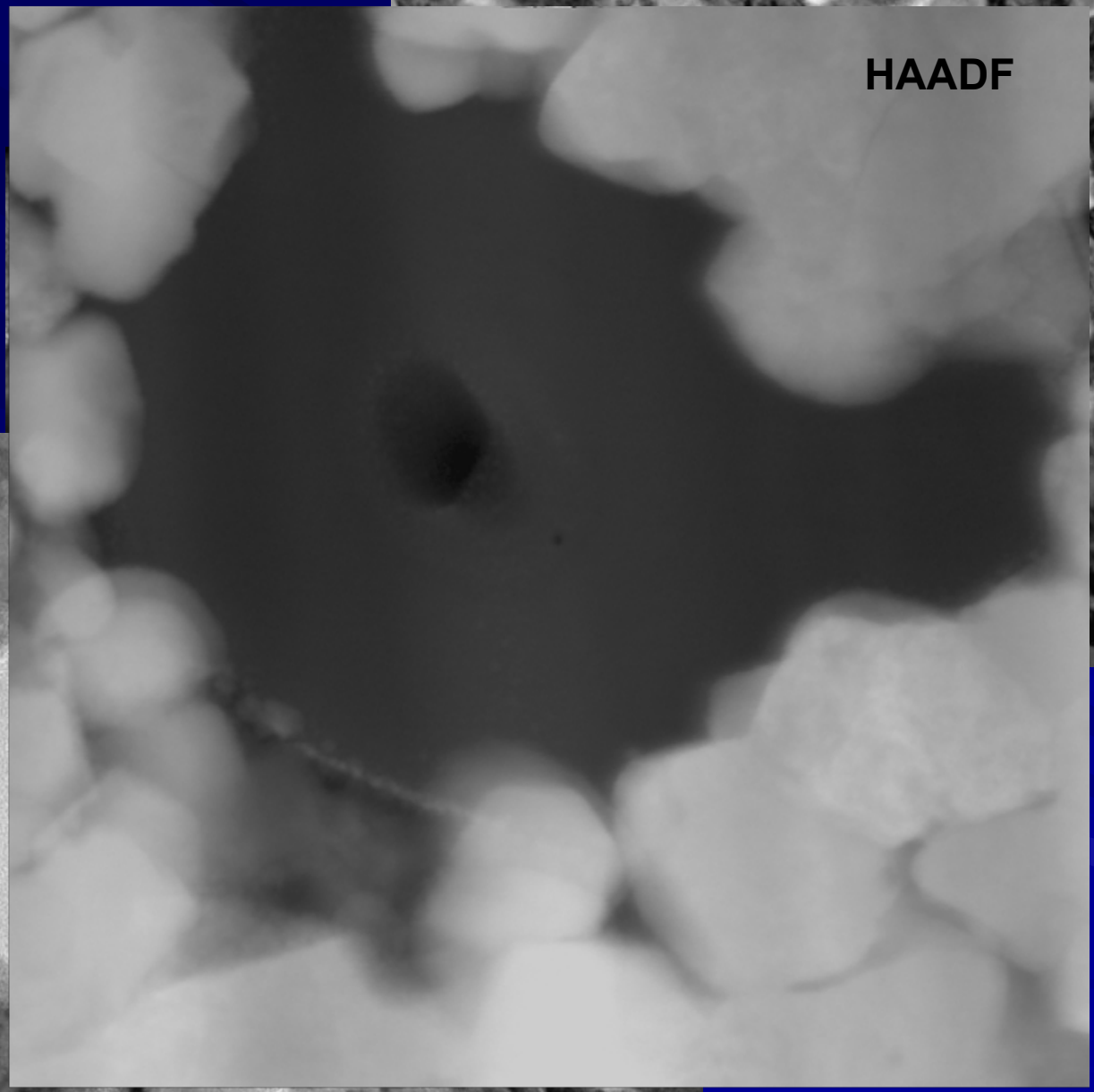


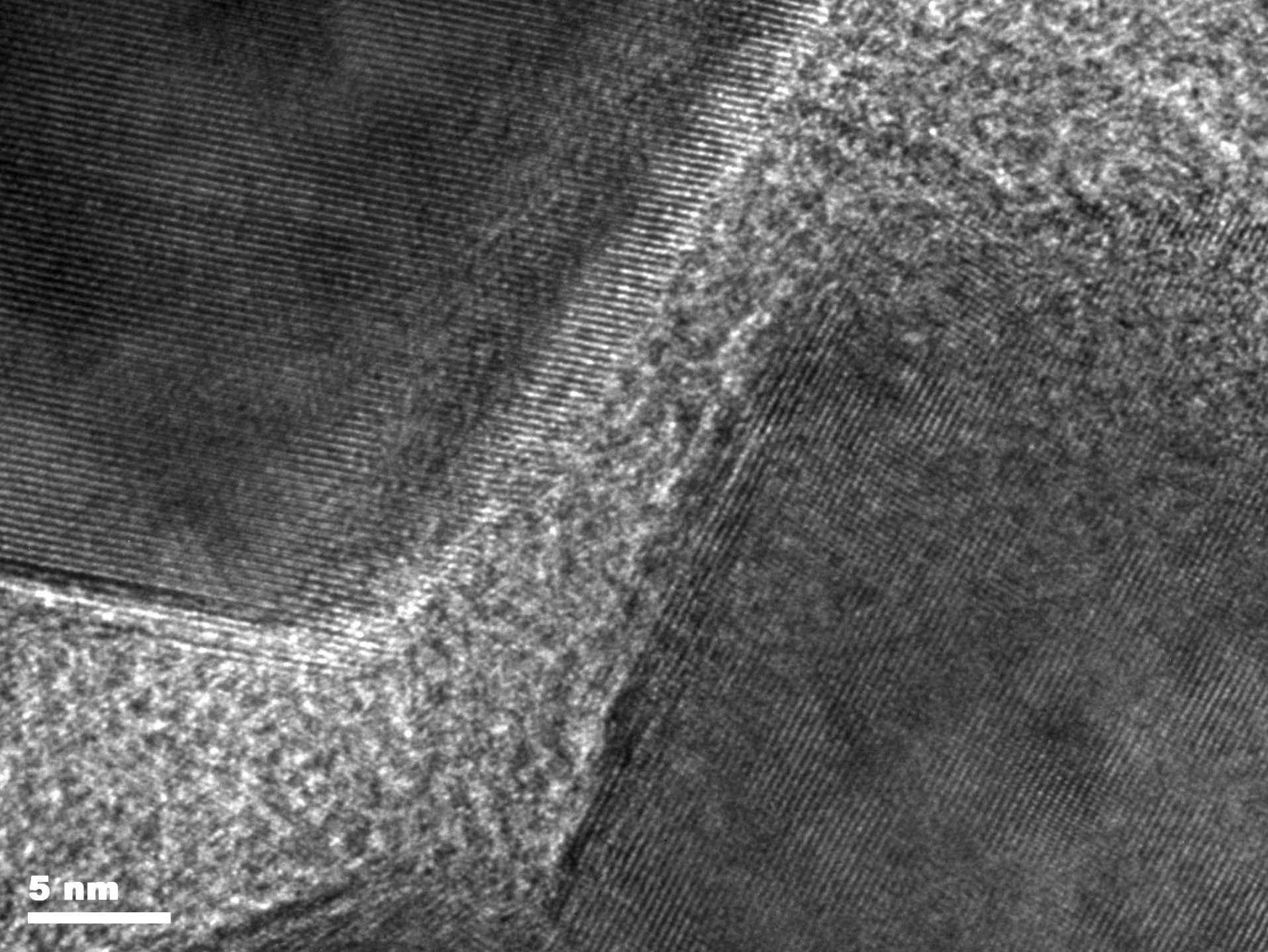


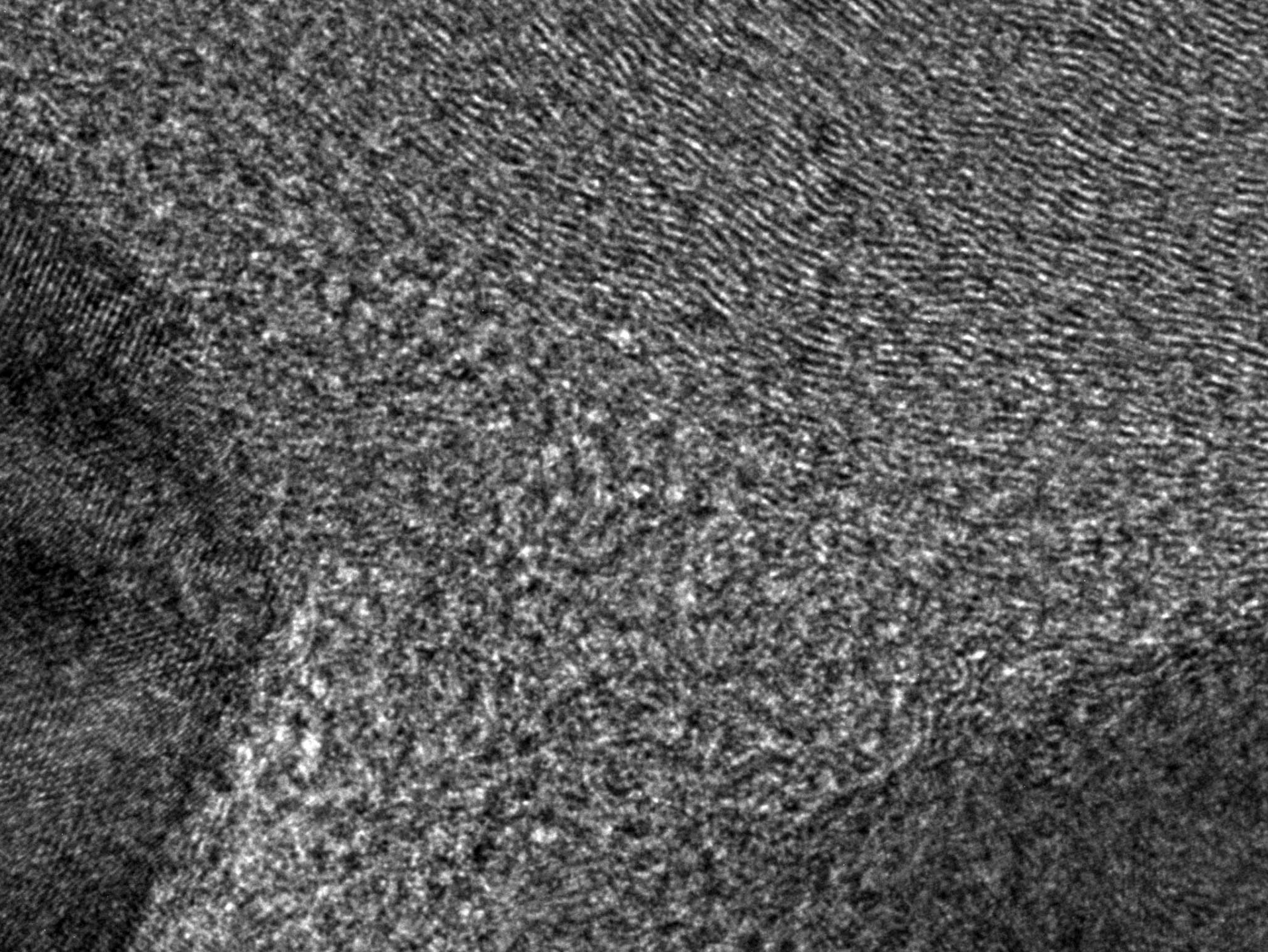
Prof. Aldo Boccaccini,
Imperial College, Londyn

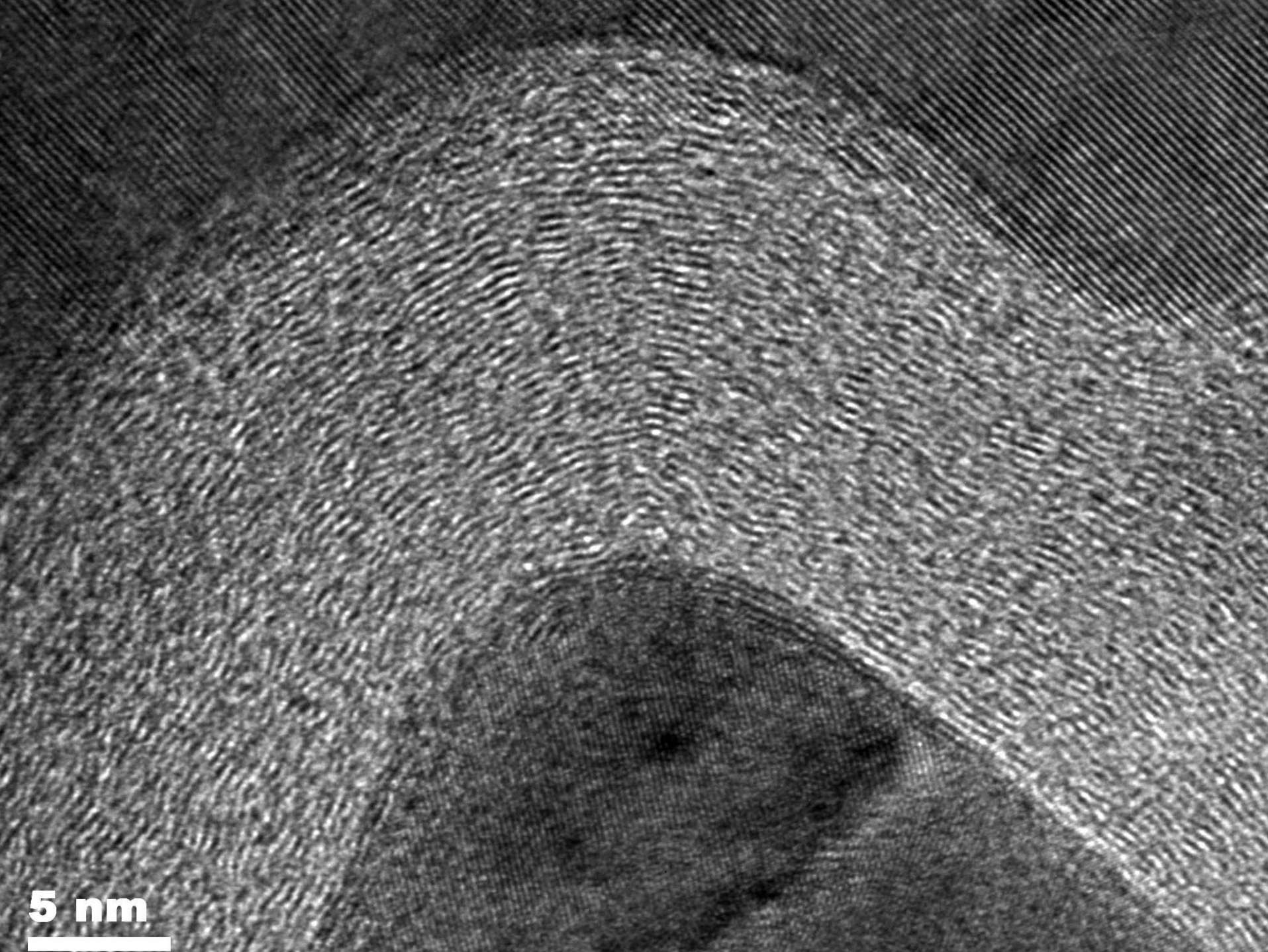

10 nm
500 nm

ZrO_2 + CNT




5 nm




5 nm

Available online at www.sciencedirect.com
ScienceDirect
Scripta Materialia 58 (2008) 520–523
Scripta MATERIALIA
www.elsevier.com/locate/scriptamat

Zirconia/carbon nanofiber composite

Annamária Duszová,[a] Ján Dusza,[b,*] Karel Tomášek,[a] Jerzy Morgiel,[c] Gurdial Blugan[d] and Jakob Kuebler[d]

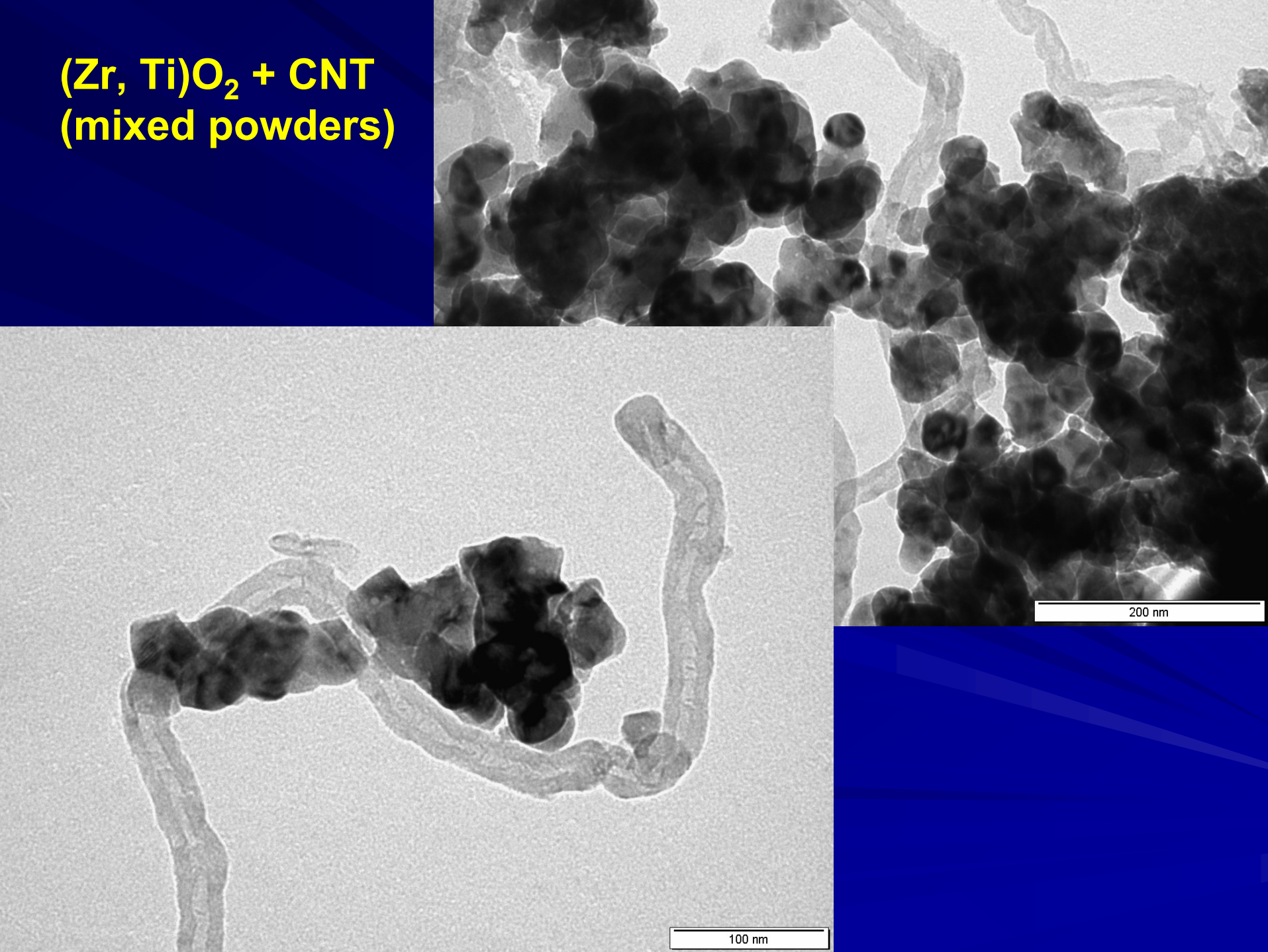
[a] *Technical University of Košice, Faculty of Metallurgy, Letná 9, 042 00 Košice, Slovak Republic*
[b] *Institute of Materials Research, Slovak Academy of Sciences, Watsonova 47, 04353 Košice, Slovak Republic*
[c] *Institute of Metallurgy and Materials Science of Polish Academy of Sciences, Reymonta 25, 30 059 Krakow, Poland*
[d] *Empa, Swiss Federal Laboratories for Materials Testing and Research, Laboratory for High Performance Ceramics, 8600 Duebendorf, Switzerland*

Received 28 September 2007; revised 2 November 2007; accepted 4 November 2007
Available online 3 December 2007

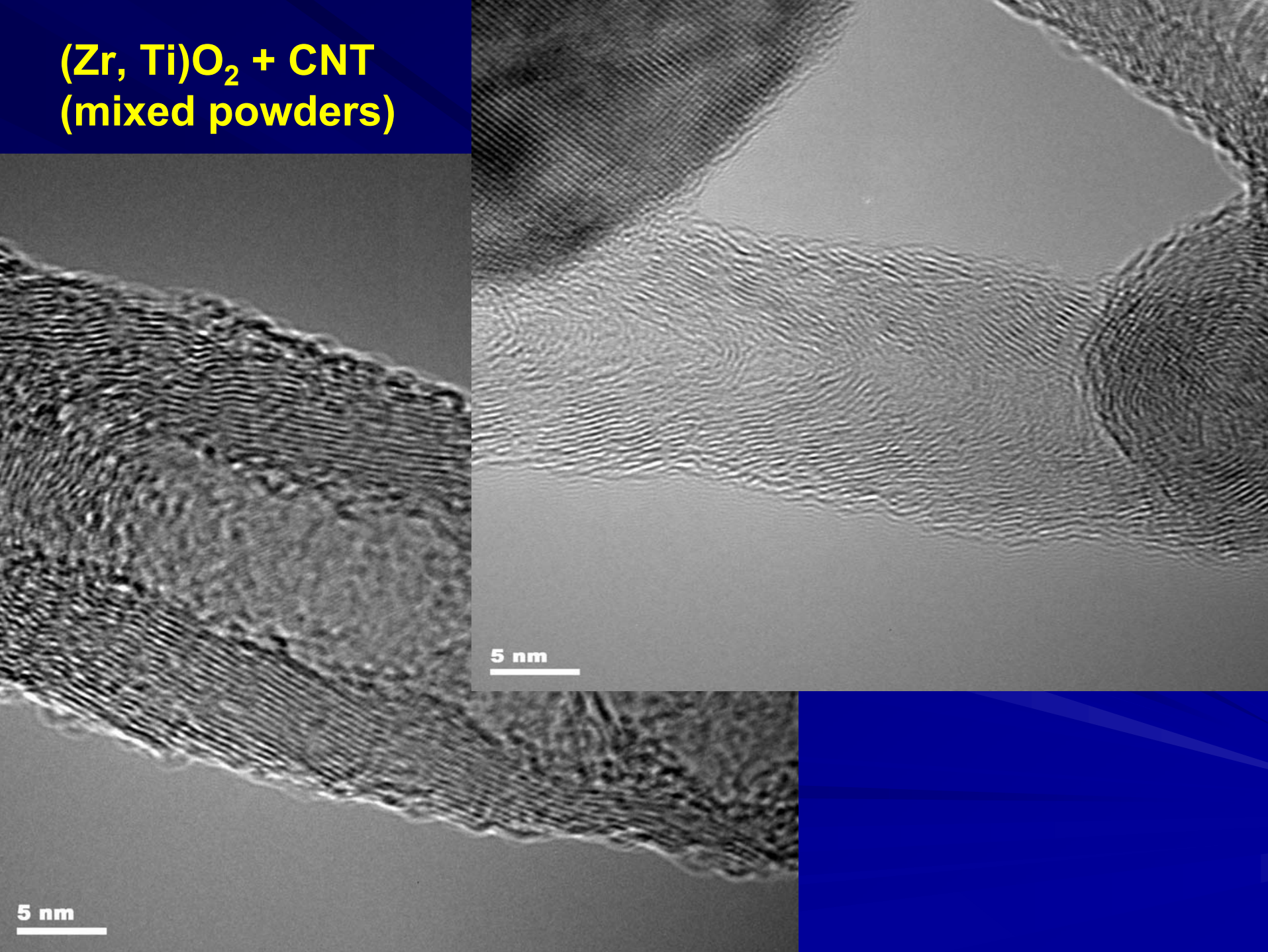
The effect of the addition of carbon nanofibers (CNFs) on the microstructure, fracture/mechanical and electrical properties of the CNF/zirconia composite has been investigated. The microstructure of both ZrO_2 and ZrO_2–CNF composites consists of a very low grain sized matrix (approximately 160 nm) with relatively well dispersed carbon nanofibers in the composite. The mechanical properties slightly decreased after the addition of CNFs to the ZrO_2 but the electrical resistivity decreased significantly, exhibiting approximately 0.1 Ω cm.

Keywords: 3Y-TZP; Carbon nanofiber; Microstructure; Fracture; Electrical resistivity

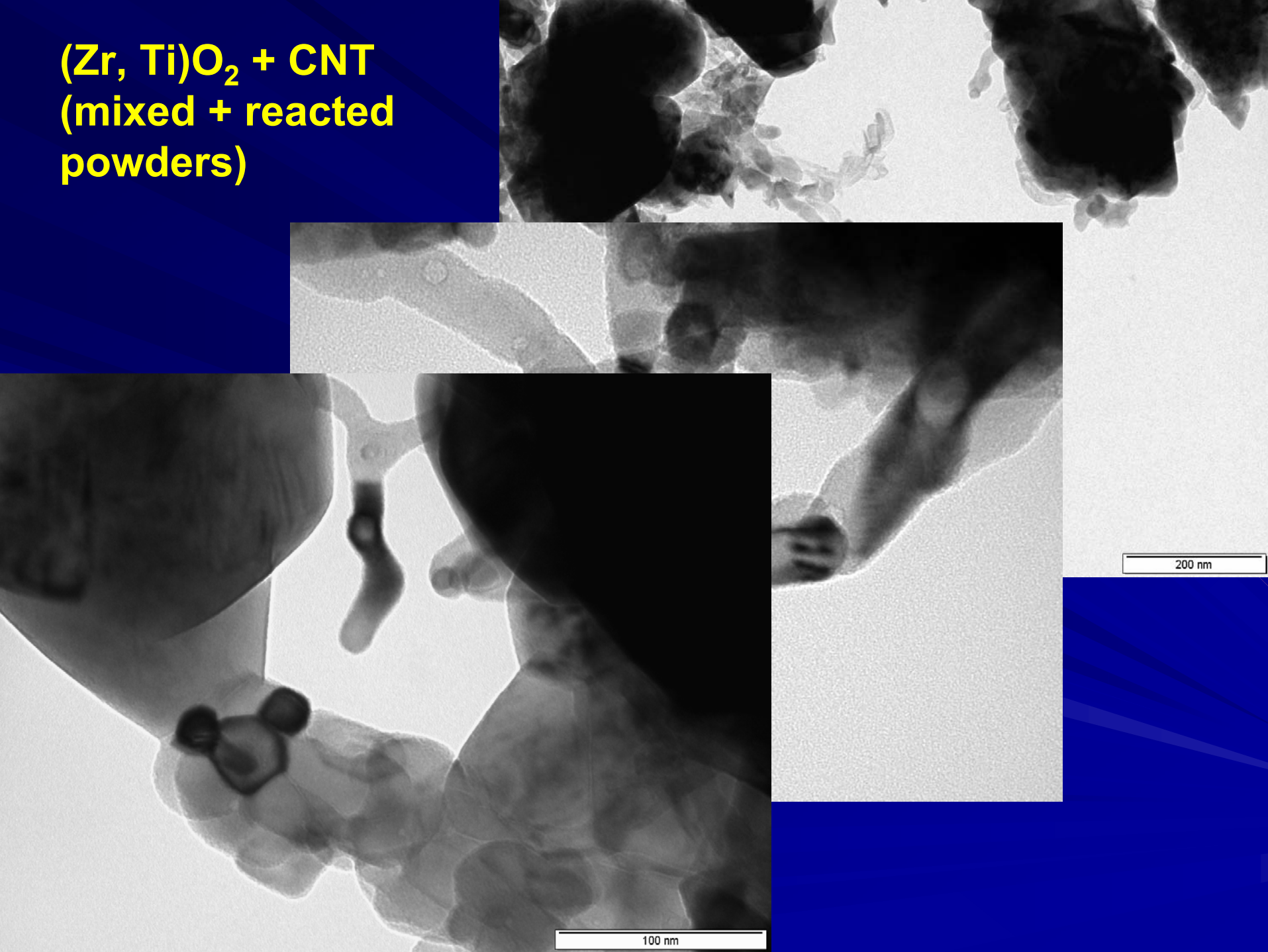
$(Zr, Ti)O_2$ + CNT (mixed powders)

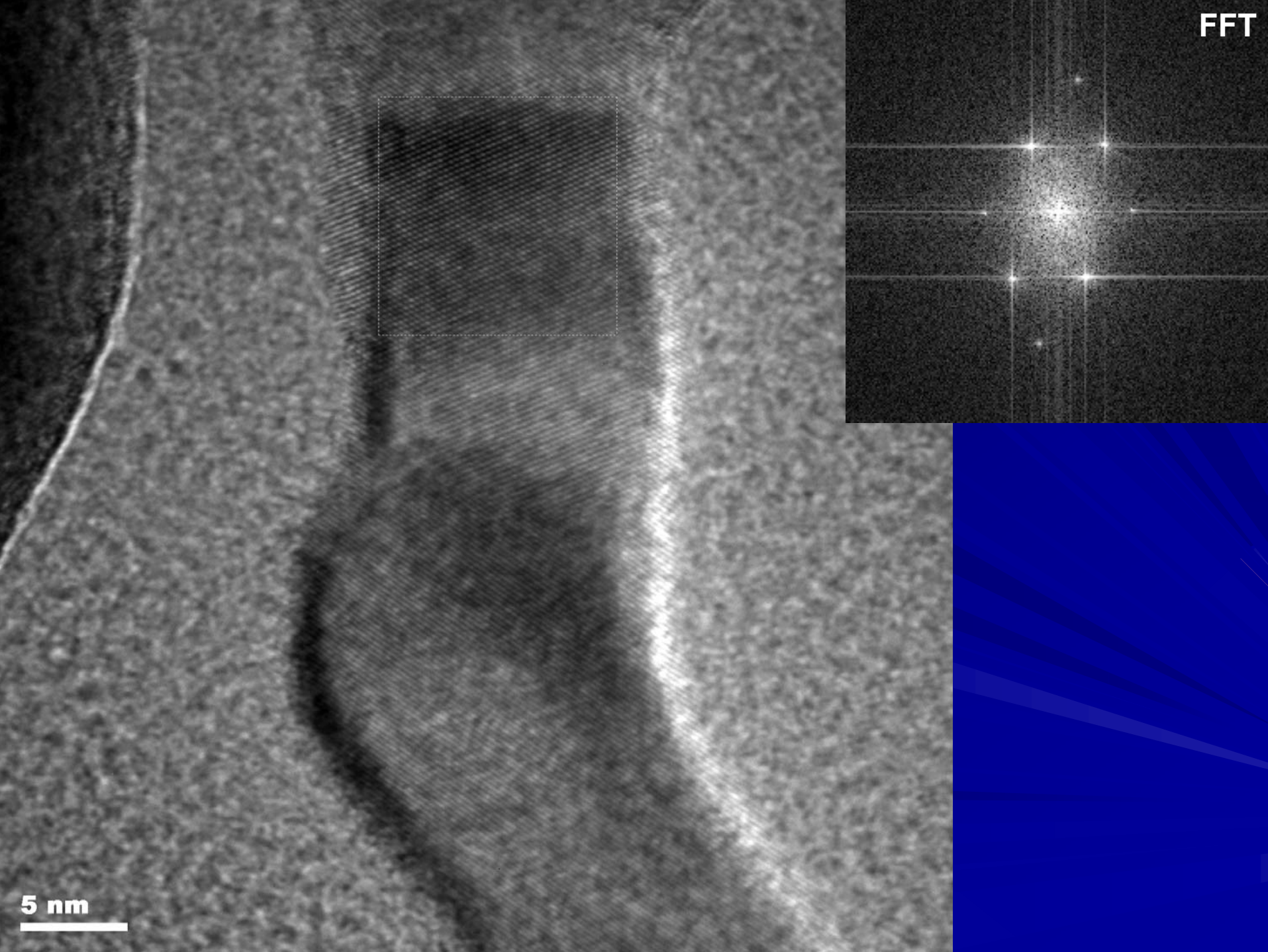


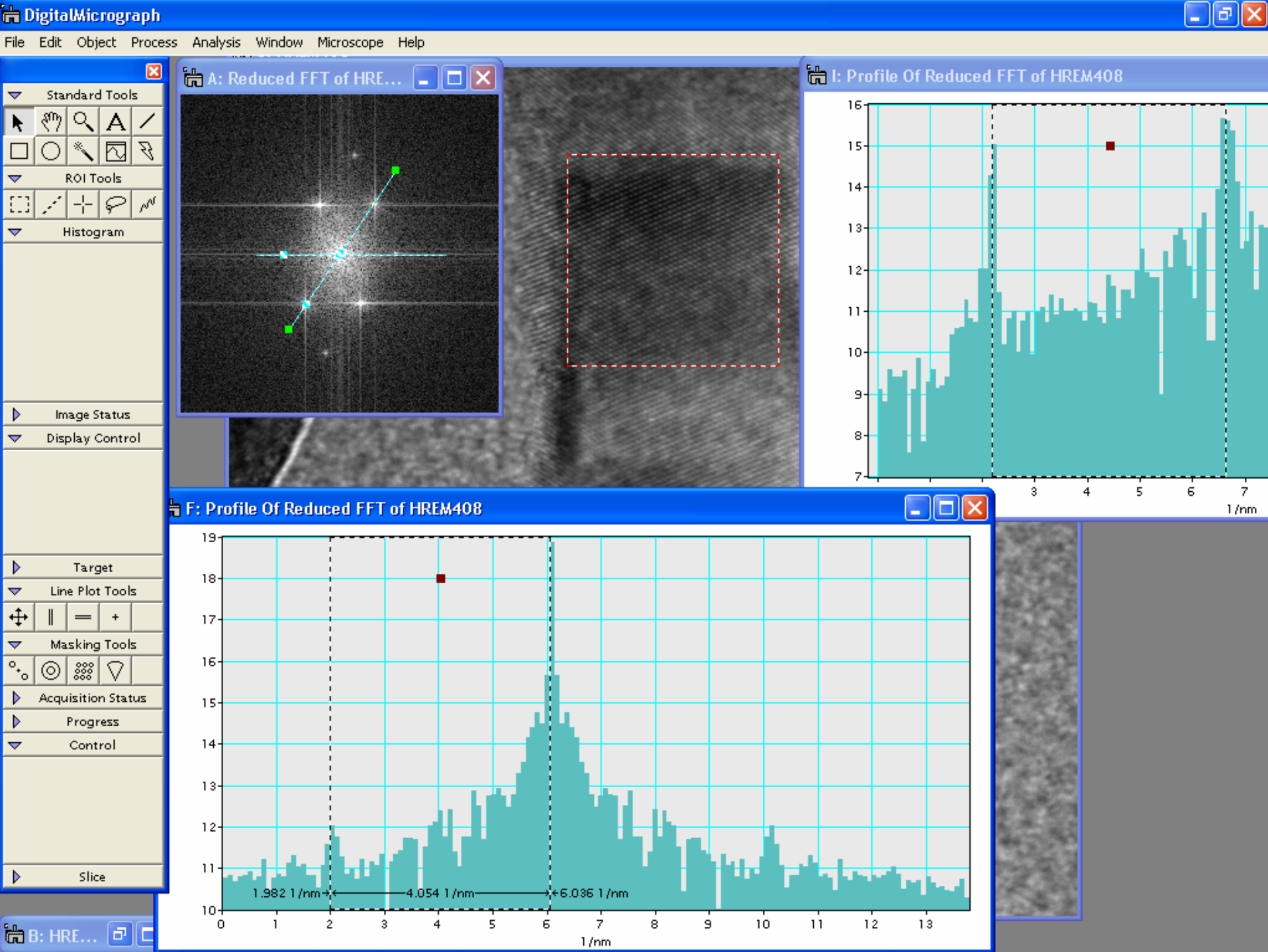
$(Zr, Ti)O_2$ + CNT (mixed powders)



$(Zr, Ti)O_2$ + CNT (mixed + reacted powders)




FFT
5 nm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File Edit Object Process Analysis Window Microscope Help
Standard Tools
ROI Tools
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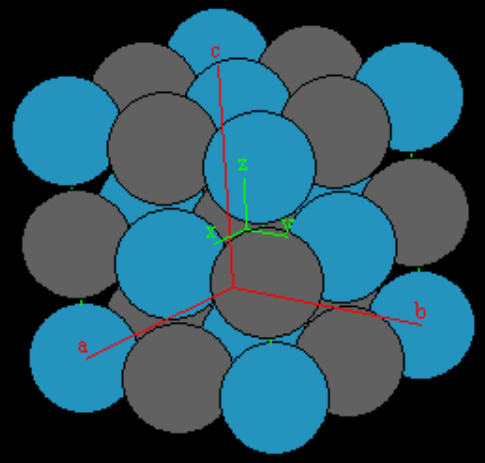
Masking Tools
Acquisition Status
Progress
Control
Slice
A: Reduced FFT of HRE...
I: Profile Of Reduced FFT of HREM408
1/nm
F: Profile Of Reduced FFT of HREM408
1.982 1/nm
4.054 1/nm
6.036 1/nm
1/nm
B: HRE...

CaRIne 3.0

File Edit Cell hkl/uvw Calcul. Specials Crystal View Window ?

C:\X-COPY1\WYMIEN~2\CARINEV3\CEL\Z_KOSZ\C\TIC...



x'n 137.30 y'n 126.65 z'n 108.77 Cmd None Nb 8 a 4.3 b 4.3 c 4.3 α 90.0 β 90.0 γ 90.0 Sy

Identification of Planes

V : (kV)

λ : (Å)

L : (cm)

K : (cm.Å)

r1 (cm)

r2 (cm)

d1 2.5 (Å)

d2 : 2.27 (Å)

α 56.2 (°)

(hkl)#1	(hkl)#2	dhkl1	dhkl2	Angle(°)	E(%)	Zone axis
1,-1,1	2,0,0	2.49	2.16	54.74	7.8	0,1,1
1,1,1	2,0,0	2.49	2.16	54.74	7.8	0,1,-1
1,-1,1	0,0,2	2.49	2.16	54.74	7.8	1,1,0
1,-1,-1	2,0,0	2.49	2.16	54.74	7.8	0,-1,1
1,1,1	0,0,2	2.49	2.16	54.74	7.8	1,-1,0
1,1,1	0,2,0	2.49	2.16	54.74	7.8	-1,0,1
1,1,-1	0,2,0	2.49	2.16	54.74	7.8	1,0,1
1,1,-1	2,0,0	2.49	2.16	54.74	7.8	0,1,1
0,2,0	1,1,-1	2.16	2.49	54.74	26.1	1,0,1
2,0,0	1,1,1	2.16	2.49	54.74	26.1	0,-1,1
2,0,0	1,-1,1	2.16	2.49	54.74	26.1	0,1,1
2,0,0	1,-1,-1	2.16	2.49	54.74	26.1	0,1,-1
2,0,0	1,1,-1	2.16	2.49	54.74	26.1	0,1,1
0,0,2	1,1,1	2.16	2.49	54.74	26.1	-1,1,0
0,2,0	1,1,1	2.16	2.49	54.74	26.1	1,0,-1
0,0,2	1,-1,1	2.16	2.49	54.74	26.1	1,1,0

Compute Print -> ASCII Help Close

Crystal

Rotations

Keyboar Control

Ster. Proj

ES Vision - Jurek - [Acquisition Window (1) - E:\JM_TECNAI\2007_KMM-NoE\AGH_C-tube+n-cryst_powder\ZrO2+CNT_reacted\STEM\STEM1+.emi]

File Edit View Display Acquire Process Tools Window Help

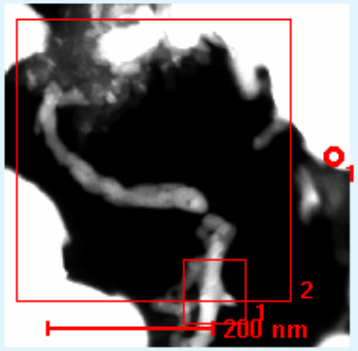
Normal Image Display

Markers

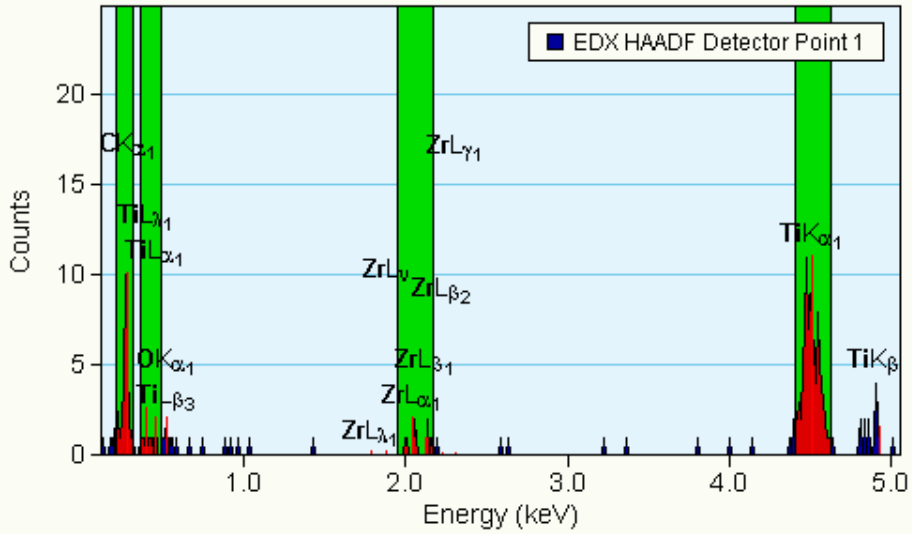
V

K L M

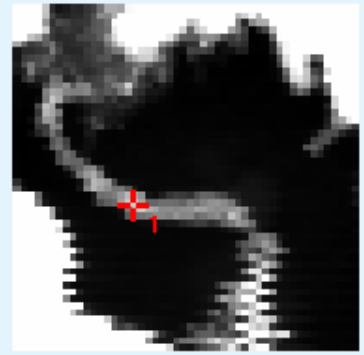
HAADF Detector



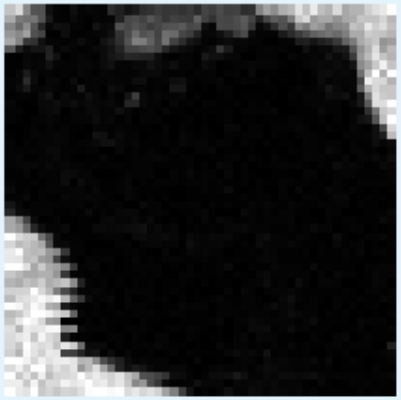
EDX HAADF Detector Point 1



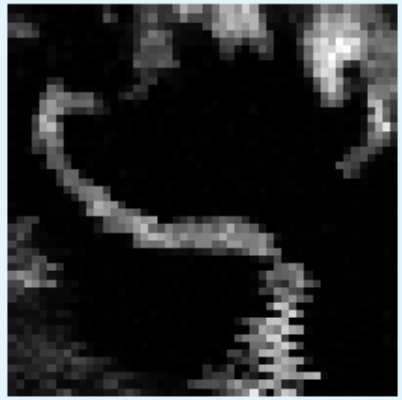
STEM HAADF Detector



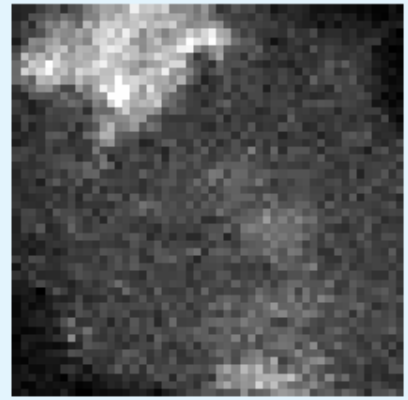
Zr_La



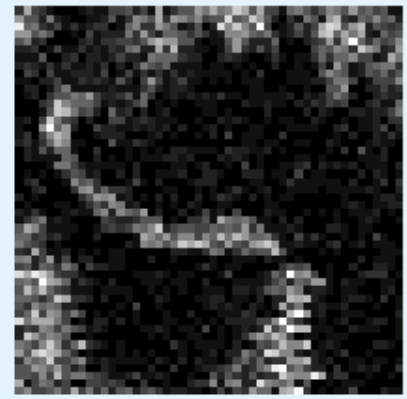
Ti_Ka



C_Ka



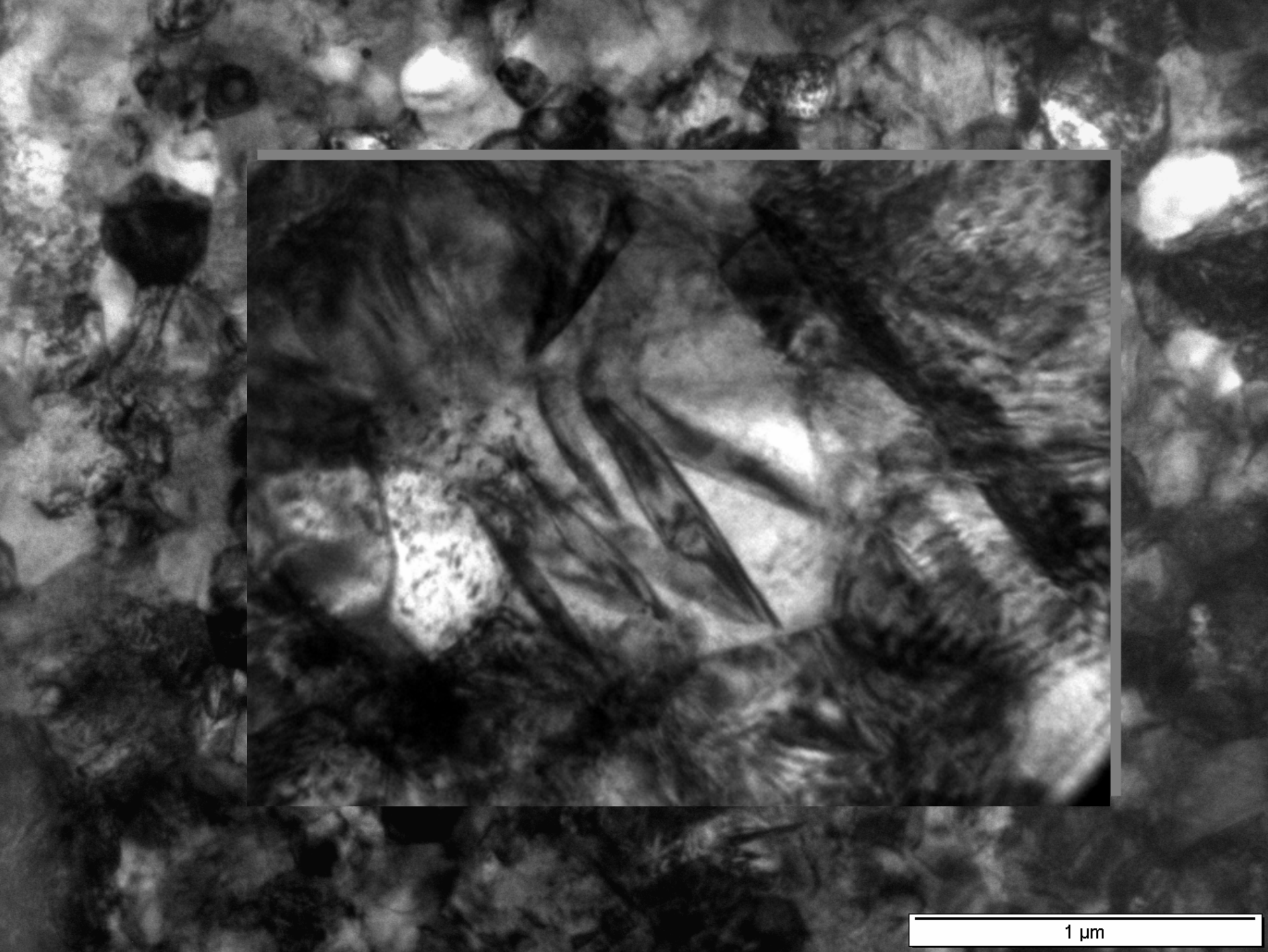
O_Ka + Ti_La

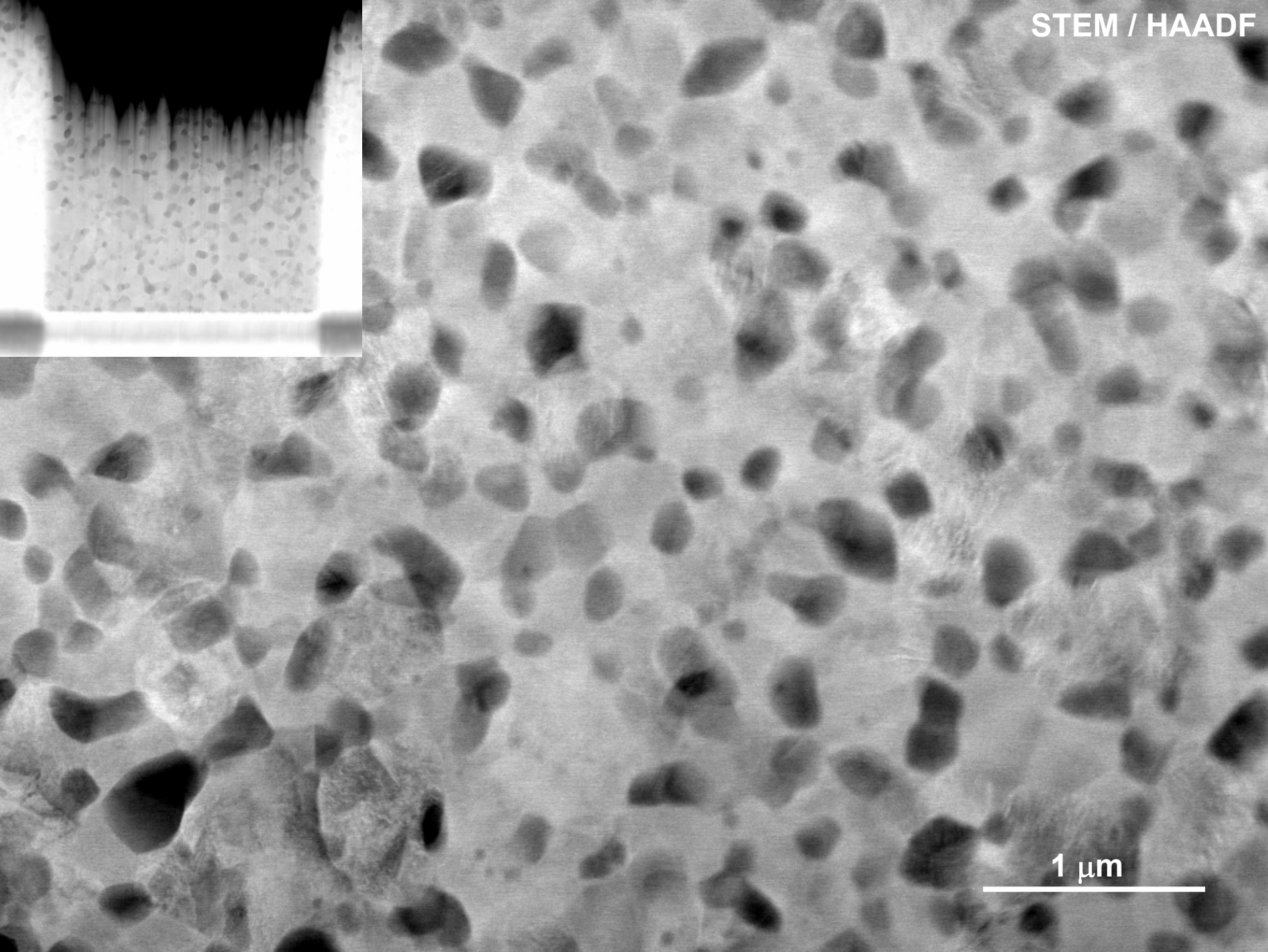


Ready

Spiek YTZP / TiC

1500°C / 10^{-4}mbara / 2 godz


1 µm

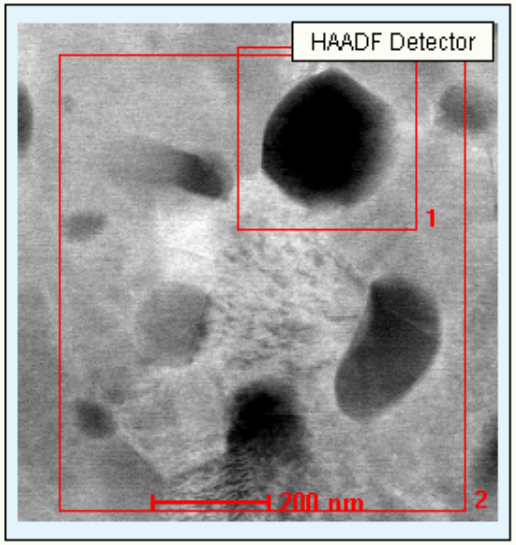

STEM / HAADF
1 μm

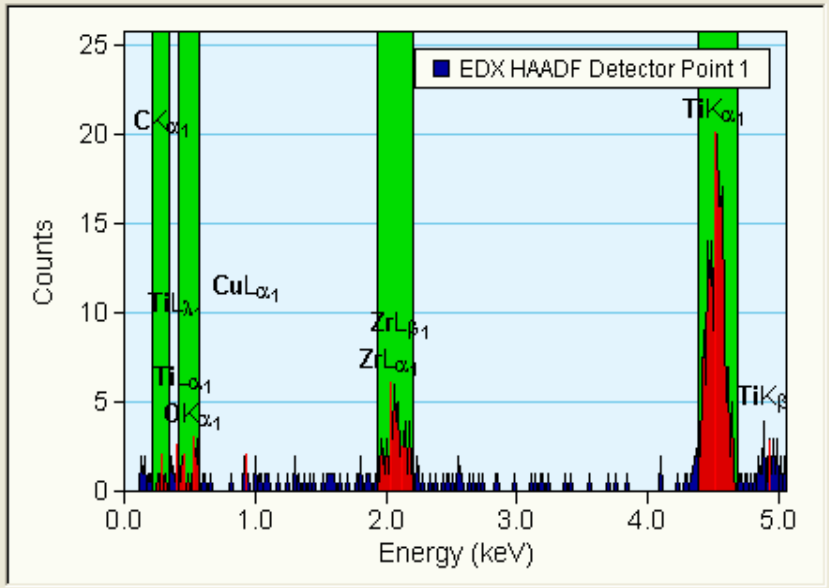
File Edit View Display Acquire Process Tools Window Help

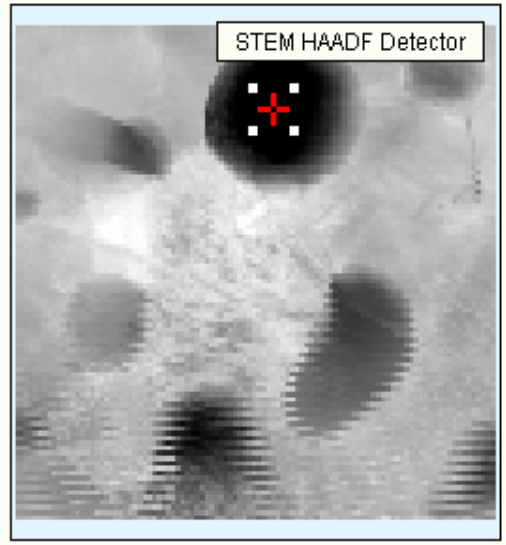
Normal

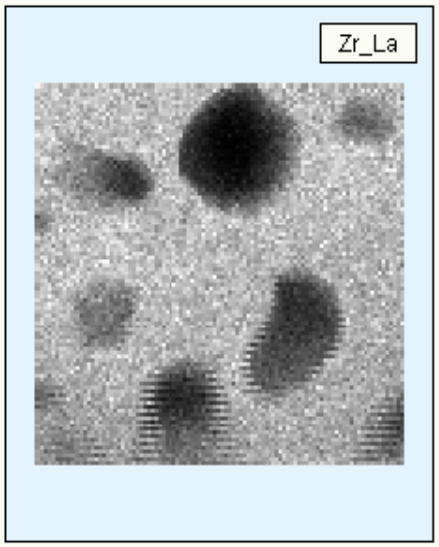
Markers

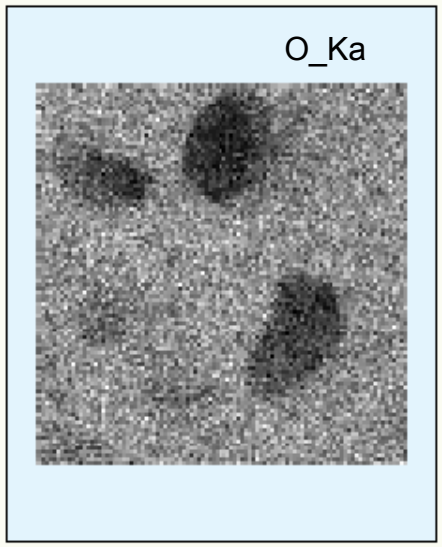
K L M

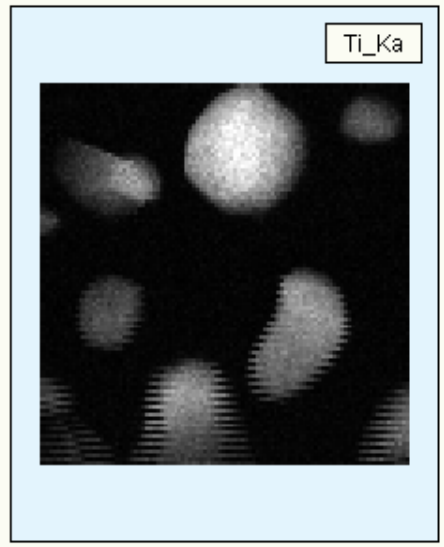


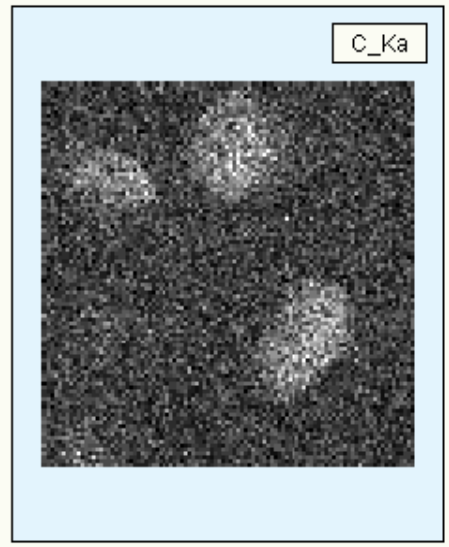












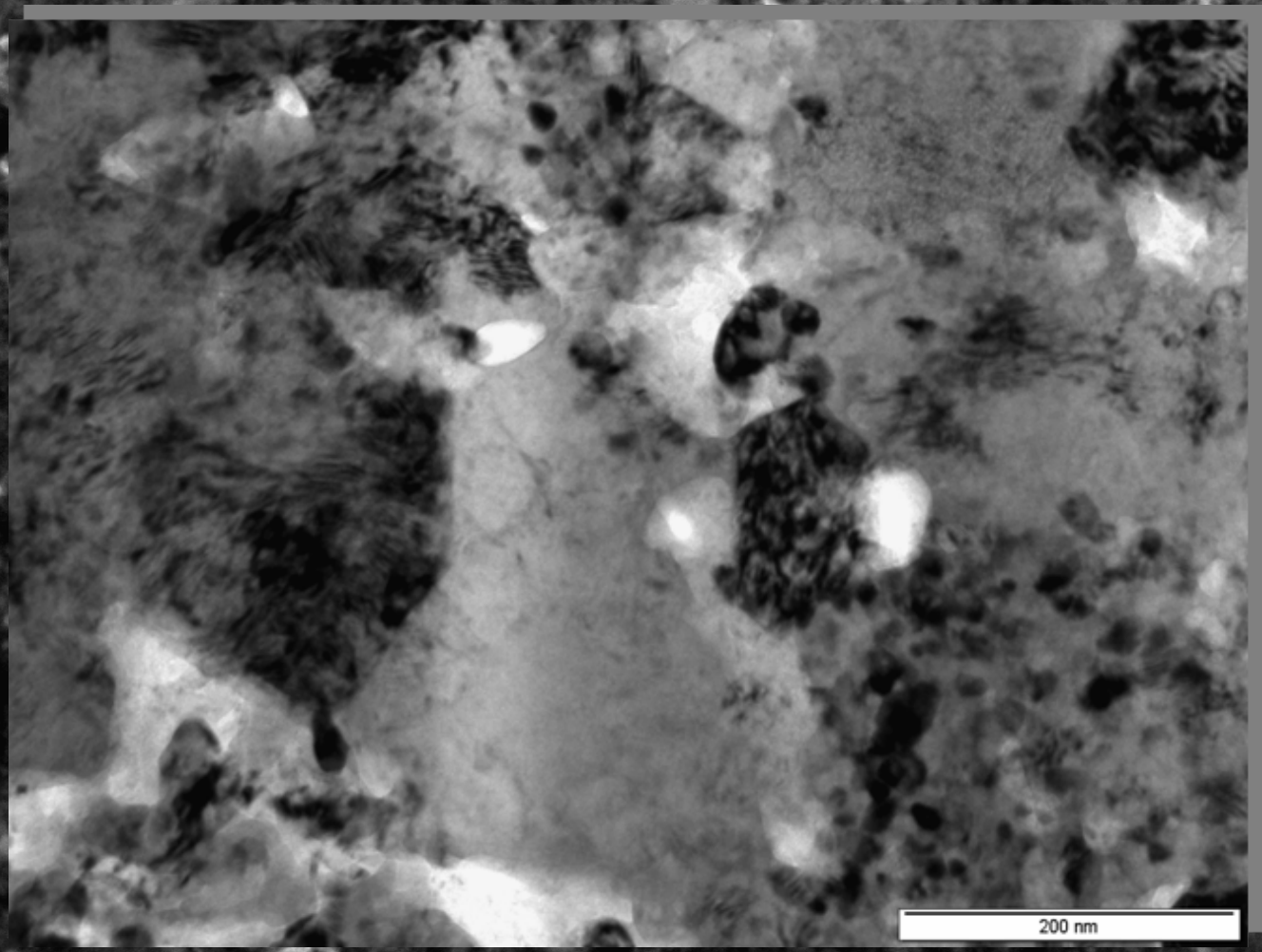
Ready

Spiek YTZP / TiC

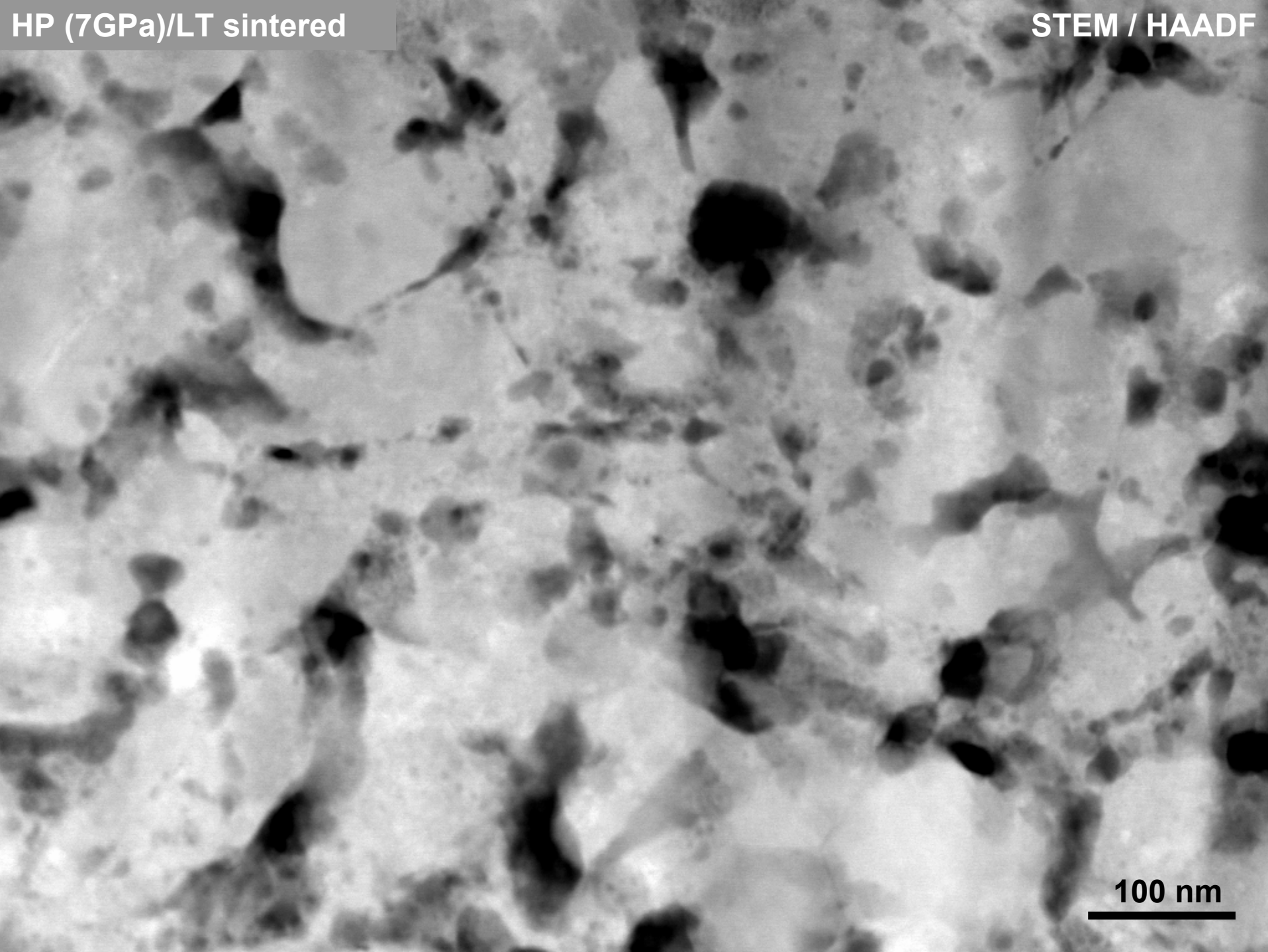
1250°C / 7,7 GPa / 30 sek

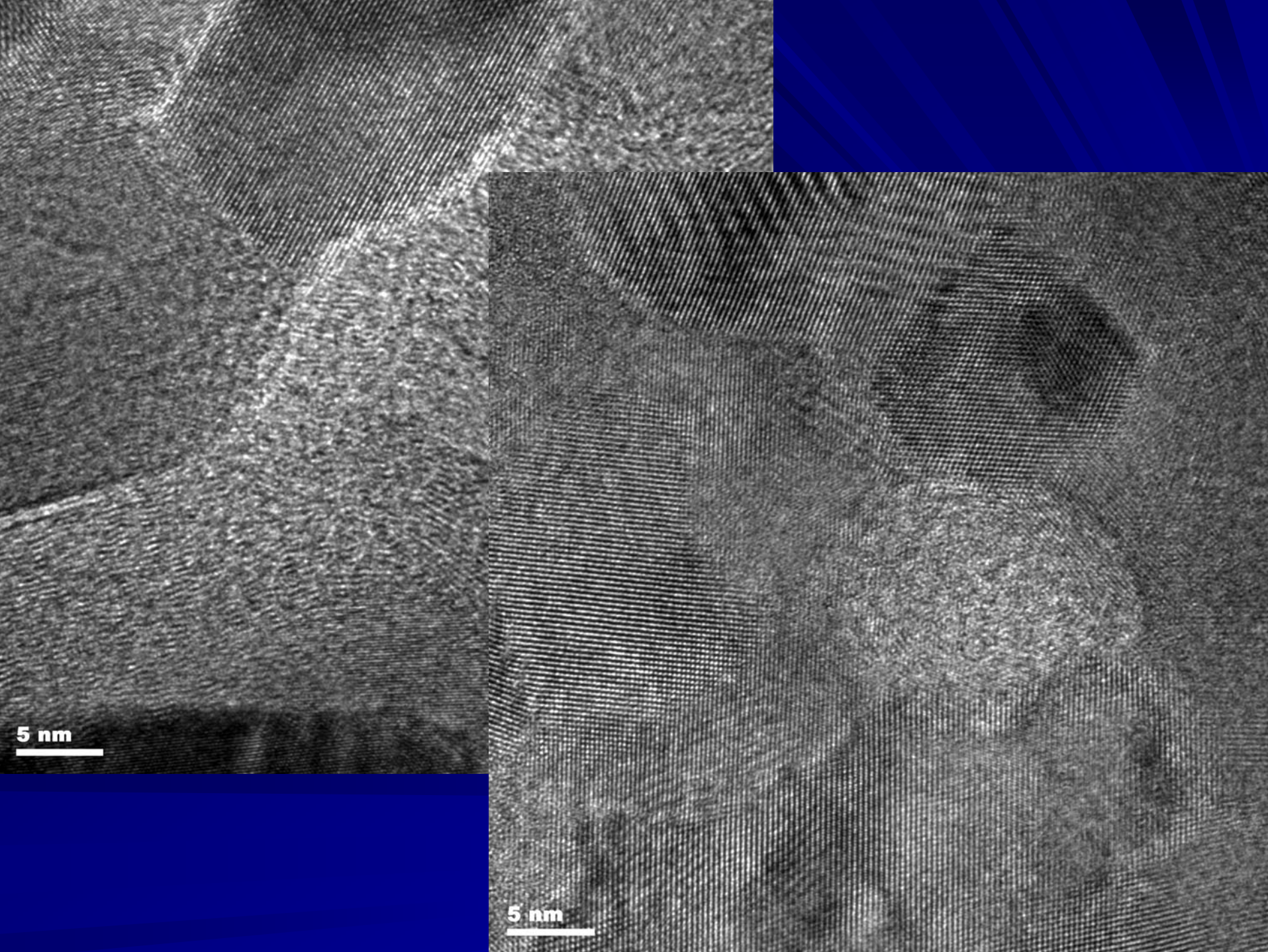
Waldemar Pyda, AGH,
Lucyna Jaworska, IOS

HP (7GPa)/LT sintering

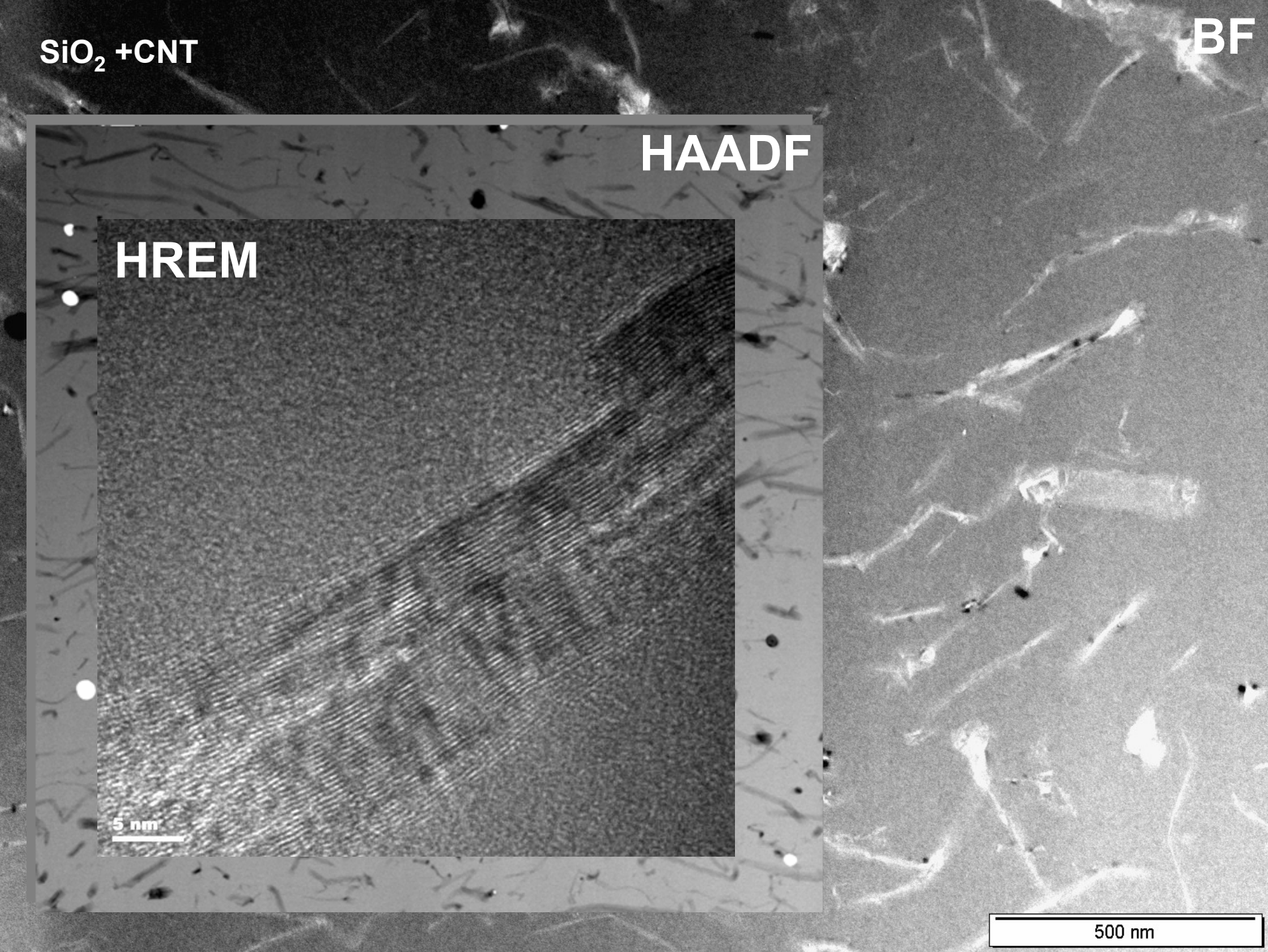


1 μm


HP (7GPa)/LT sintered
STEM / HAADF
100 nm


5 nm
5 nm

Aldo Boccaccini


SiO_2 +CNT
BF
HAADF
HREM
5 nm
500 nm

Cz. II. Nanokompozyty ceramika + CNT - podsumowanie

Problemy rozwiązane:

- Opisano mikrostrukturę proszków oraz spieków ZrO_2 z udziałem CNT
- Wykazano tendencje do amorfizacji CNT w trakcie spiekania
- Potwierdzono możliwość tworzenia „nanodrutów" TiC
- Potwierdzo utrzymanie kształtu i struktury CNT w spiekach z „bioszkła"

Problemy do podjęcia:

- Analiza procesu tworzenia „nanodrutów" TiC

Projekty: iNTeg-Risk (negocjowany), OPTIMAN (odrzucony)

Cz. III. Wielowarstwy

Powłoki funkcjonalne:
(SHS)

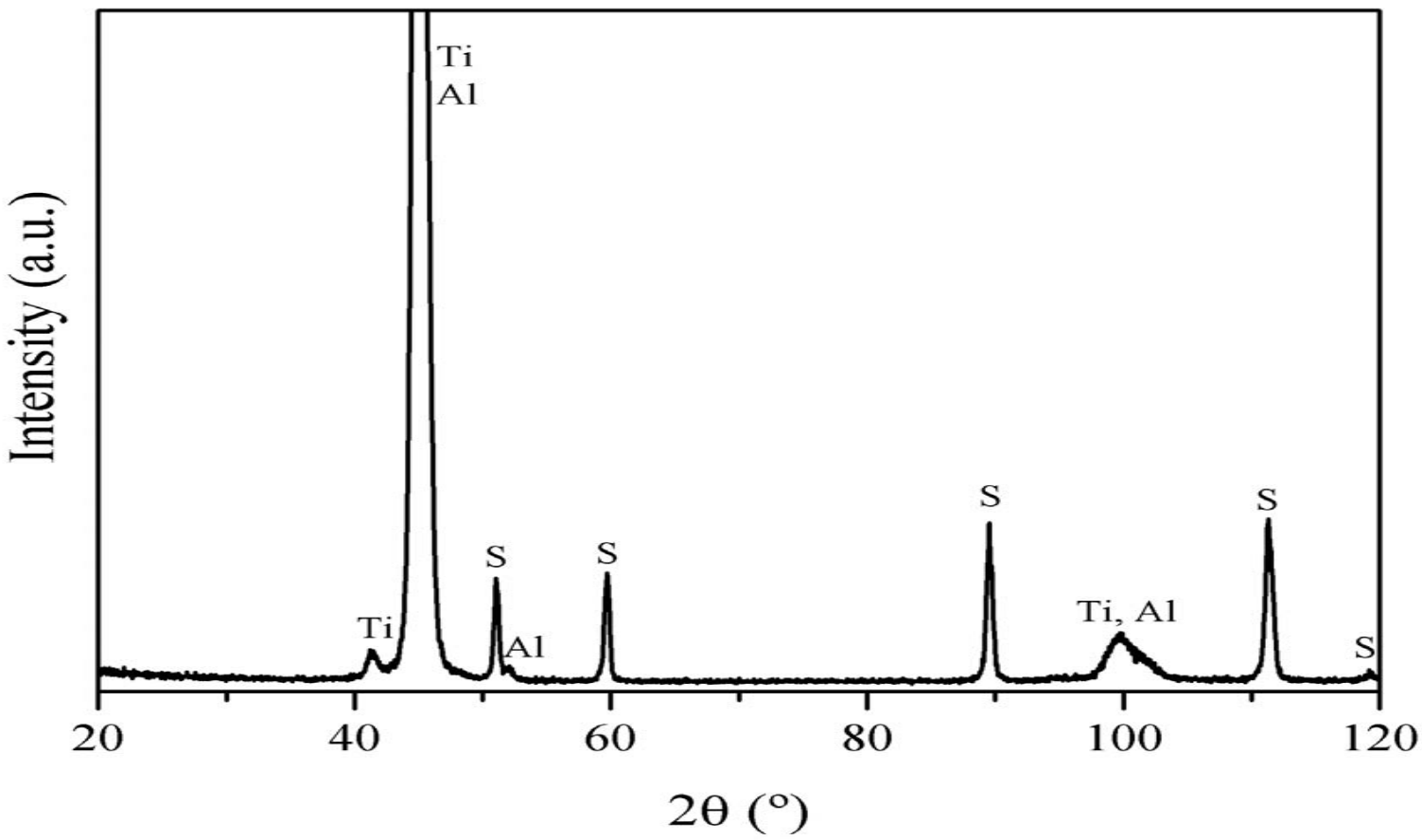
- **AlTi (20 nm)**
  (Ana Sofia Ramos
  University of Coimbra)

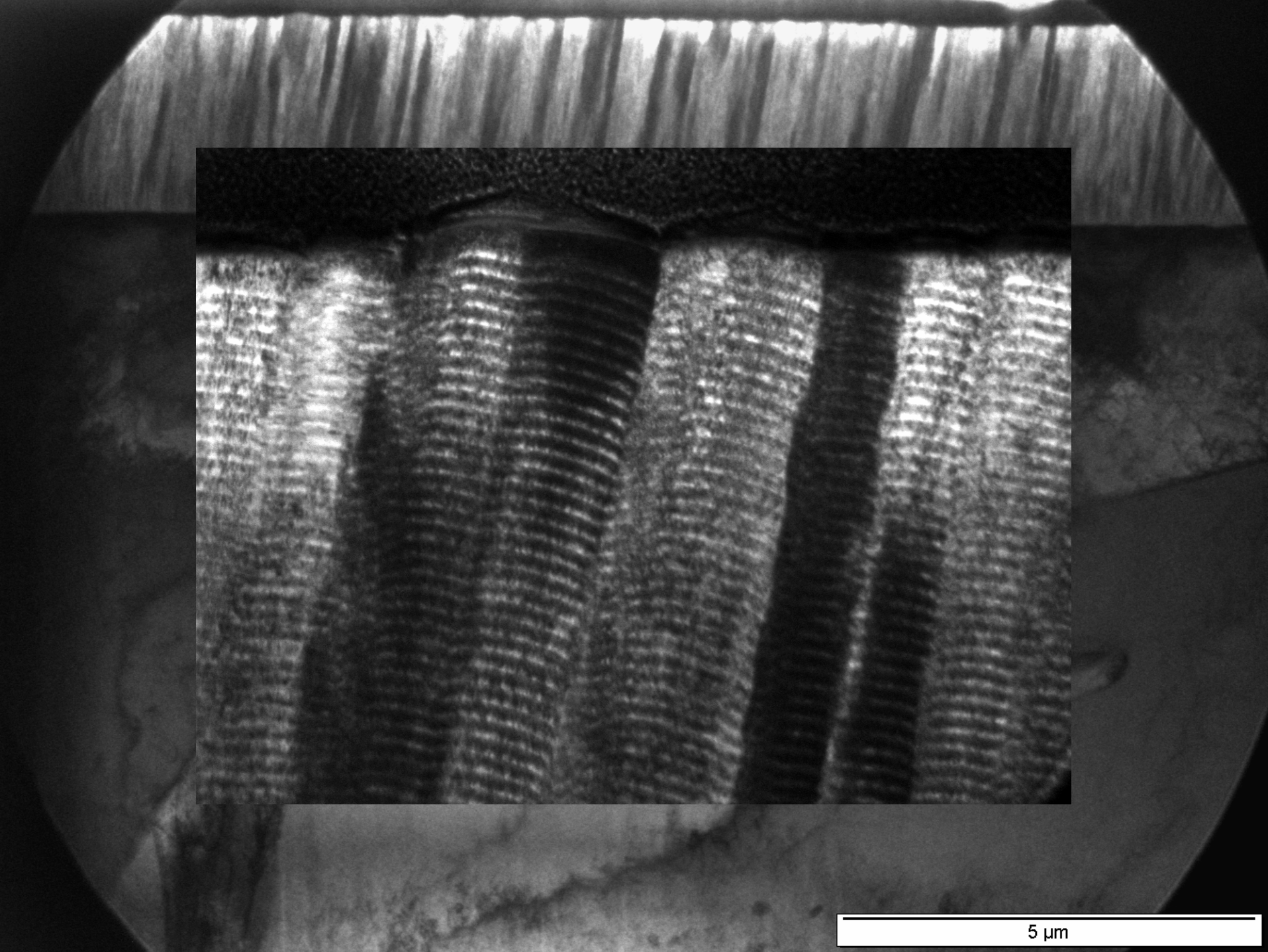
Podniesienie wytrzymałości:
(„przecwzużyciowe”)

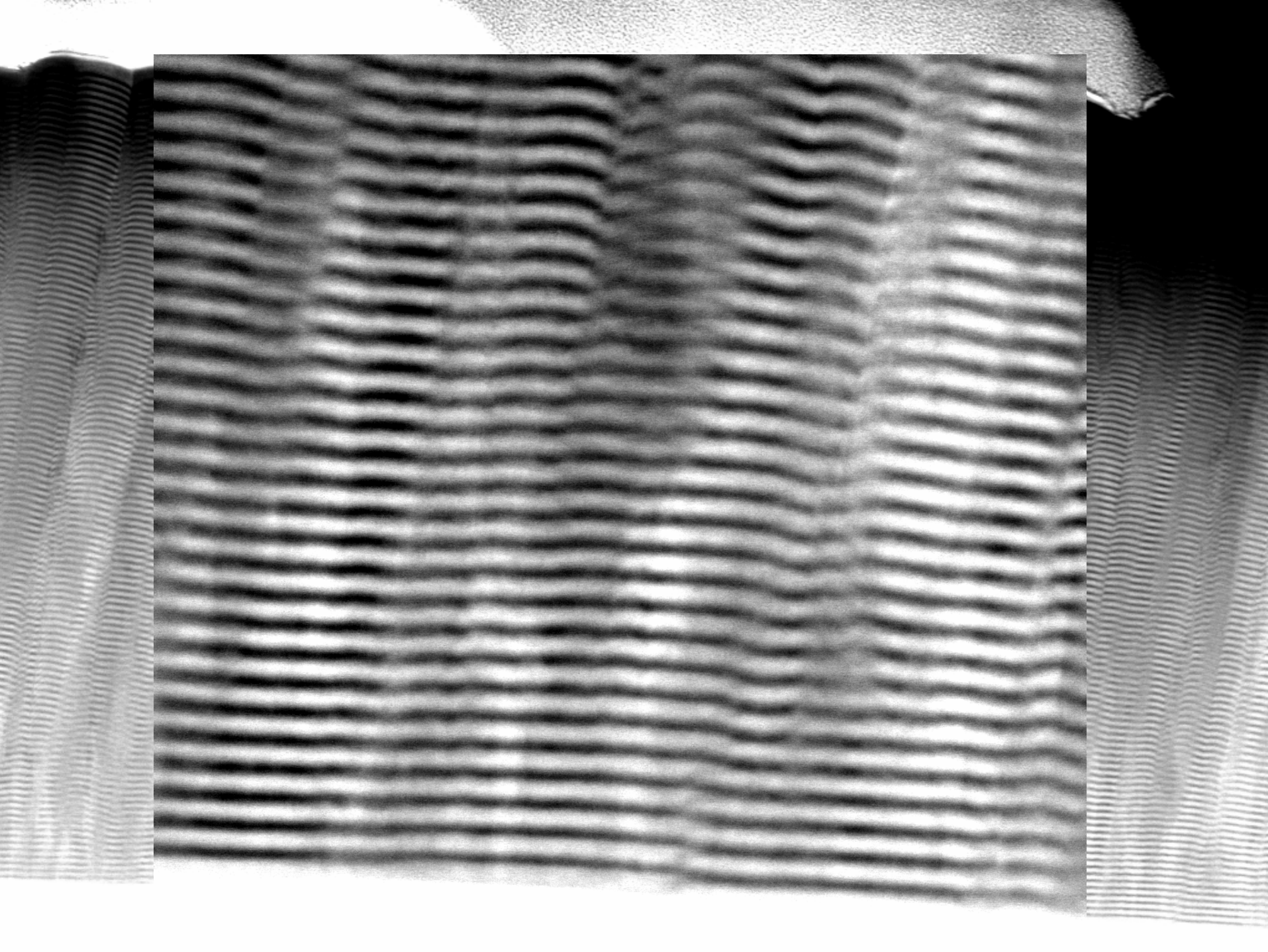
- **CuNi 5 / 5 nm**
  (Paweł Wieczorek/
  Politechnika Częstochowska)

Ana Sofia Ramos
Mechanical Engineering Department
Polo II,
University of Coimbra

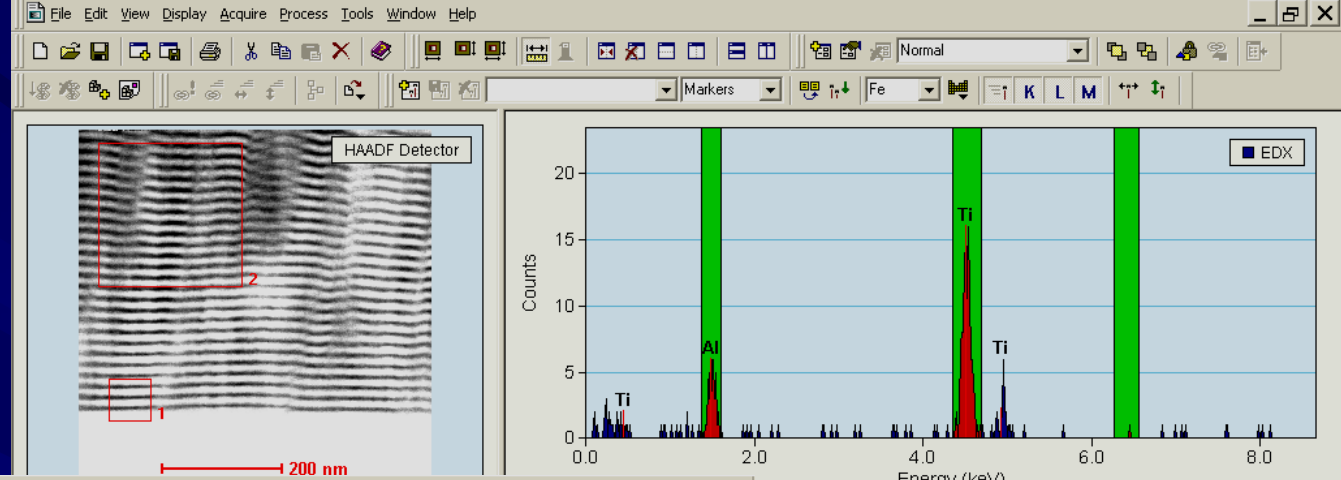
TiAl / 20 nm

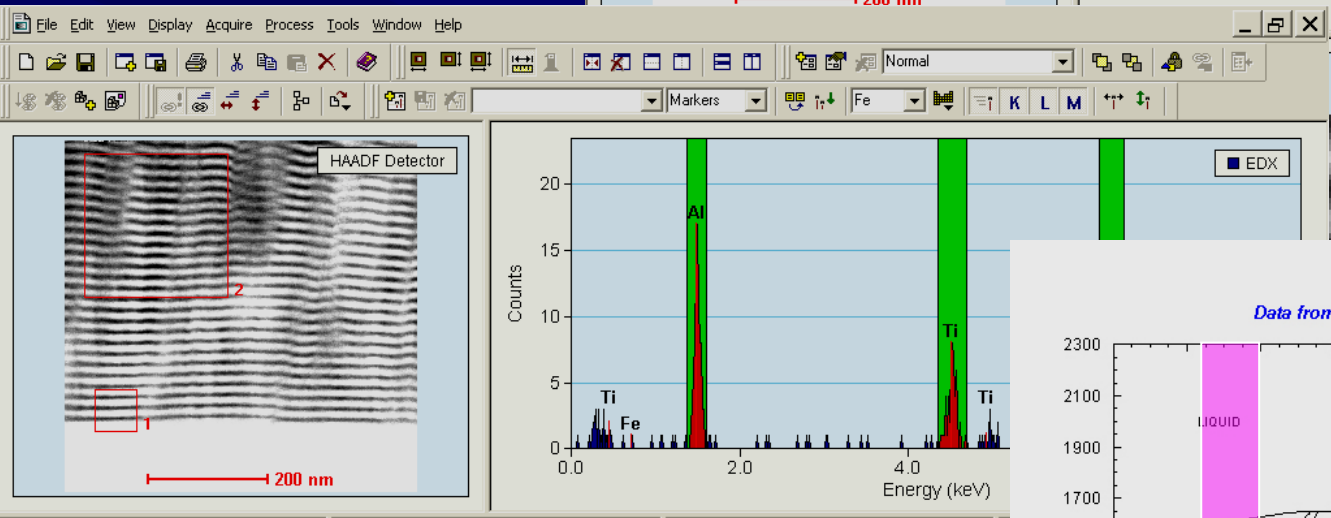


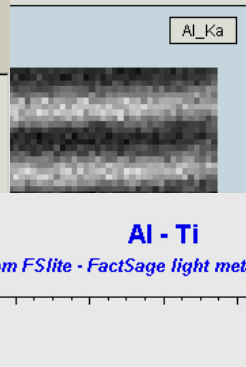

5 µm

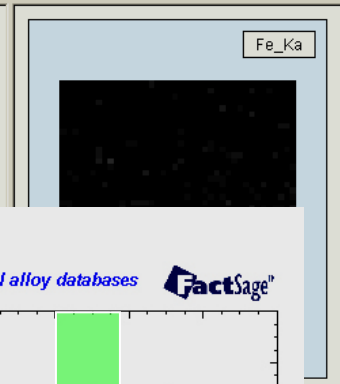


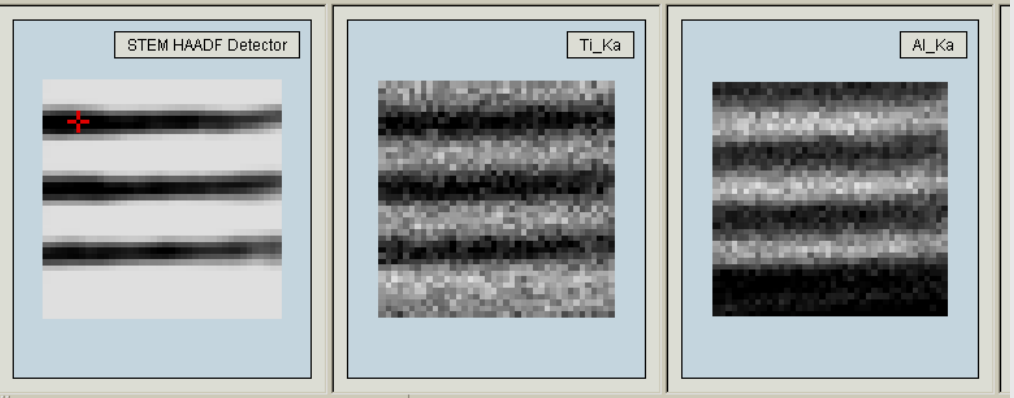
EDS / mappings

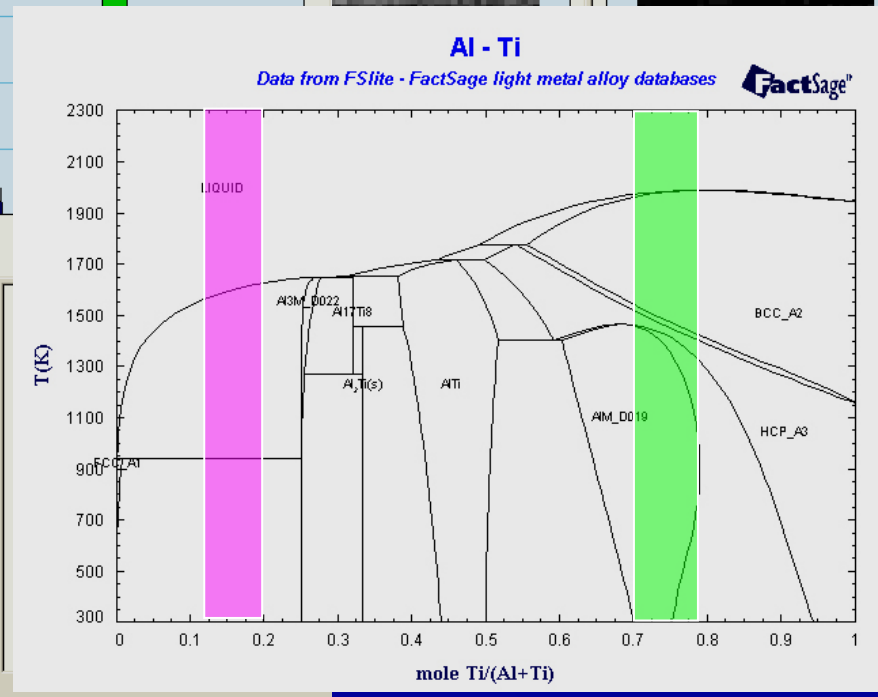












Ready

Wielowarstwy Cu/Me

Deposition method

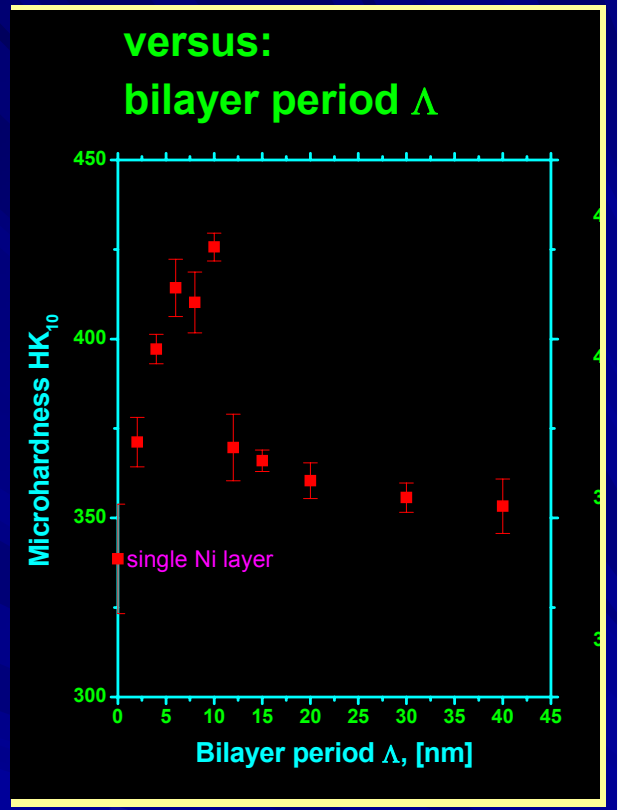
- *single solution, potentiostatic electrodeposition*

Substrates:

- n-type Si (100) Sb - 2×10^{18} 1/cm^3, resistivity - 0.017 Ω·cm
- polycrystalline Cu (99,9 %)

Multilayer system	Bath compsition
Cu/Ni	1.5 M $Ni(SO_3NH_2)_2$ + 0.01 M $CuSO_4$ + 0.5 M H_3BO_3
Co/Cu	1,4 M $CoSO_4$ + 0.008 M $CuSO_4$ + 0,64 M H_3BO_3
NiFe/Cu	0.5 M $Ni(SO_3NH_2)_2$ + 0.01 M $CuSO_4$ + 0.04 M $FeSO_4$ + + 0.4 M H_3BO_3

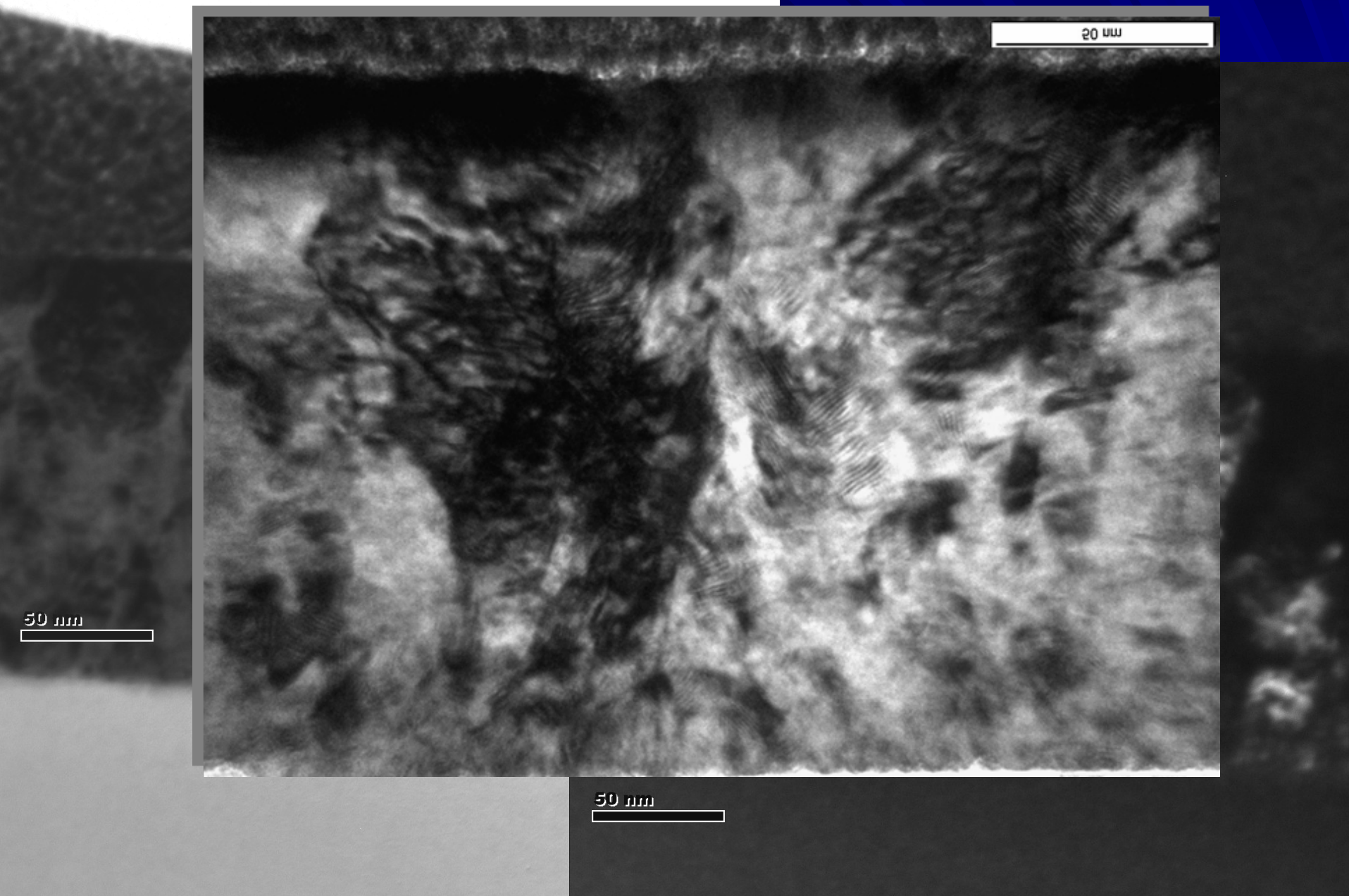
Nr	Multilayer system	Subst.	t_{Cu} [nm]	$t_{Ni, Co, NiFe}$ [nm]	Λ [nm]	n	E_{Cu} [mV]	E_{Ni} [mV]
T14	Cu/Ni	Cu	10	10	20	150	-500	-1300
T98	Cu/Ni	Si	5	5	10	20	-500	-1300
P37	Cu/Co	Si	5	5	10	20	-600	-1200
N11	Cu/NiFe	Si	4	4	8	20	-500	-1200

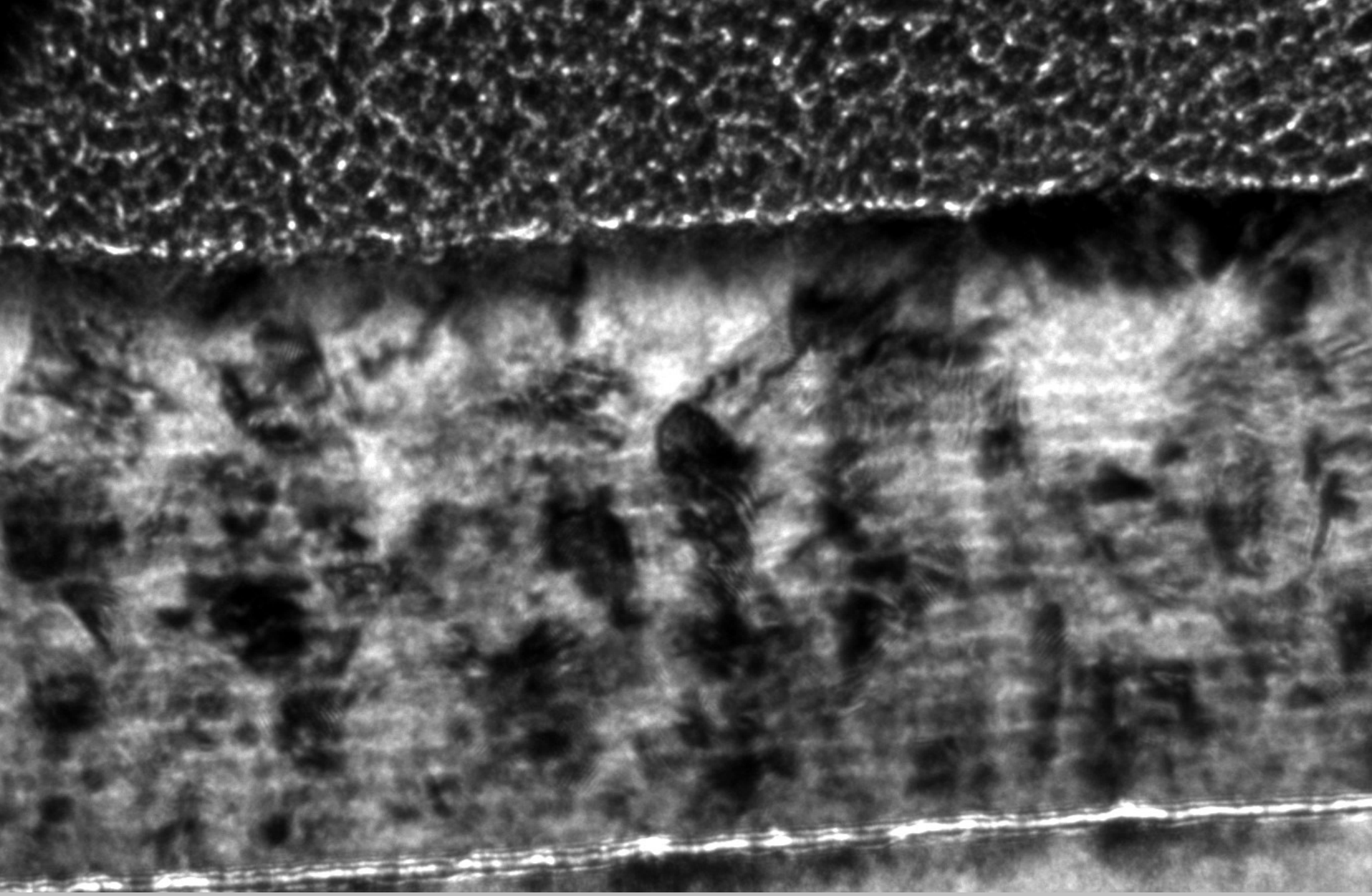


Paweł Wieczorek

Philips CM20

CuNi, 5/5nm (Λ=10nm)

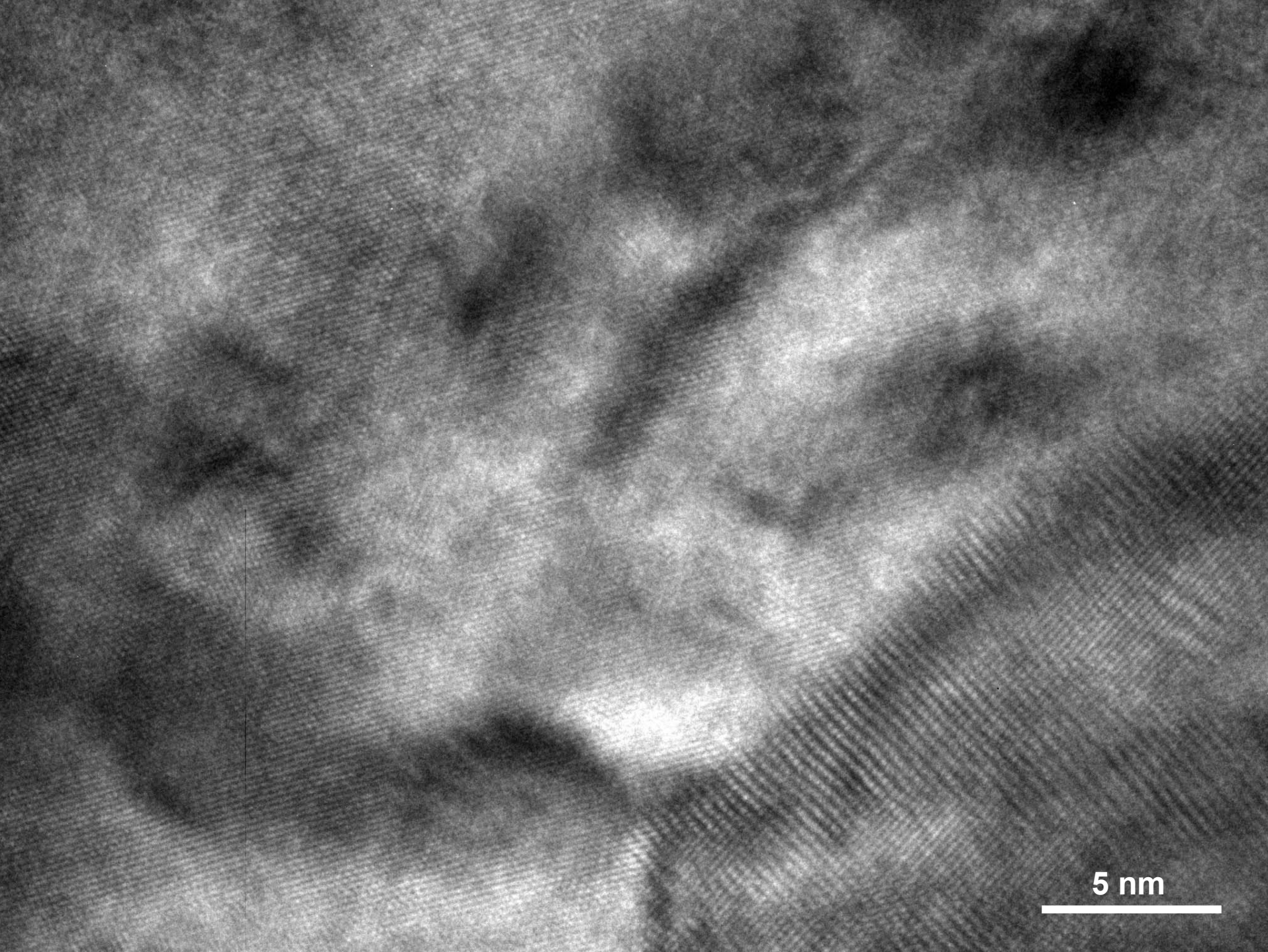


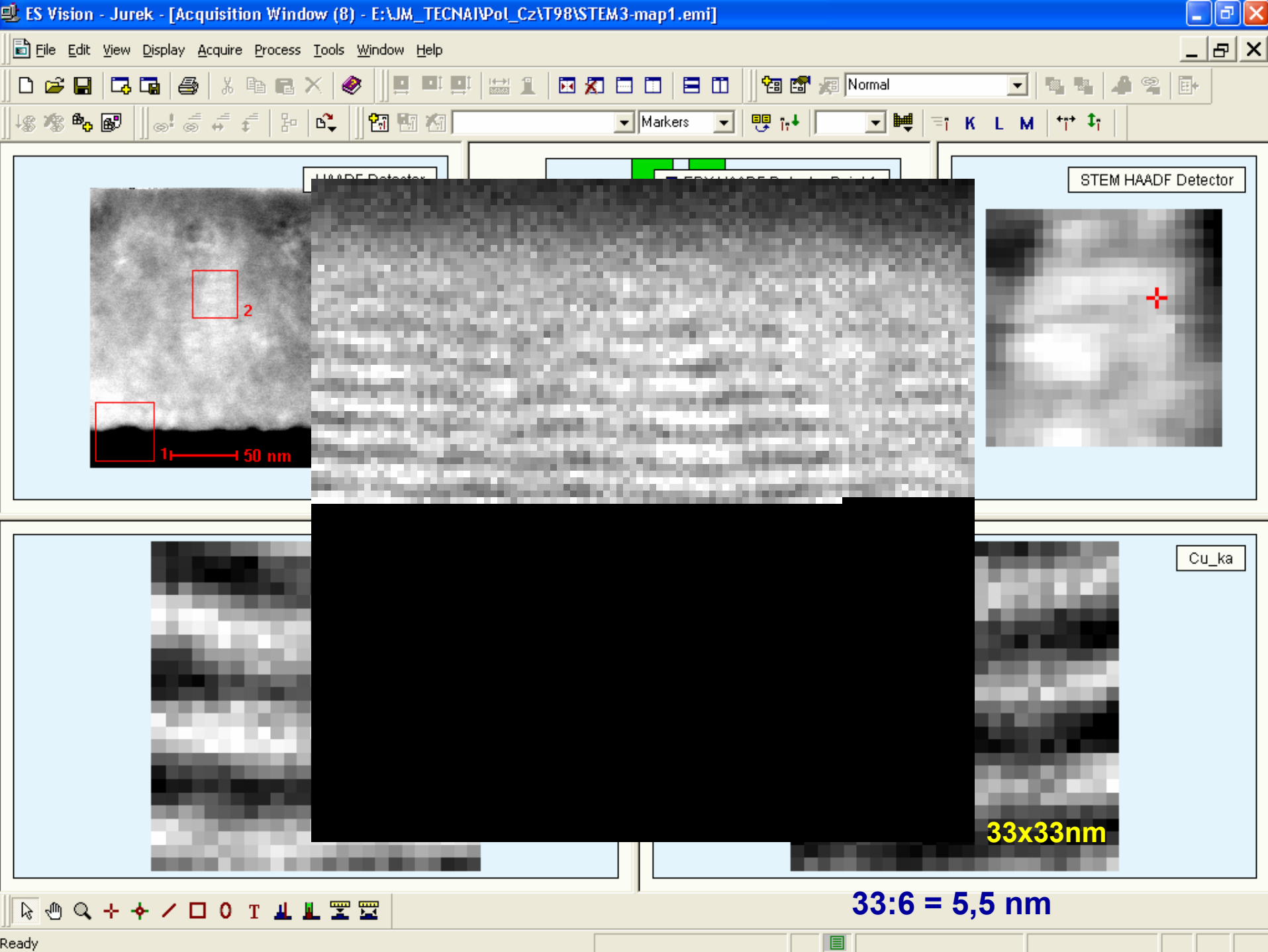


Physics of X-ray Multilayer Structures Technical Digest, ***7*** *(1992) 94-96.*

Effects of Fresnel Fringes on TEM Images of Interfaces in X-Ray Multilayers

Tai D. Nguyen, Michael A. O'Keefe, Roar Kilaas, Ronald Gronsky, Jeffrey B. Kortright


5 nm


ES Vision - Jurek - [Acquisition Window (8) - E:\JM_TECNAI\Pol_Cz\T98\STEM3-map1.emi]
File Edit View Display Acquire Process Tools Window Help
Normal
Markers
K L M
STEM HAADF Detector
2
1
50 nm
Cu_ka
33x33nm
33:6 = 5,5 nm
Ready

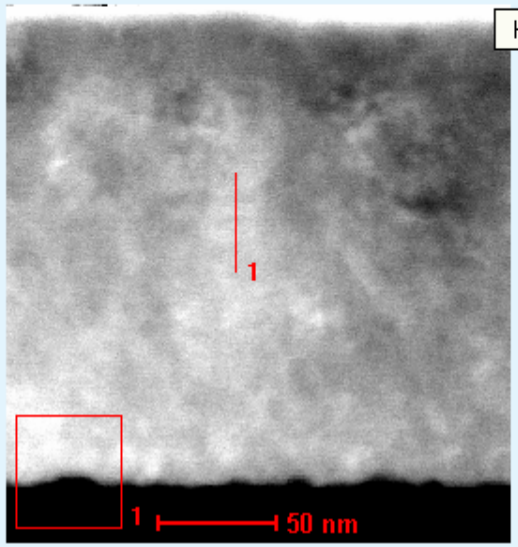
File Edit View Display Acquire Process Tools Window Help

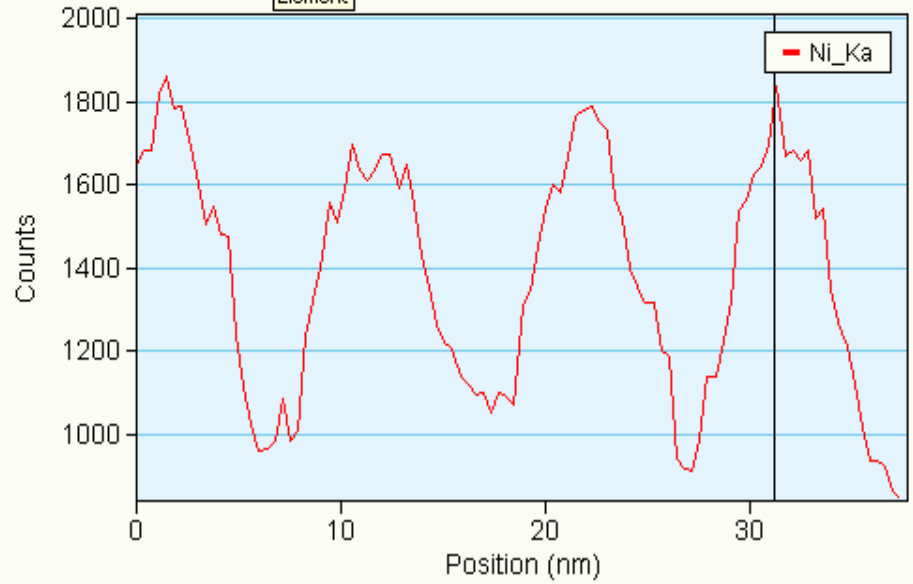
Normal

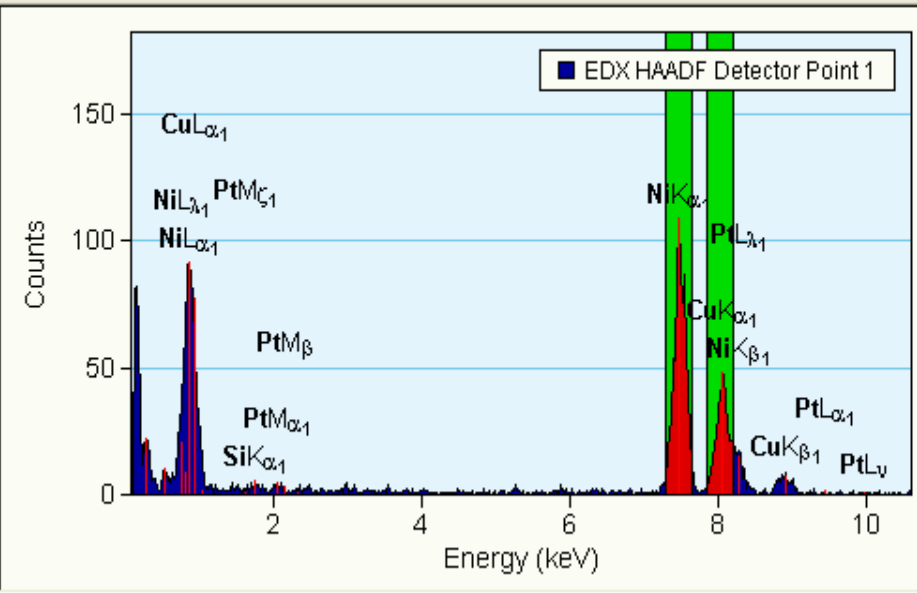
Markers

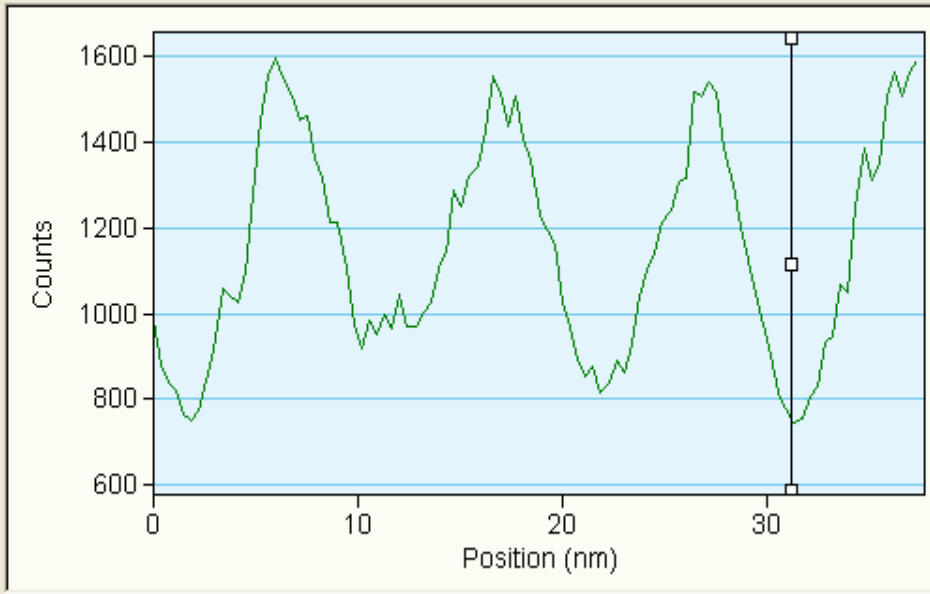
Element

K L M









Cz. III. Wielowarstwy

- podsumowanie

Problemy rozwiązane:

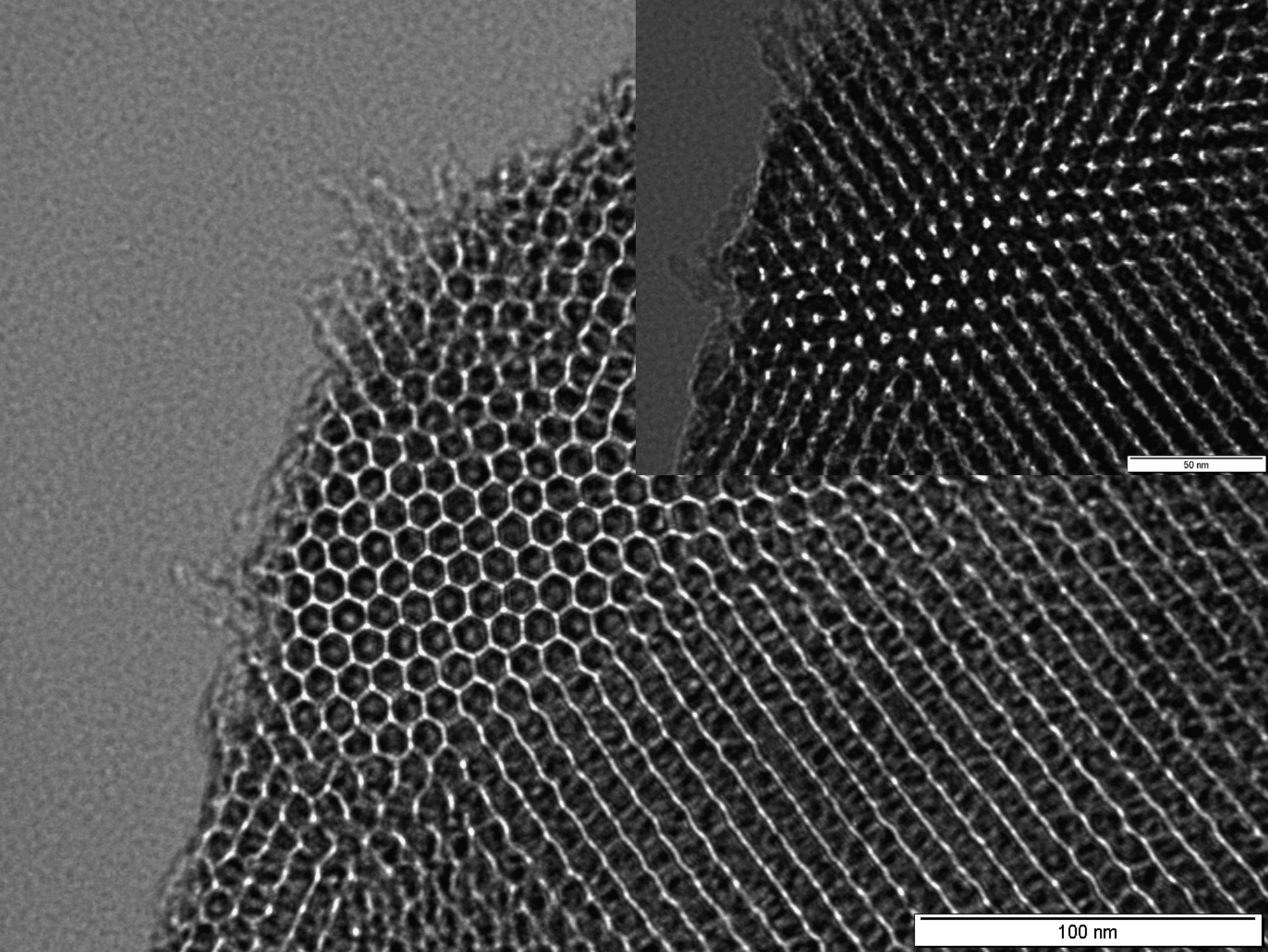
- **Opisano mikrostrukturę, skład fazowy i jakościowo skład chemiczny powłok n(Ti/Al) oraz n(Cu/Me)**

Problemy do podjęcia:

- **Analiza defektów układu warstw**
- **Ilosciowa ocena lokalnego składu chemicznego**

Convergence **Ro**utes for **Na**nomaterials **Ch**aracterization (odrzucony)

HArd **N**ano**CO**mposite **C**oatings (zgłoszony)


50 nm
100 nm