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Winter College on Optics and Energy

8 - 19 February 2010

Nanostructured inorganic thin films in solar energy conversion
Part I: Vacuum deposited selective absorber coatings

A. Schuler

Ecole Polytechnique Federale De Lausanne
Switzerland

Nanostructured inorganic thin films in solar energy conversion

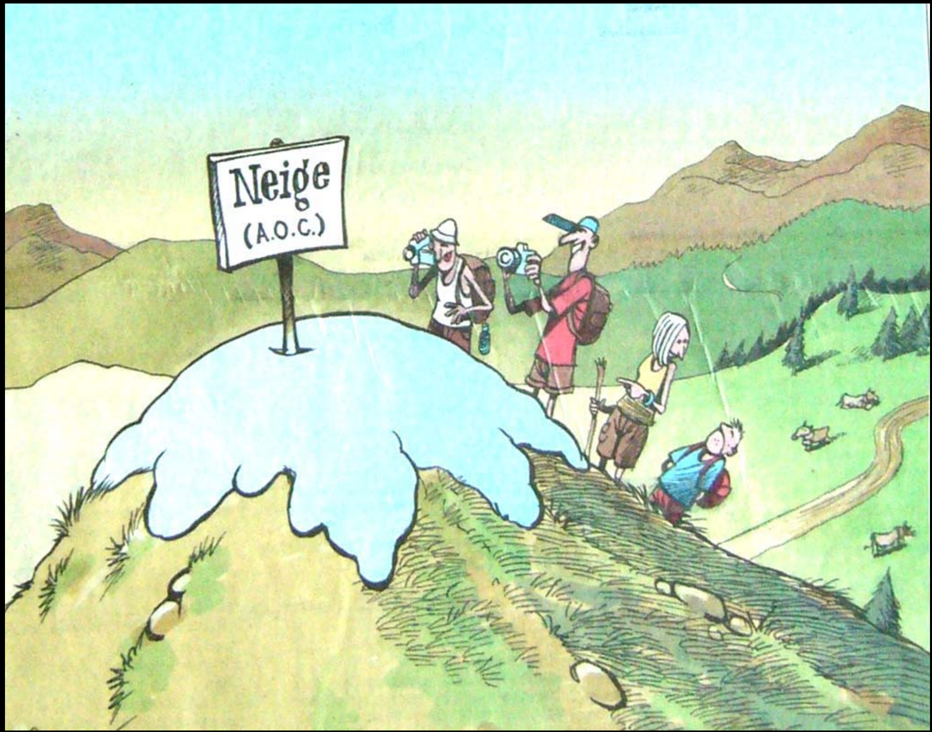
Part I: Vacuum deposited selective absorber coatings

Andreas Schüler

Ecole Polytechnique Fédérale de Lausanne
Solar Energy Laboratory LESO

LESO-PB
LABORATOIRE D'ENERGIE SOLAIRE
EPFL
ÉCOLE POLYTECHNIQUE FÉDÉRALE DE LAUSANNE

Climate Change



Swiss Perspective: Melting Glaciers

Grindelwaldgletscher, OcCC/ProClim, 2007.

Approaches in Nanotechnology

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UV, X-ray lithographies
« top-down »

manipulation of atoms by AFM/STM-tips
« bottom-up »

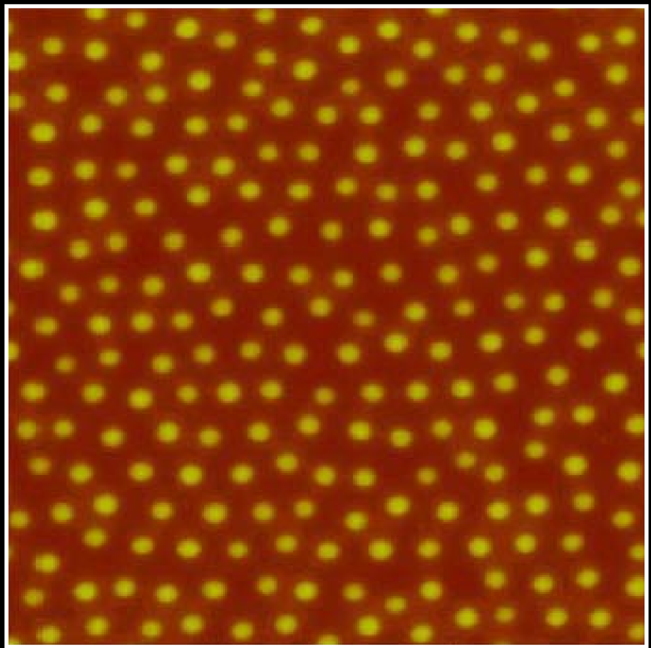
self-organized growth of nanostructures (e.g. nanocomposite thin films)

parallel processes

building up atom by atom

Nanometer-sized metal clusters

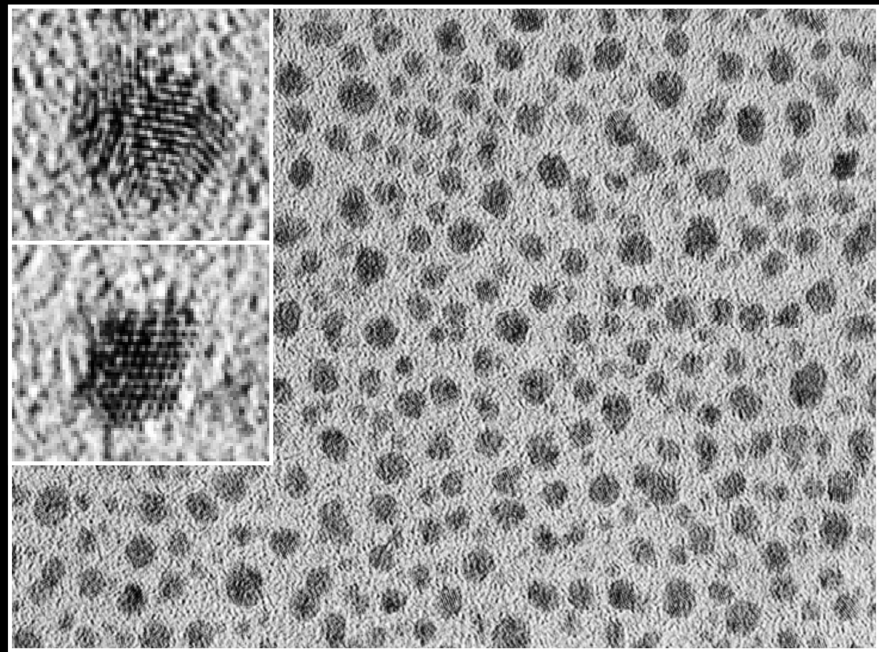
on substrates



AFM of Au clusters deposited by micellar method

H.G. Boyen, G. Kästle, F. Weigl, B. Koslowski, C. Dietrich, P. Ziemann, J.P. Spatz, S. Riethmüller, C. Hartmann, M. Möller, G. Schmid, M.G. Garnier, P. Oelhafen, Science 297, 1533 (2002)

in thin films



HRTEM of a-C:H/Au

P. Oelhafen, A. Schüler, Solar Energy 79, 110 (2005)

Solar energy applications of nanostructured materials

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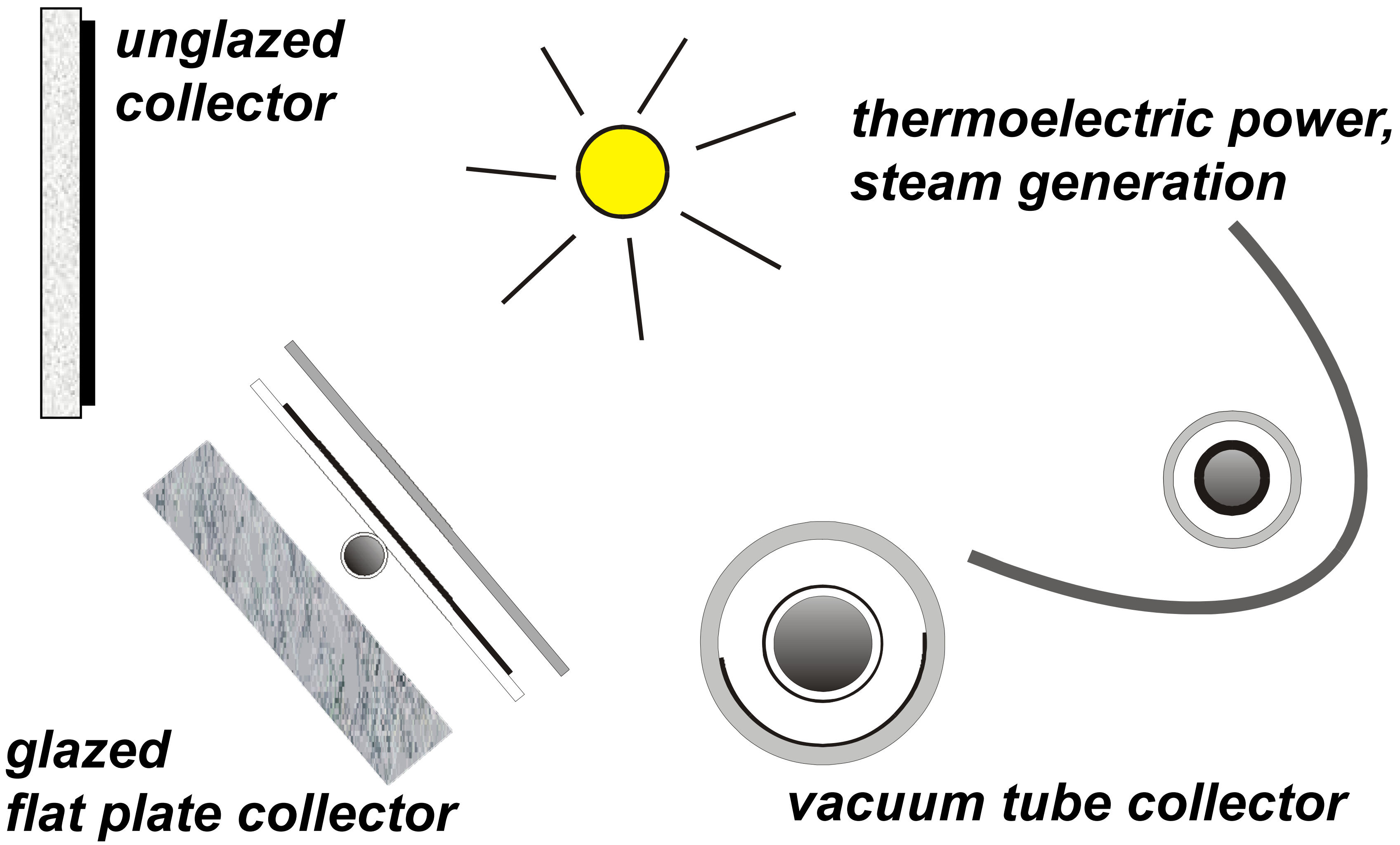
Examples from our work:

- nanopores: anti-reflection coatings on collector glazing
- dielectric nanocrystals: colored coatings for solar thermal facades
- semiconductor nanocrystals:
  quantum dot solar concentrators for photovoltaics
- metallic clusters: selective solar absorbers

…and there are many more applications…

switchable optical coatings, quantum well solar cells, dye-sensitized solar cells, carbon nanotube containing polymeric PV cells, ...

Thermal solar energy



Parabolic trough collectors for thermoelectric power generation

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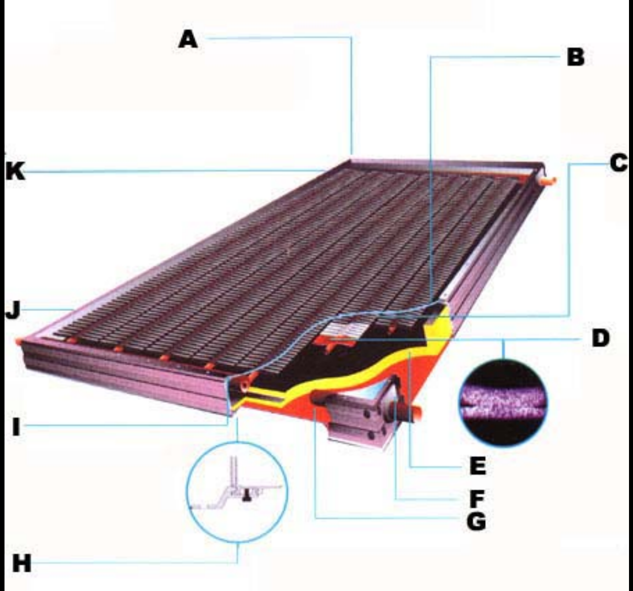
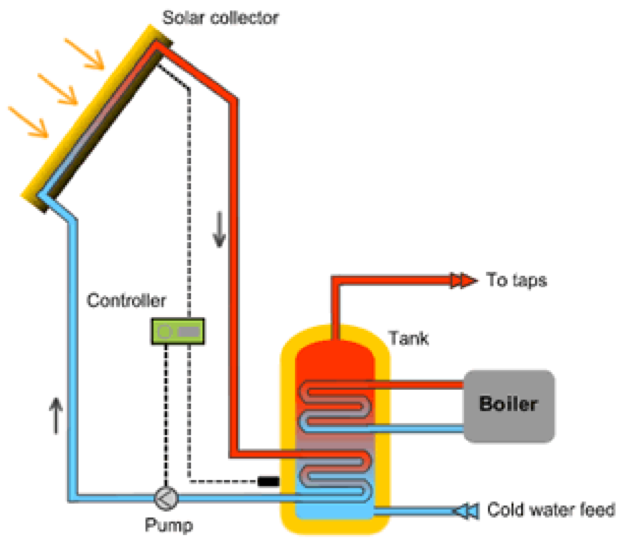
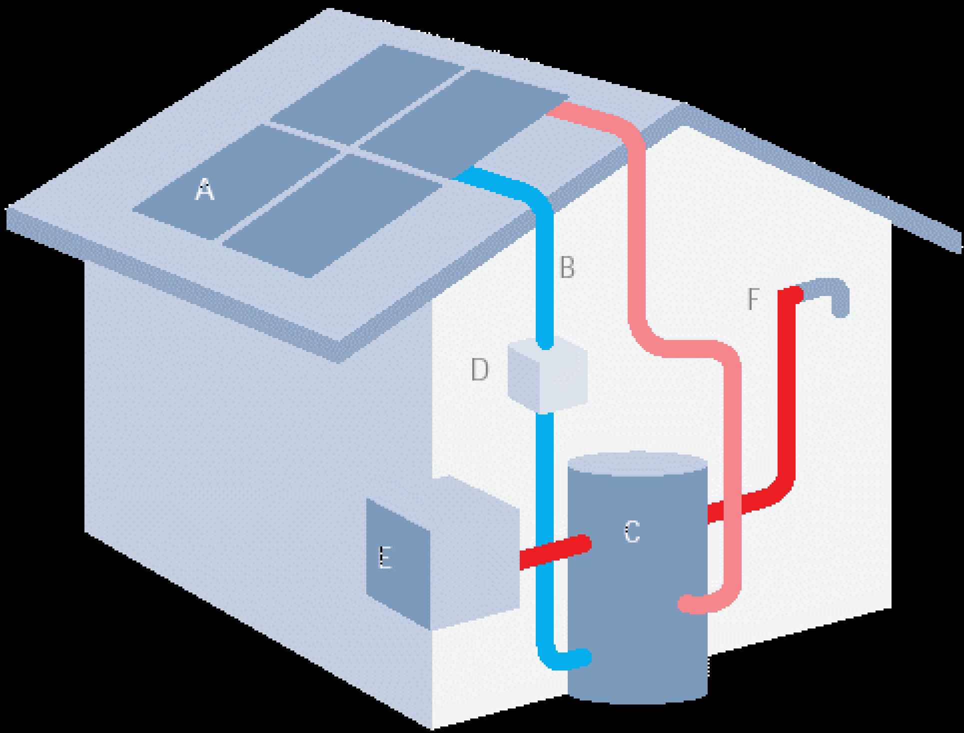
Space heating and domestic hot water production







Glazed facade collectors

U p p e r s t a g e   c e n t r e

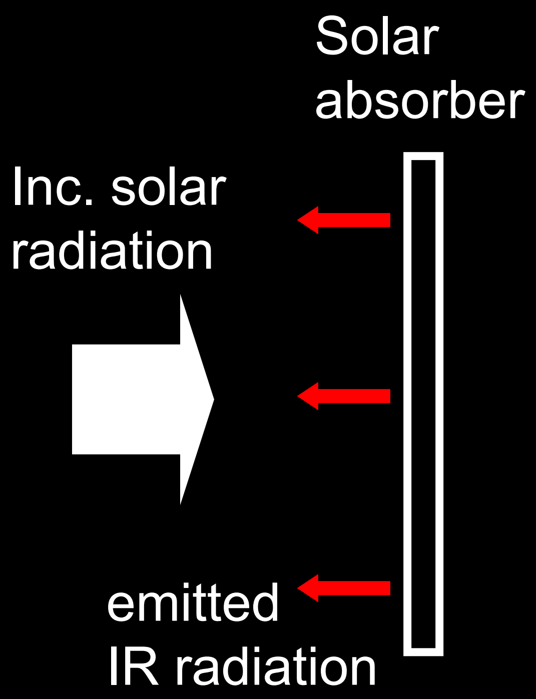
source: questionnaire SOLABS

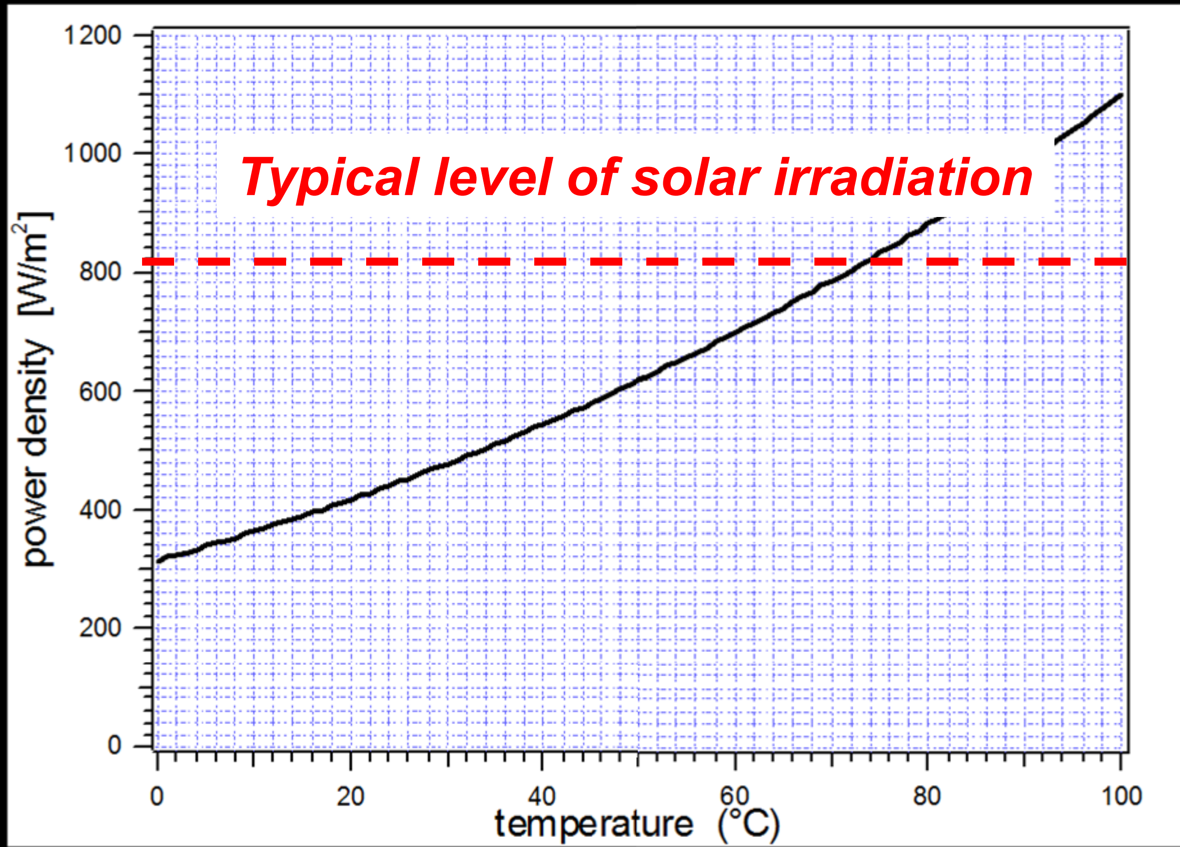
Unglazed roof collectors

E n e r g i e   S o l a i r e   s . a .

source: questionnaire SOLABS

Solar thermal collectors and Stefan's law

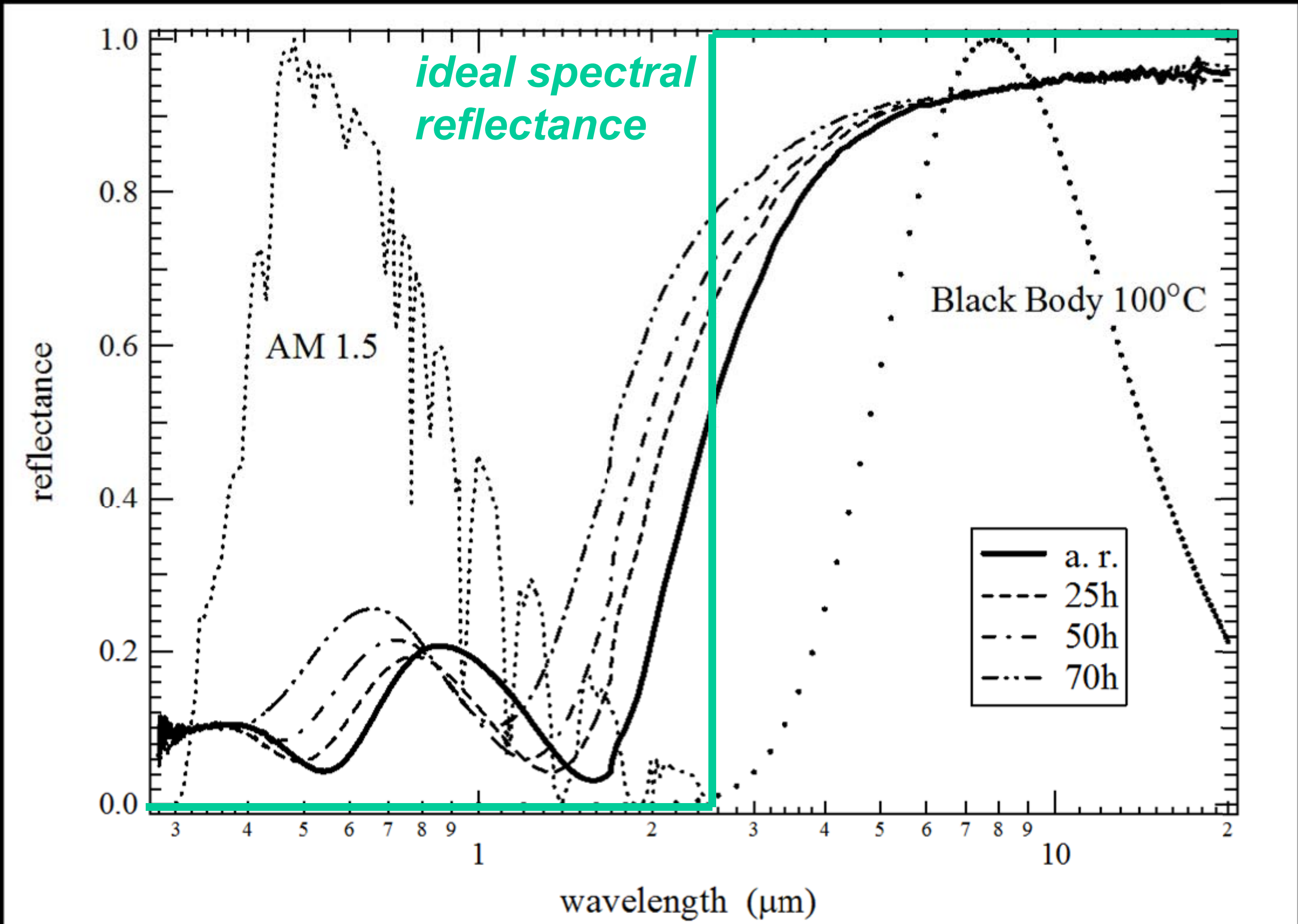




$$E = \sigma T^4 \ \ [W/m^2]$$

$$\sigma = 6.67\ 10^{-8}\ \ [W/m^2\,K^4]$$

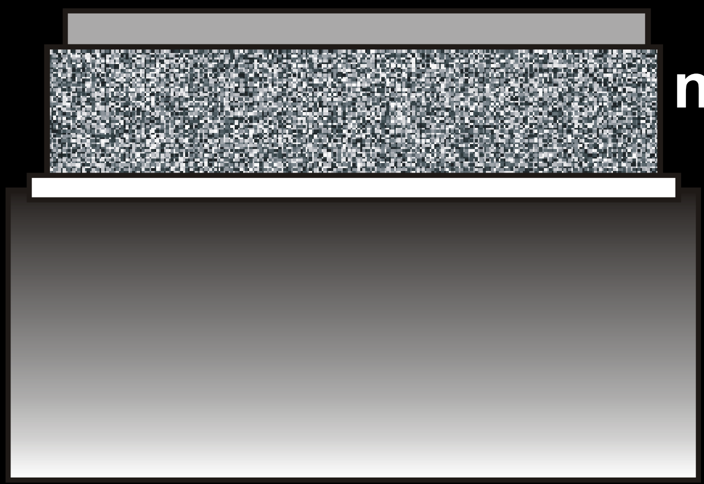
Optical selective solar absorber coating



coating based on a-C:H/Ti,
(accelerated aging @ 250°C)

A. Schüler et al., SEMSC (2001)

Multilayered solar absorber coating



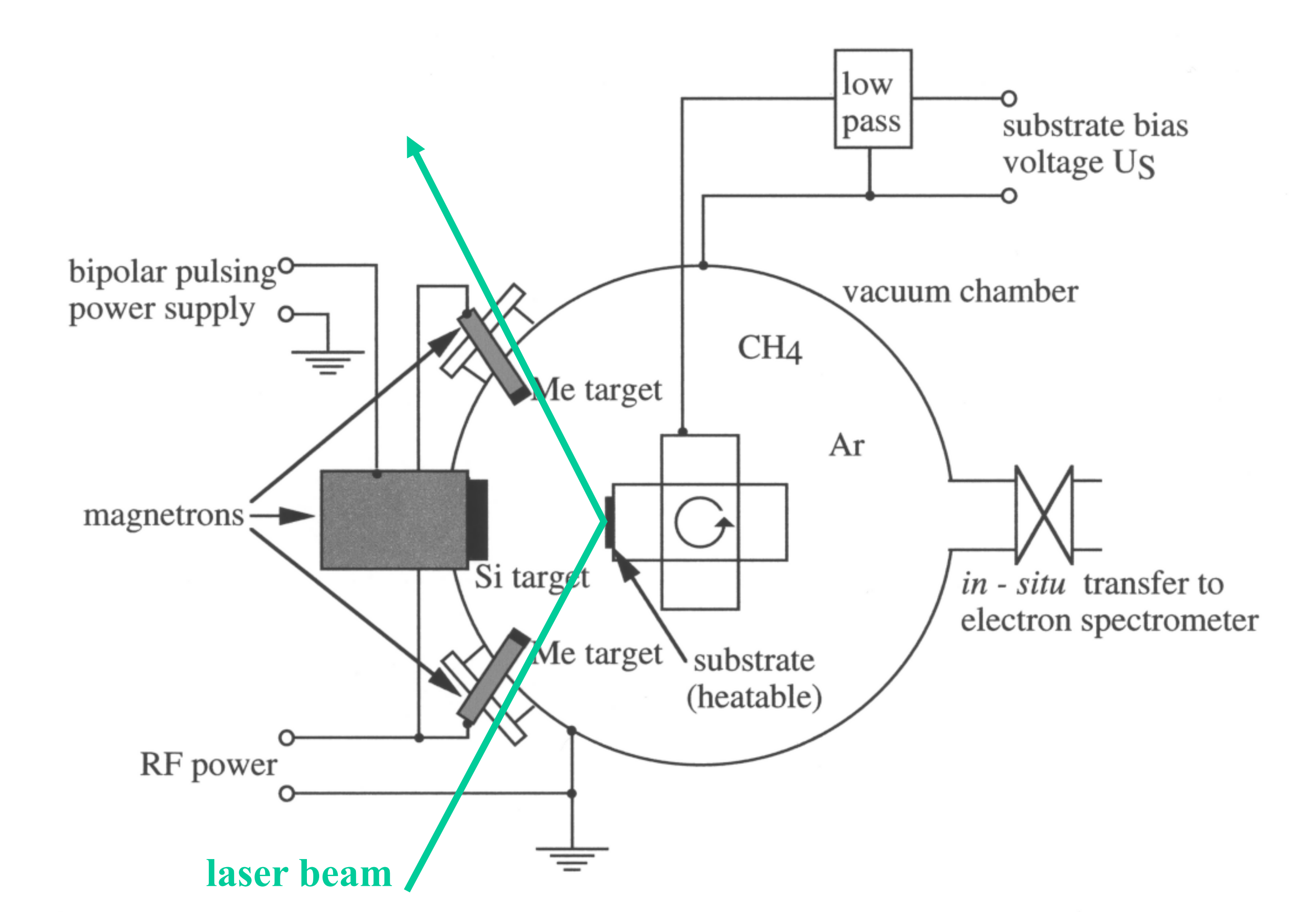
oxidation barrier (water repellent)

nanocomposite absorber layer

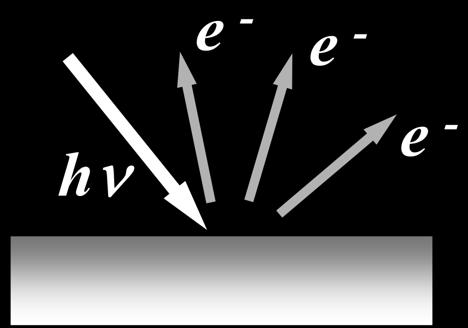
interlayer for good adhesion
and as diffusion barrier

infrared – reflecting
metal sheet (Al, Cu)

Vacuum deposition:
Reactive magnetron sputtering



In-situ photoelectron spectroscopy

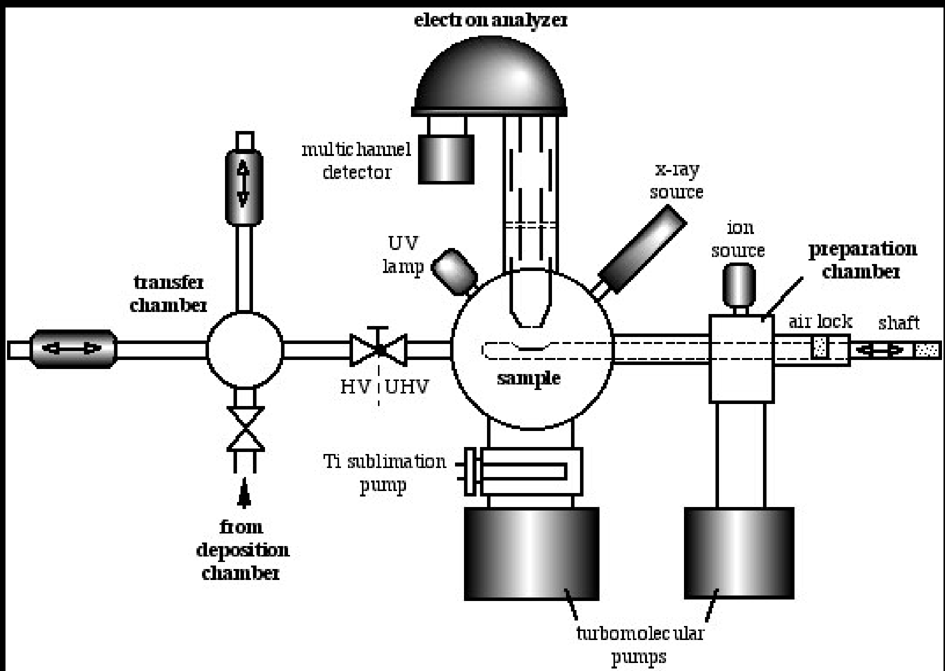


Excitation with X-rays (XPS):

- core levels
- atom concentrations
- chemical shifts
- characteristic energy losses

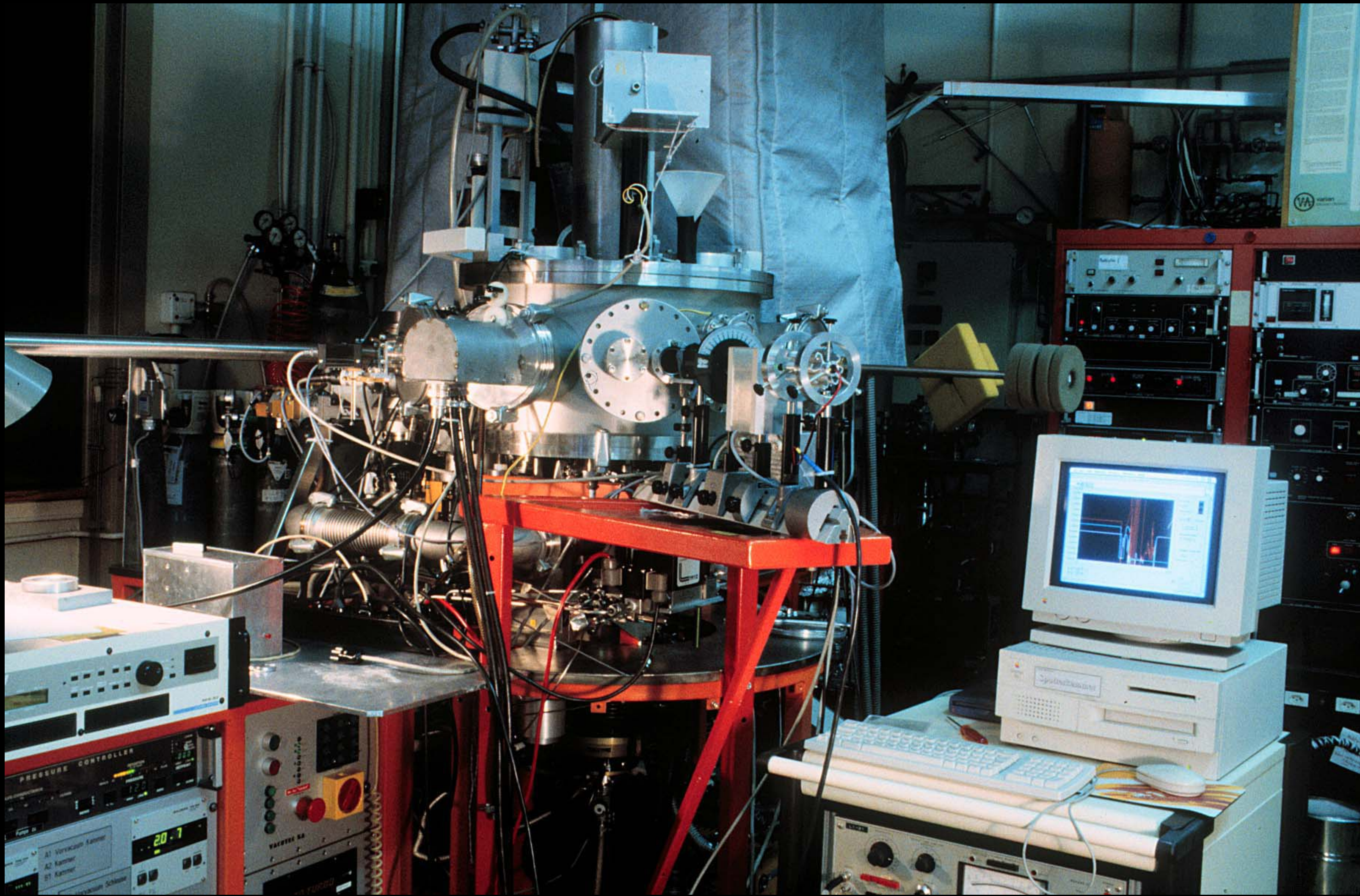
UV excitation (UPS):

- valence band
- extremely surface sensitive
- need for in-situ experiments (sample transfer in vacuum)

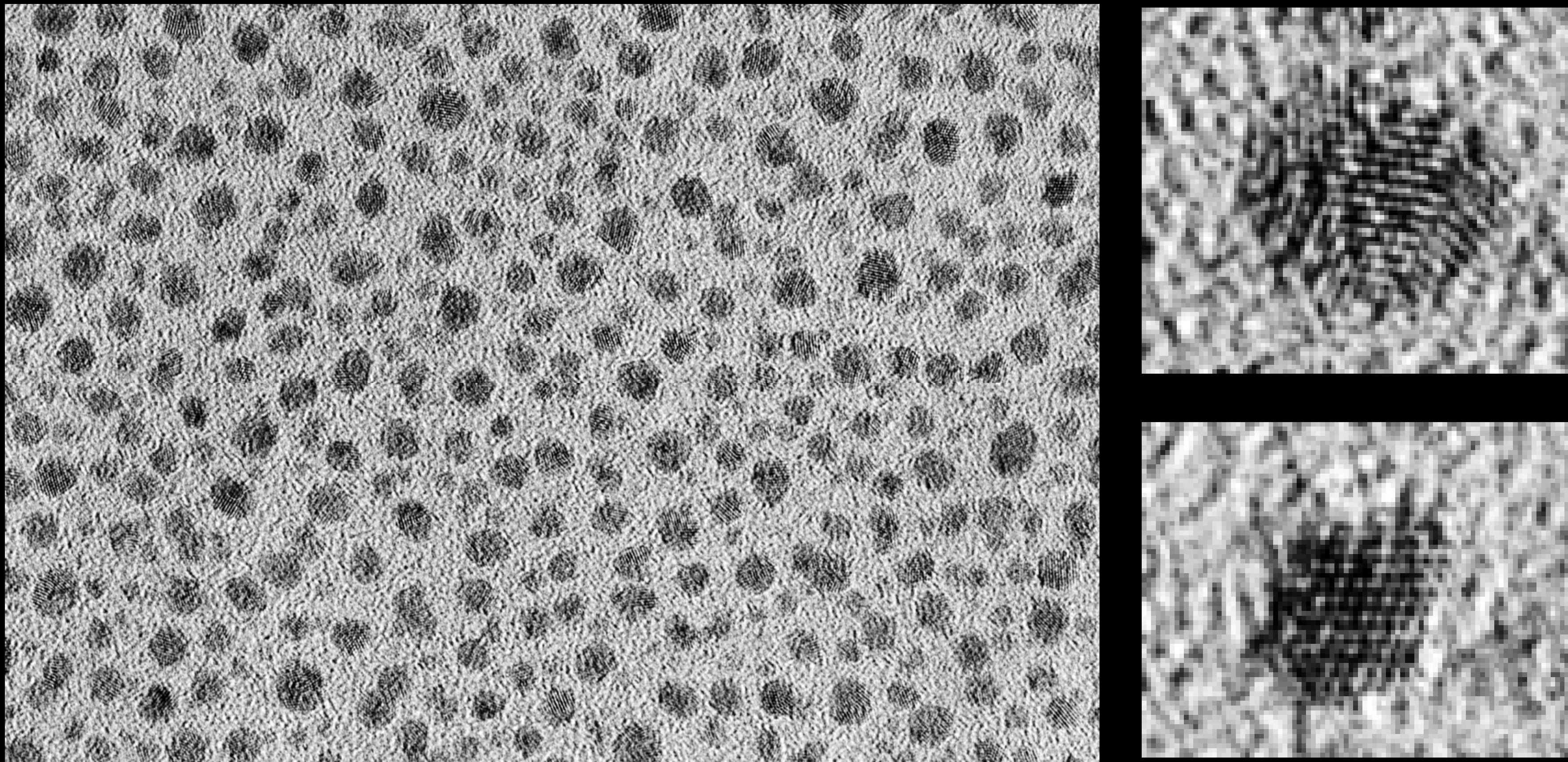


LEYBOLD EA10/100 MCD

View of experimental setup



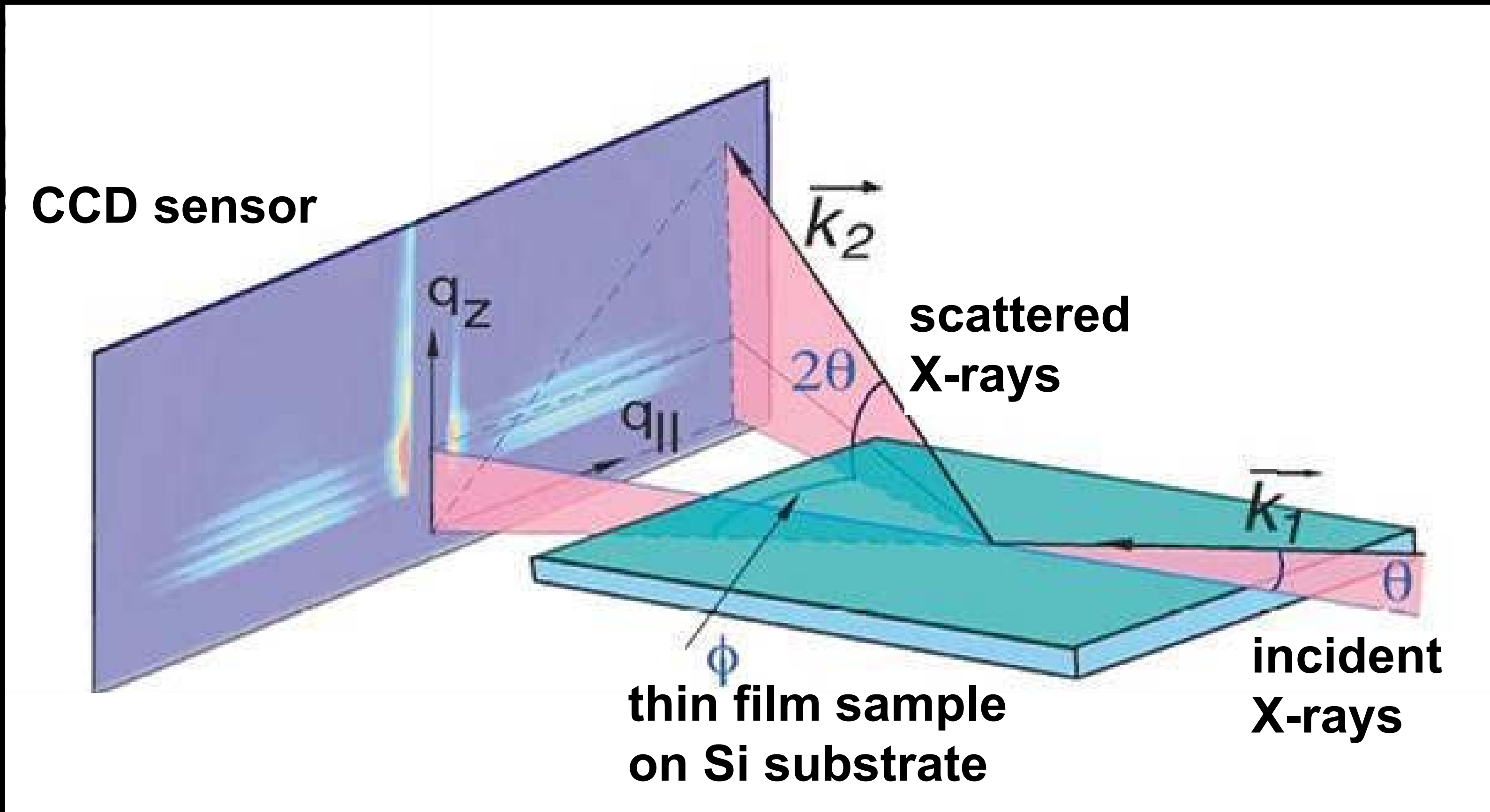
Nanostructured thin films a-C:H/Au



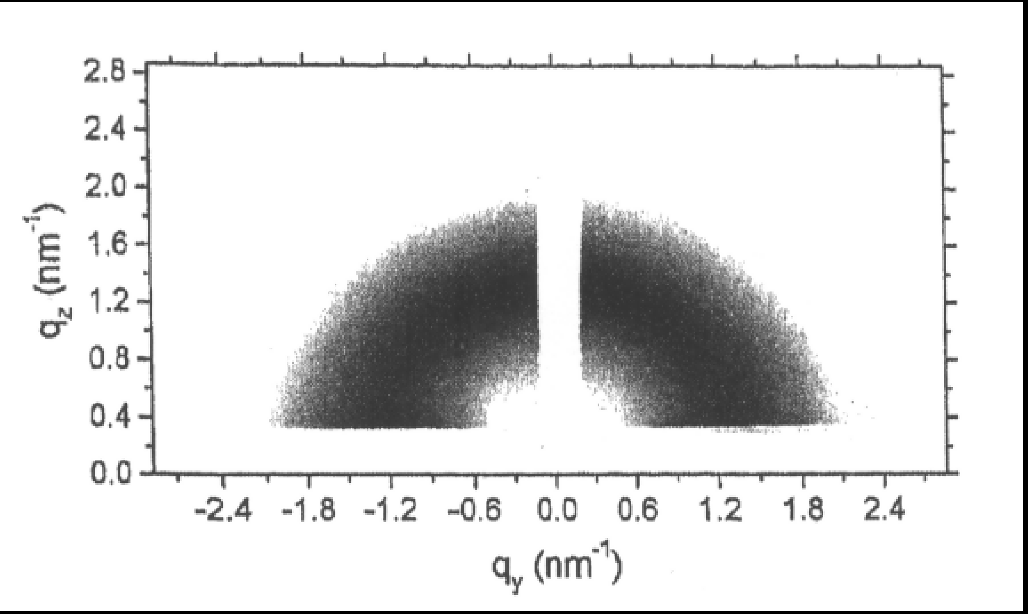
HRTEM of a-C:H/Au

Gampp, Portmann

Grazing Incidence Small Angle X-ray Scattering GISAXS: principle



Structural information in third dimension



GISAXS of a-C:H/Au

(grazing incidence small-angle X-ray scattering, synchrotron radiation 9 keV)

Babonneau et al., PRB 63 (2001)

films are to a good approximation isotropic

- oblate and prolate ellipsoidal clusters, but rather close to spherical shape

- correlation distance between clusters isotropic

Optical material constants

The complex symmetric dielectric tensor in general :

$$D_k = \sum_l \varepsilon_{kl} E_l$$

In principal axis :

$$D_x = \varepsilon_x E_x \qquad D_y = \varepsilon_y E_y \qquad D_z = \varepsilon_z E_z$$

In isotropic media :

$$\vec{D} = \varepsilon \vec{E}$$

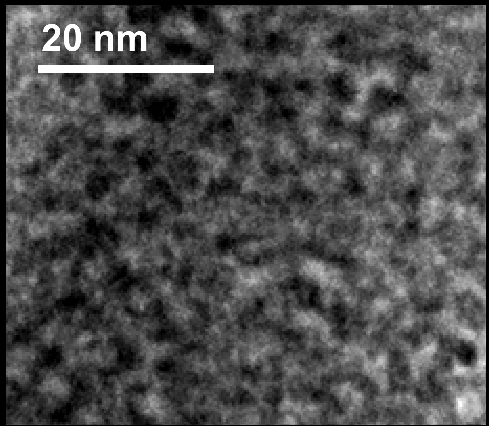
The complex refractive index :

$$N = n - ik = \sqrt{\varepsilon}$$

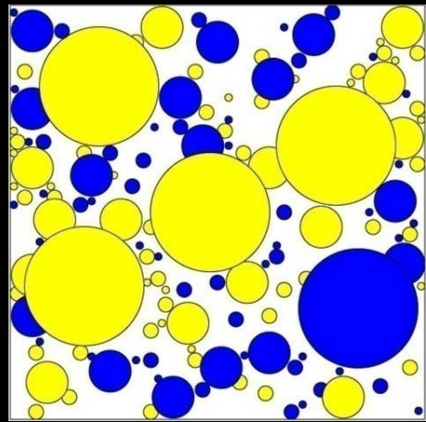
The absorption coefficient in Beer's law:

$$I(x) = I_0 e^{-\alpha x} \qquad \alpha = \frac{4\pi}{\lambda} k$$

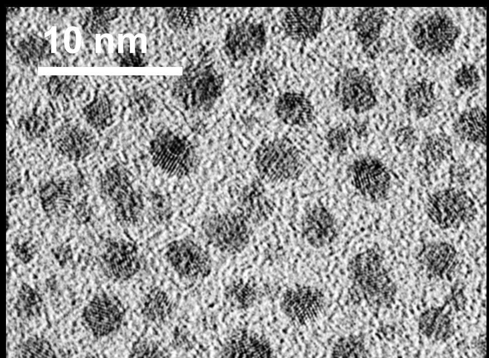
Effective medium theories



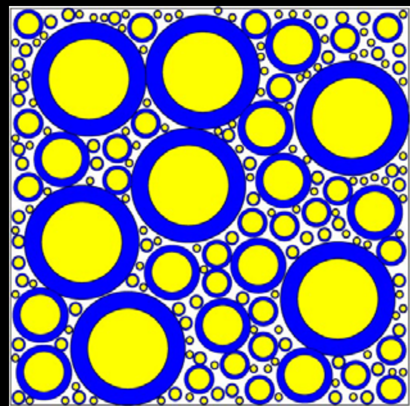
TEM of TiO_2:SiO_2 nanocomposite film



model structure Bruggeman type

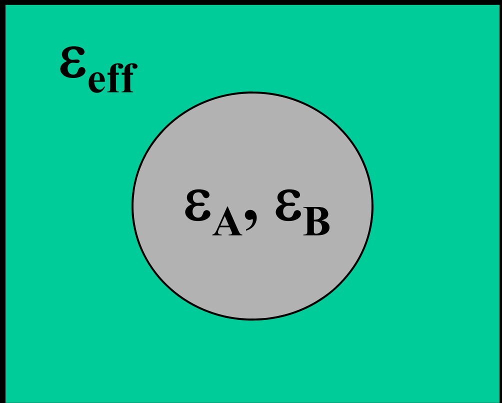


HTEM of Au clusters in a-C:H film



model structure Ping Sheng type

Bruggeman theory



the symmetric approach with respect to permutation of materials A and B yields

$$f_A * \frac{\varepsilon_A - \varepsilon_{eff}}{\varepsilon_A + 2\,\varepsilon_{eff}} + (1 - f_A) * \frac{\varepsilon_B - \varepsilon_{eff}}{\varepsilon_B + 2\,\varepsilon_{eff}} = 0$$

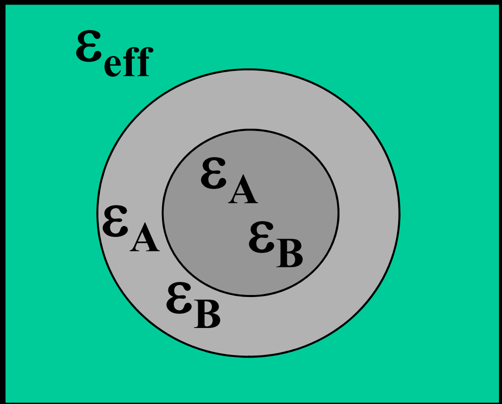
probability f_A of being A

probability $1\text{-}f_A$ of being B

high filling factors possible,
but no internal interfaces between A and B,
surface plasmon resonance?

Bruggeman, Ann. Phys. 5 24, 236 (1935)

Ping-Sheng theory



ratio of volumes determines f_A

probability $(1-f_A^{1/3})^3$ of being A with shell of B

probability $(1-(1-f_A)^{1/3})^3$ of being B with shell of A

Ping Sheng, Phys. Rev. Lett. 45, 60 (1980)

Niklasson et al., J. Appl. Phys. 55, 3382 (1984)

symmetric approach:
high volume fractions f_A and f_B

$$v_1 * \frac{(\varepsilon_B - \varepsilon_{eff})(\varepsilon_A + 2\varepsilon_B) + f_A(2\varepsilon_B + \varepsilon_{eff})(\varepsilon_A - \varepsilon_B)}{(\varepsilon_B + 2\varepsilon_{eff})(\varepsilon_A + 2\varepsilon_B) + 2 f_A(\varepsilon_B - \varepsilon_{eff})(\varepsilon_A - \varepsilon_B)}$$

$$+ v_2 * \frac{(\varepsilon_A - \varepsilon_{eff})(\varepsilon_B + 2\varepsilon_A) + (1 - f_A)(2\varepsilon_A + \varepsilon_{eff})(\varepsilon_B - \varepsilon_A)}{(\varepsilon_A + 2\varepsilon_{eff})(\varepsilon_B + 2\varepsilon_A) + 2(1 - f_A)(\varepsilon_A - \varepsilon_{eff})(\varepsilon_B - \varepsilon_A)} = 0$$

with

$$v_1 := (1 - f_A^{1/3})^3 \qquad \text{and}$$

$$v_2 := (1 - (1 - f_A)^{1/3})^3$$

internal interfaces of A and B:
surface plasmon resonance !

Effect of finite cluster size

some parameters
for « free » conduction electrons in Au :

room temp. relaxation time τ	$9.3 * 10^{-15}$ sec
Fermi velocity v_F	$1.40 * 10^{6}$ m/s
=> electron mean free path l	13 nm

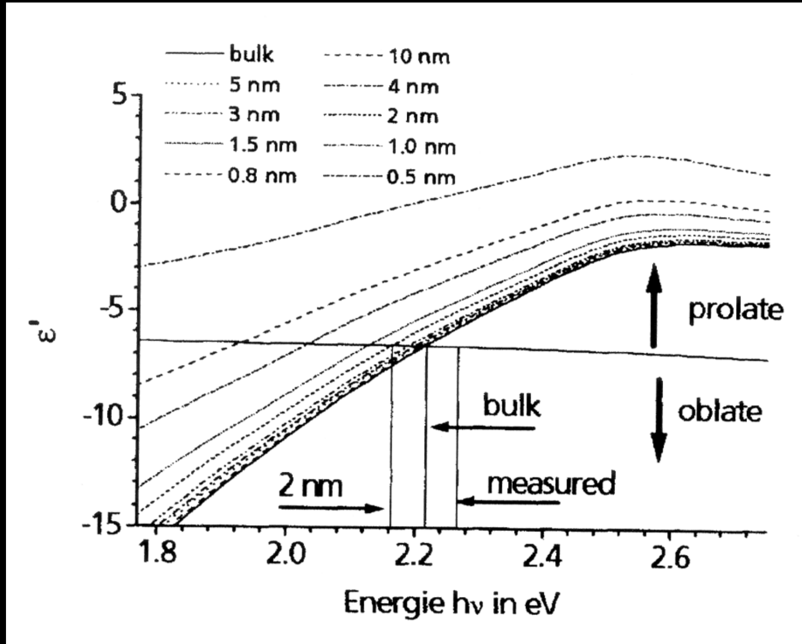
➡ for cluster sizes < 13 nm the dielectric function must be modified !

Correction for free conduction electrons at Fermi-edge

corrected relaxation time :

$$\frac{1}{\tau_R} = \frac{1}{\tau} + \frac{v_F}{R}$$

correction of ε´ for small Au clusters



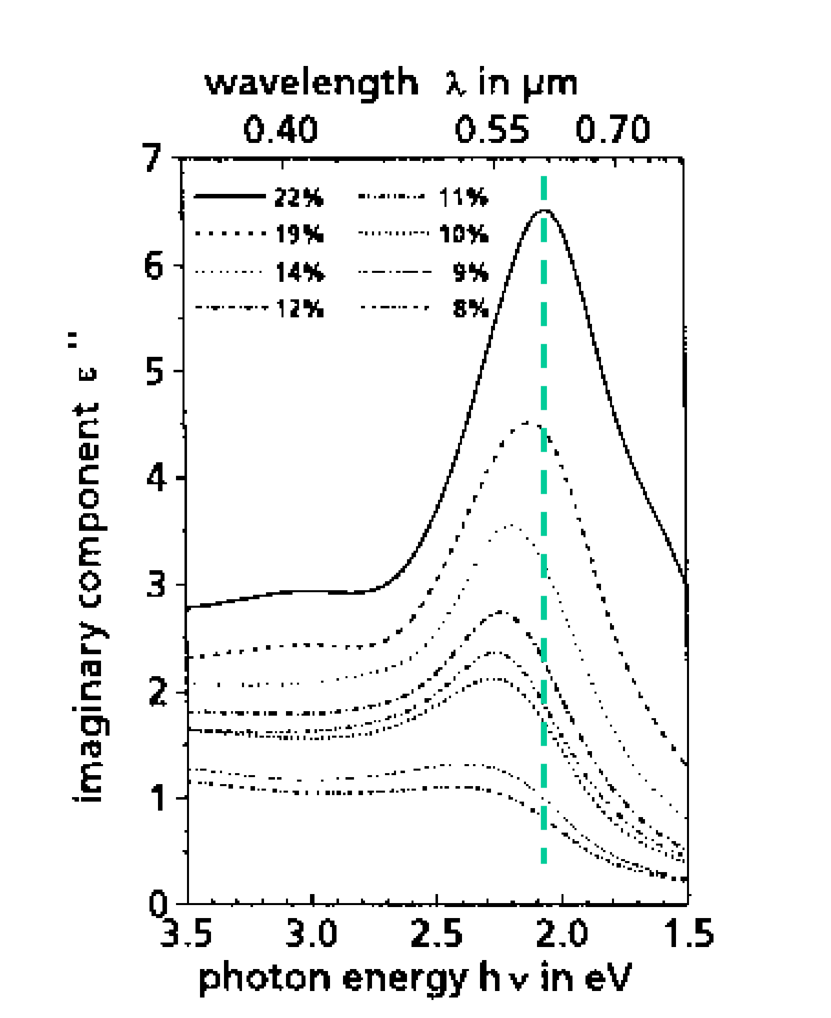
Joerger et al., SEMSC 54, 351 (1998)

modification of dielectric function with Drude theory :

$$\varepsilon(\omega,R) = \varepsilon(\omega) + \omega_p^2 \left(\frac{1}{\omega^2 + \tau^{-2}} - \frac{1}{\omega^2 + \tau_R^{-2}} \right) + i\,\frac{\omega_p^2}{\omega} \left(\frac{\tau_R^{-1}}{\omega^2 + \tau_R^{-2}} - \frac{\tau^{-1}}{\omega^2 + \tau^{-2}} \right)$$

Granqvist, J. Appl. Phys. 50, 2916 (1979)
Hövel et al., Phys. Rev. B 48,18178 (1993)

Surface plasmon resonance in a-C:H/Au



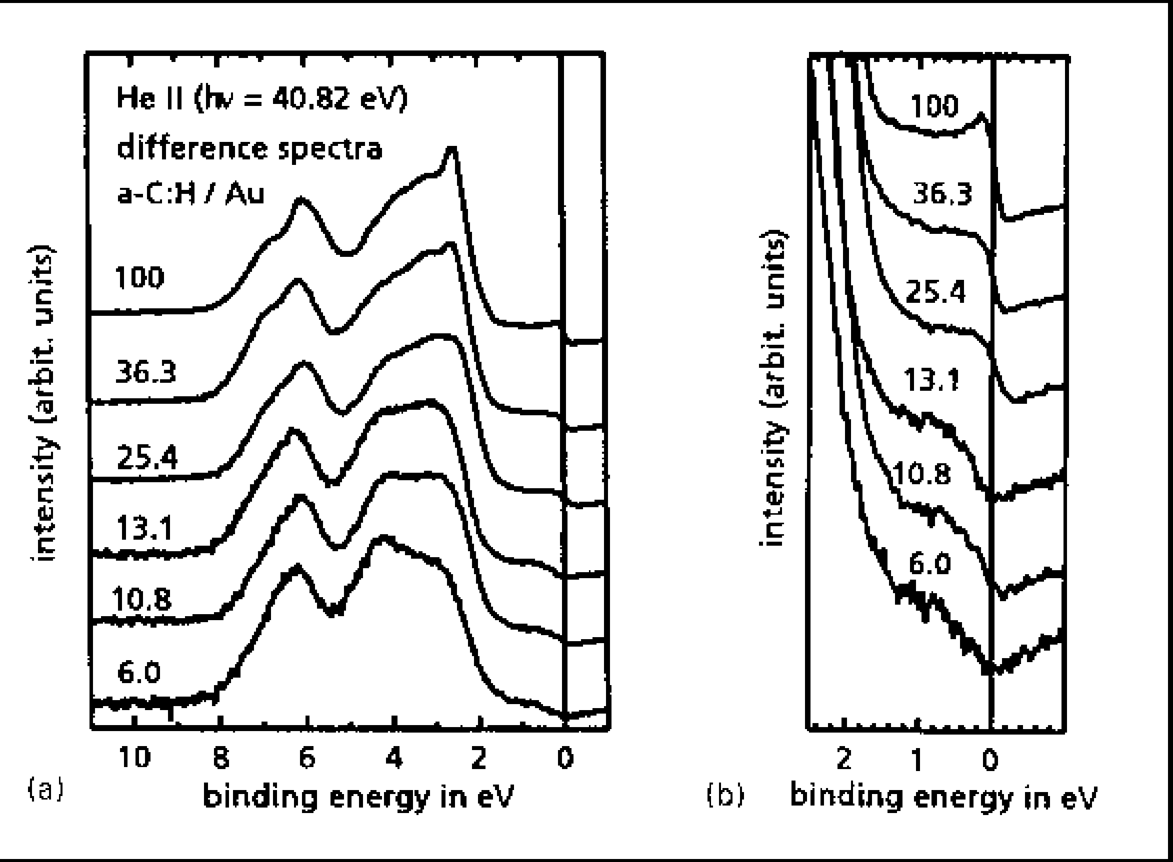
Joerger, Gampp

blueshift for small Au concentrations

⬇

size-dependent optical properties

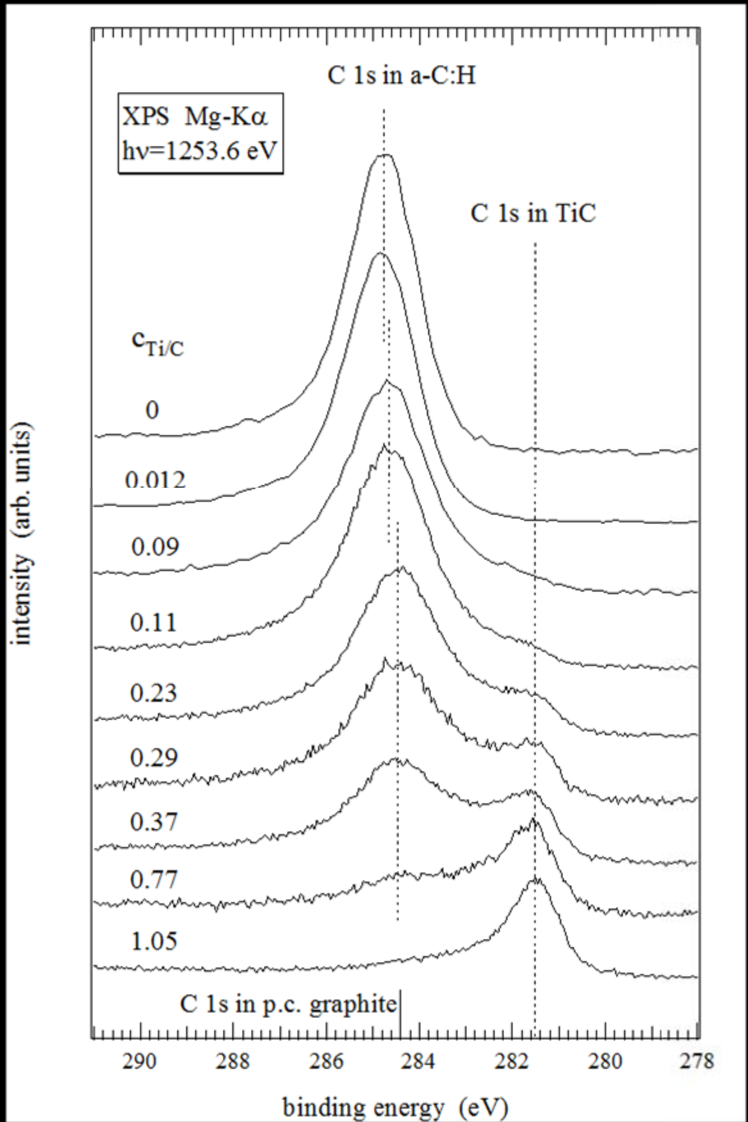
Valence band spectroscopy of a-C:H/Au



Gampp, Joerger

→ modification of d - band for decreasing cluster size

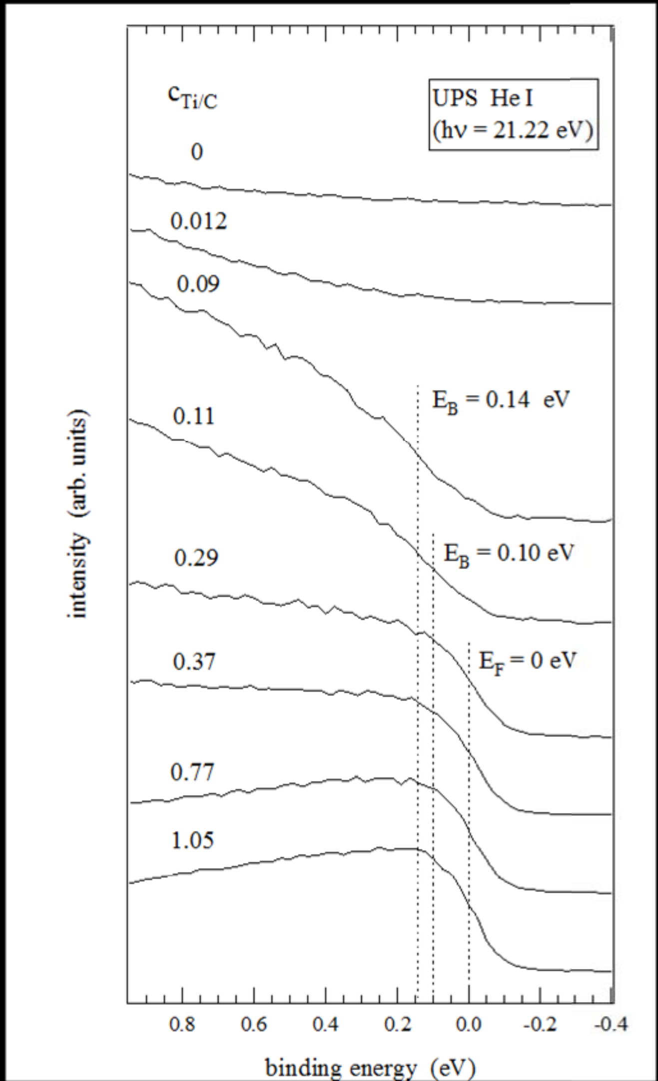
Core level spectroscopy of a-C:H/Ti



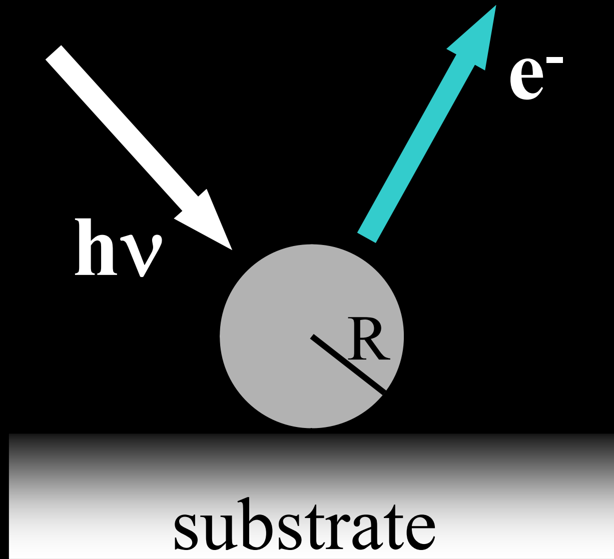
presence of two phases: a-C:H and TiC

Schüler et al., Phys. Rev. B 60, 16164 (1999)

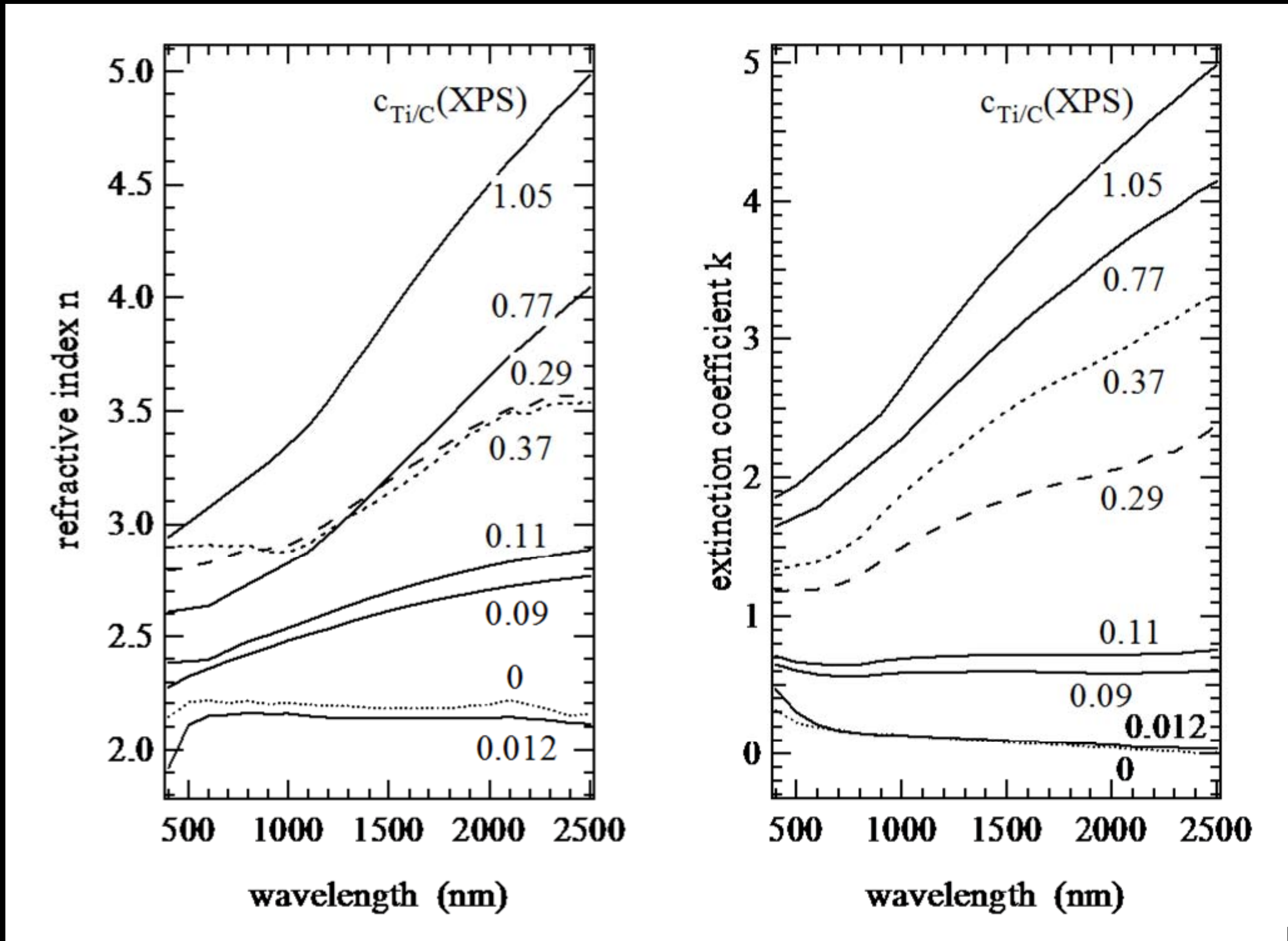
Fermi-edge in a-C:H/Ti



one-electron charging of nanometer-sized metallic TiC clusters



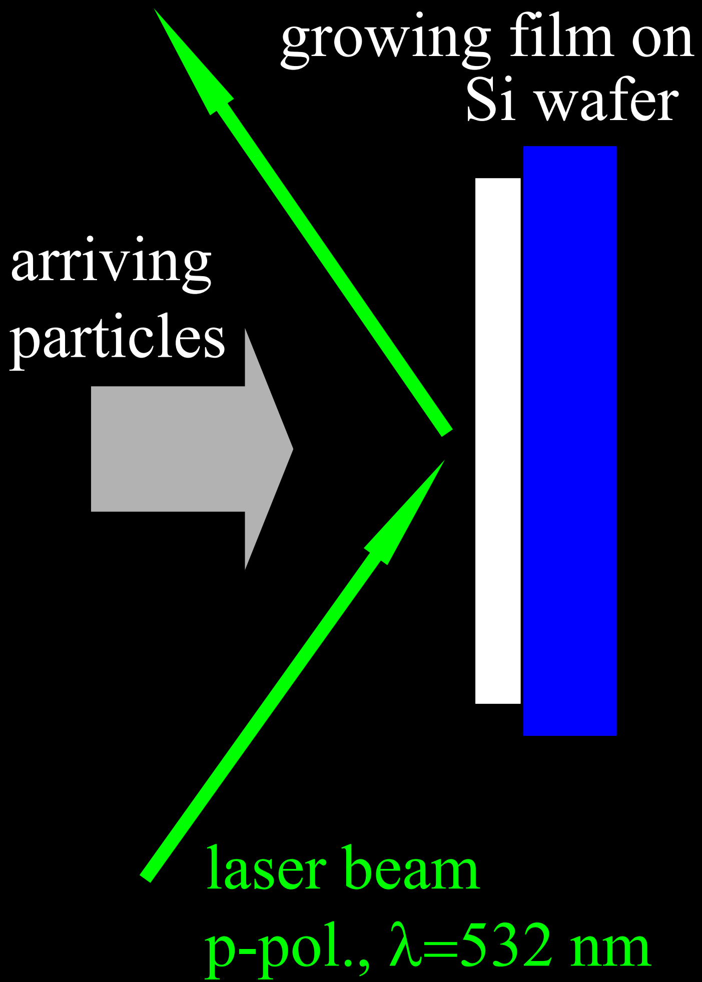
Experimantal determination of the optical properties of a-C:H/Ti

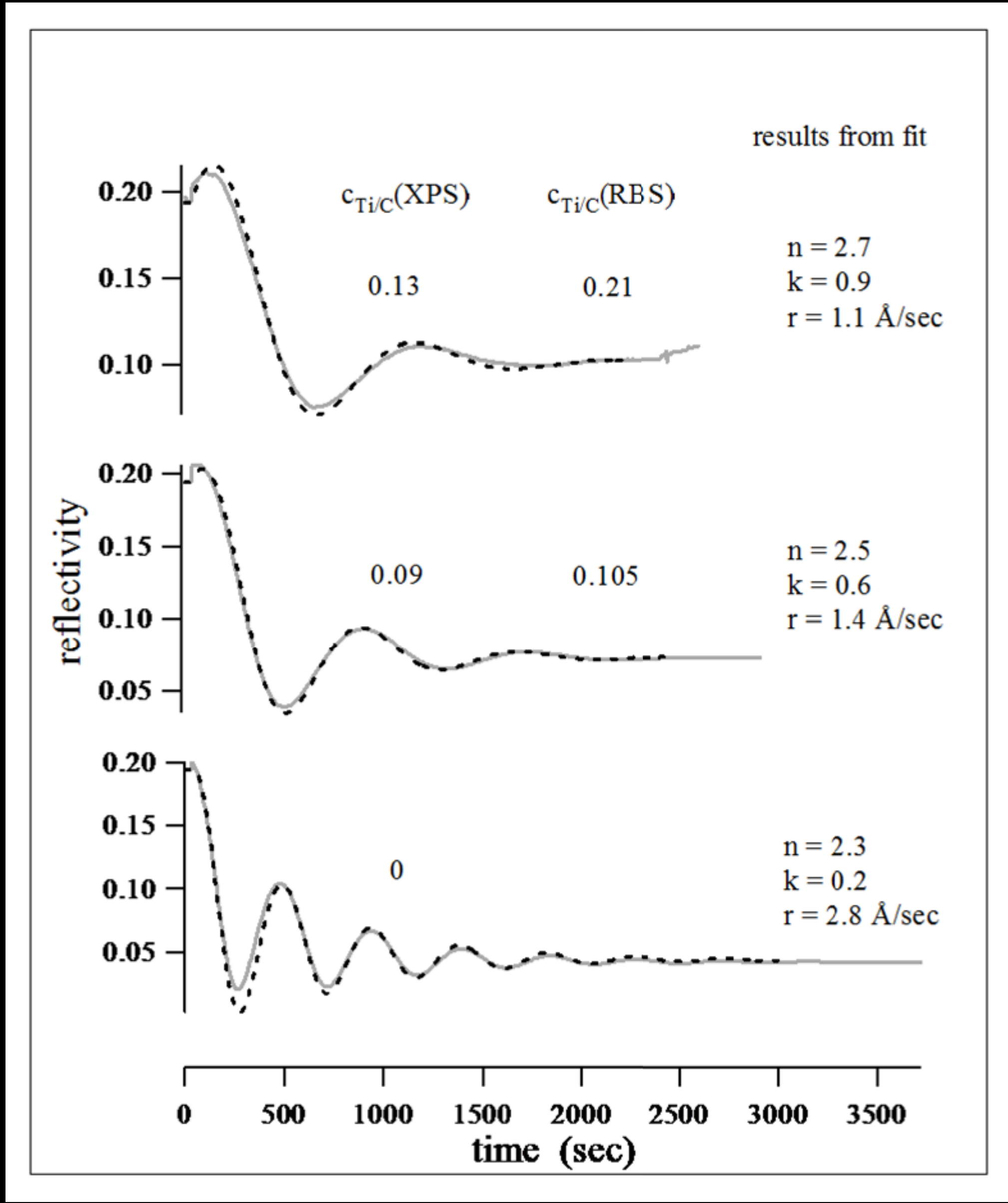


Schüler et al., J. Appl. Phys. 87, 4285, (2000)

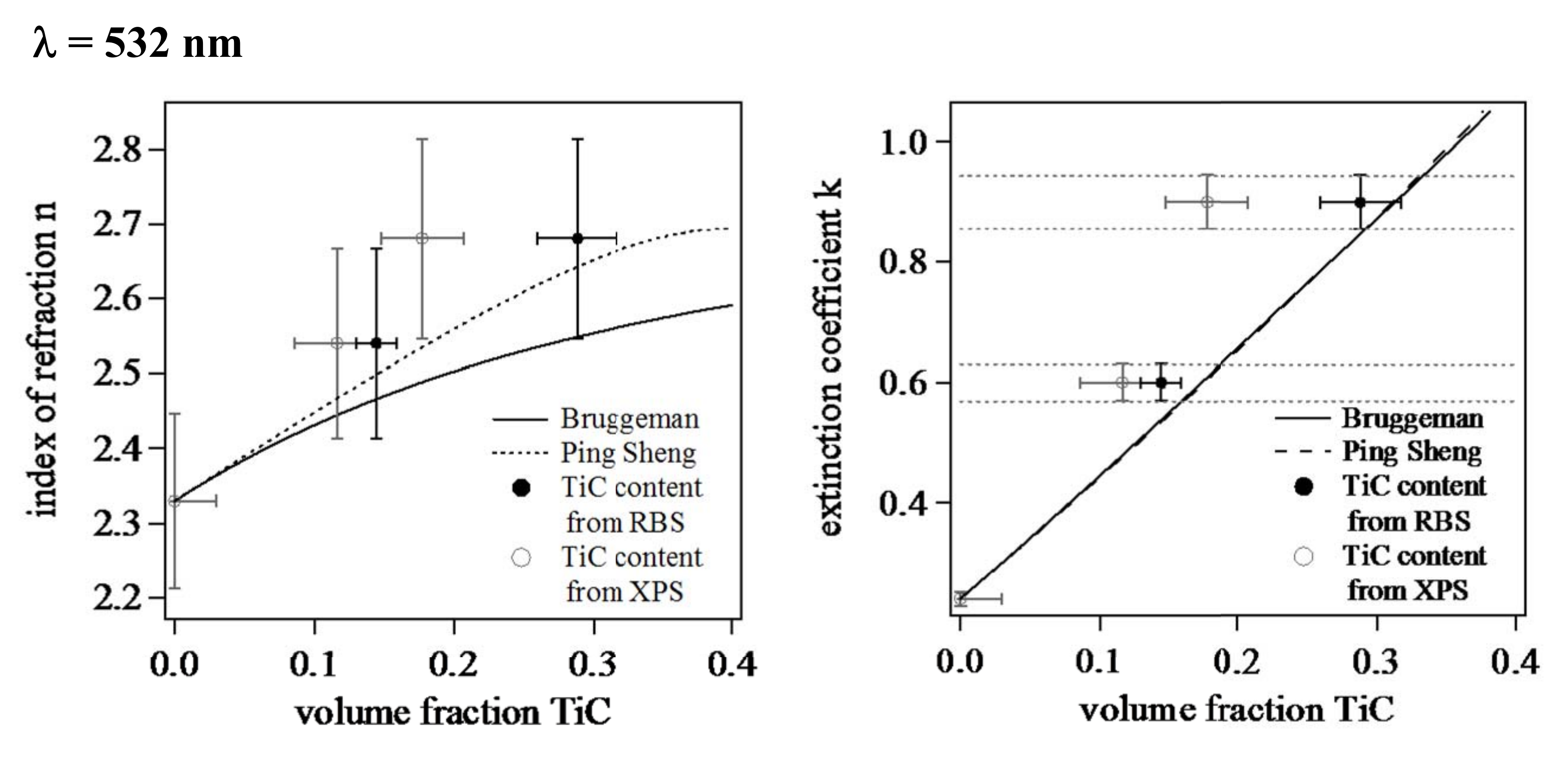
→ **control of optical constants in a wide range**

Real-time laser reflectometry





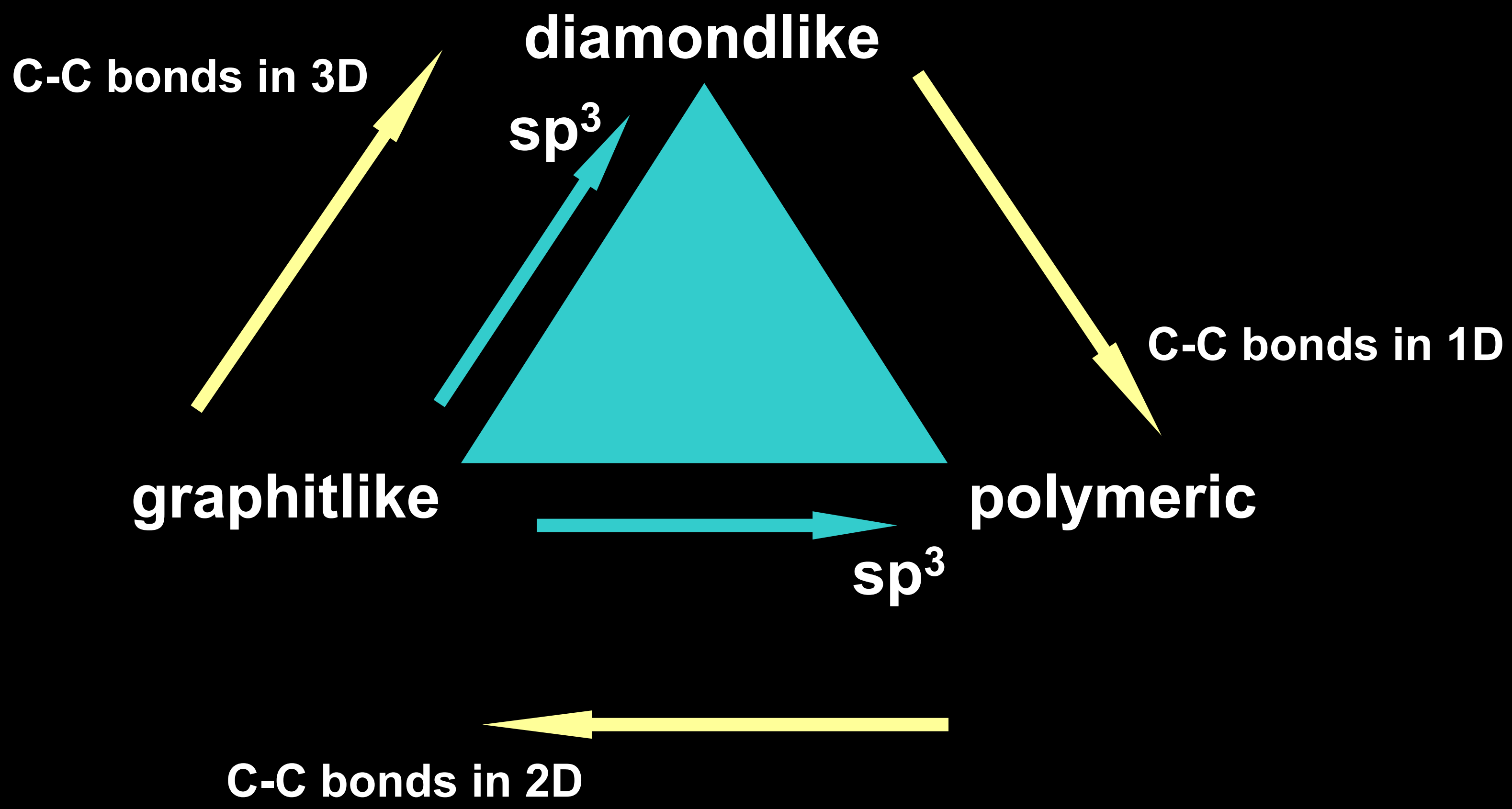
Experiment vs. theories



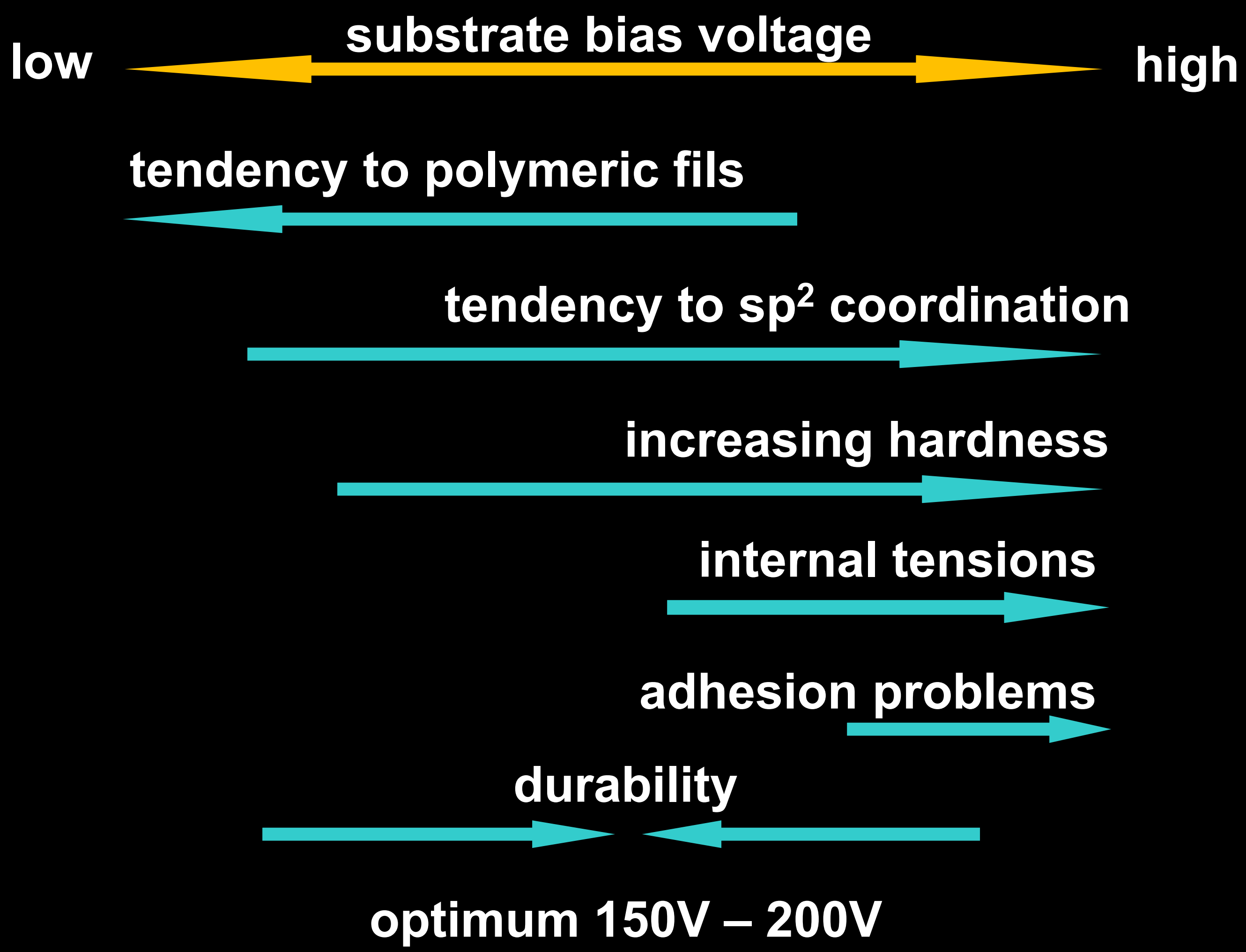
- Ping-Sheng theory closer to experiment than Bruggemann theory

- surface stoichiometry differs from bulk stoichiometry

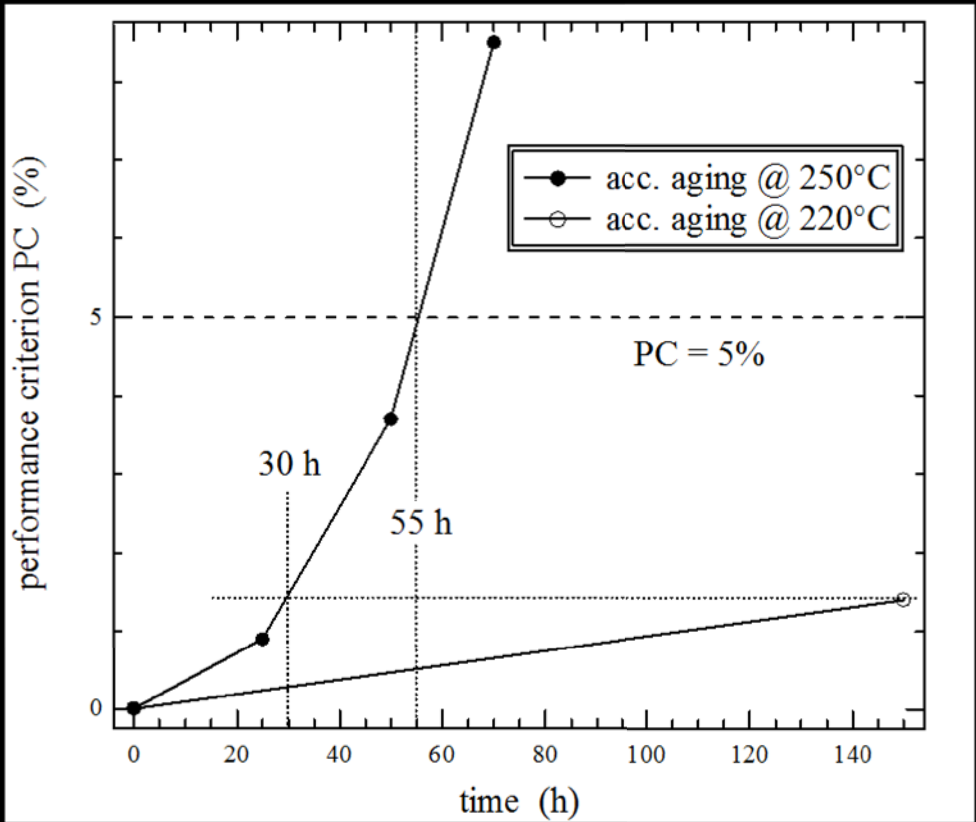
Properties of carbon based films



Important process paramater « substrate bias voltage »



Performance criterion



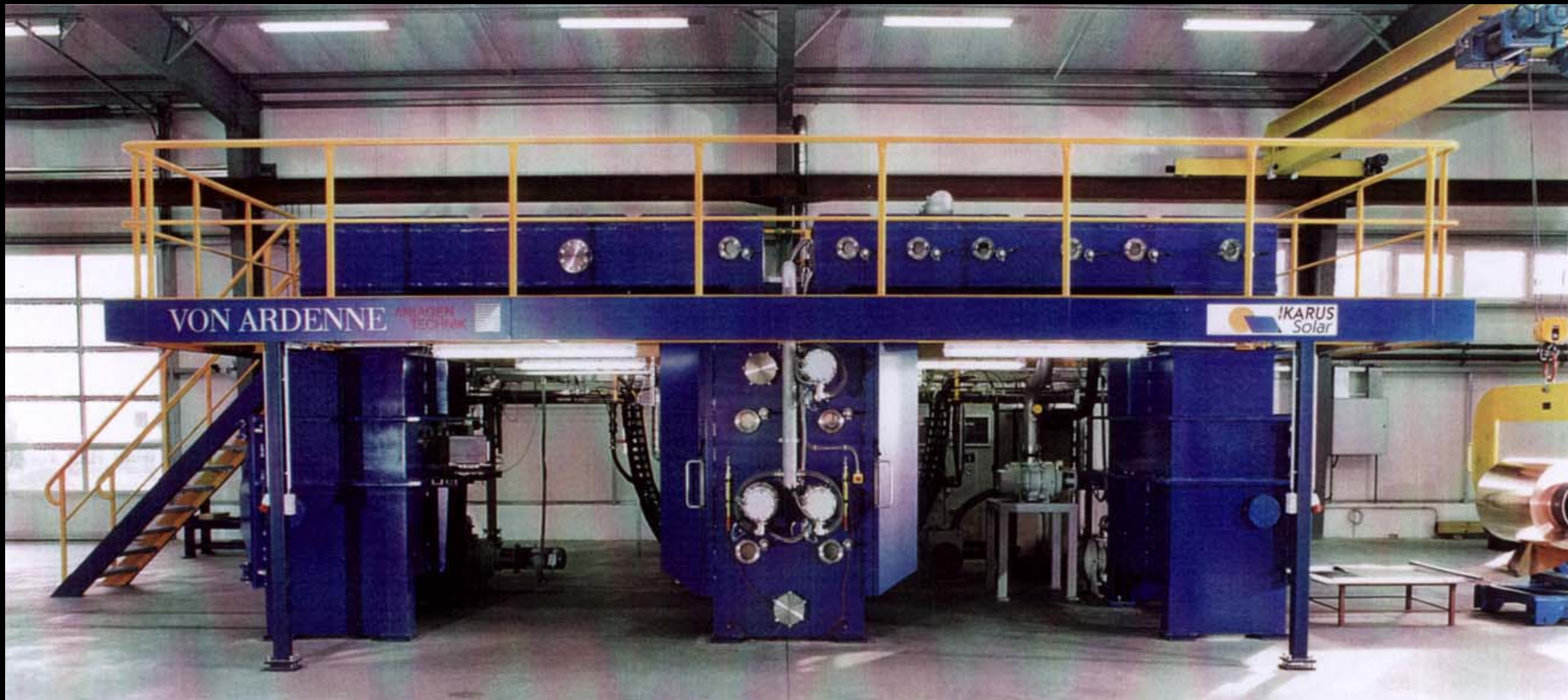
A.Schüler et al.,
Sol. Energy Mater. and Sol. Cells 60, 295 (2000)

$PC = -\Delta\alpha_S + 0.25\Delta\varepsilon_T \leq 5\ \%$

aging test passed!

activation energy of dominant aging mechansism
116 +/- 8 kJ/mol

Industrial large-scale production of selective absorber coatings



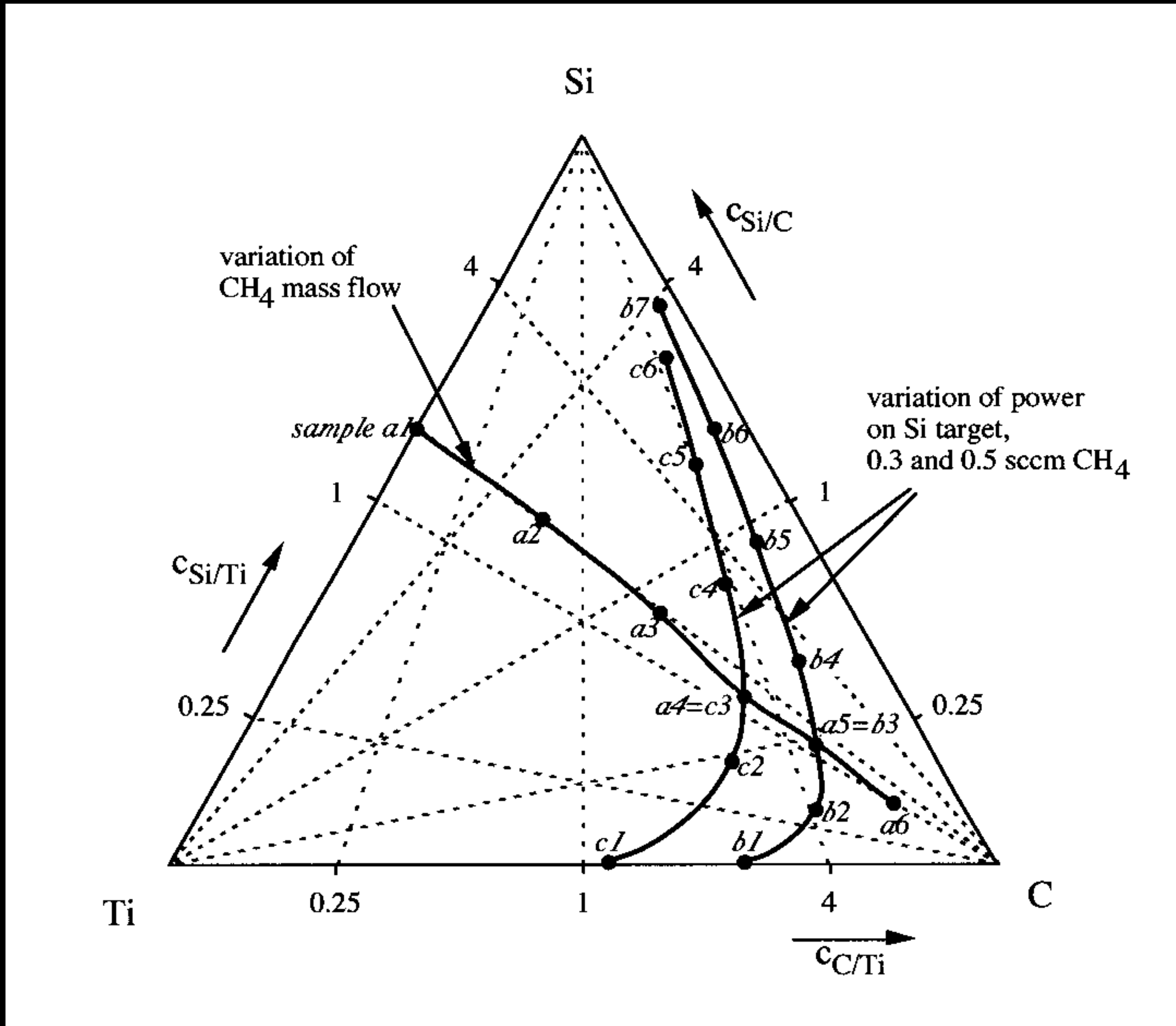
Production line for selective absorber coatings based on a-C:H/Cr (IKARUS COATINGS, FRG)

Doping a-C:H/Me with Si

Improving film stability?

(inhibition of crystallization, passivating oxide, …)

Concentration triangle Si-C-Ti



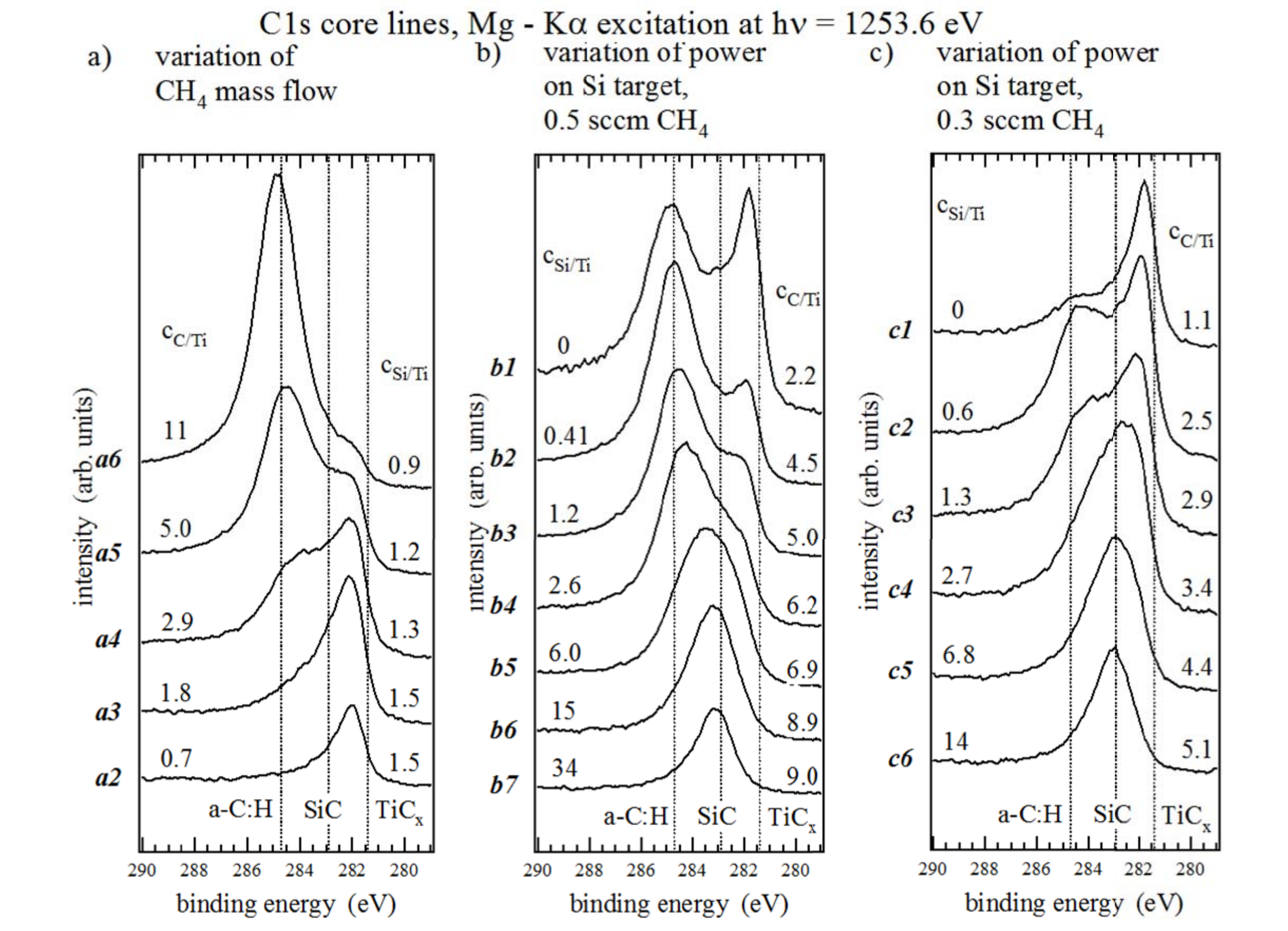
A. Schüler , P. Oelhafen, Appl. Phys. A 73, 237 (2001)

Does the silicon bind

to the metallic cluster

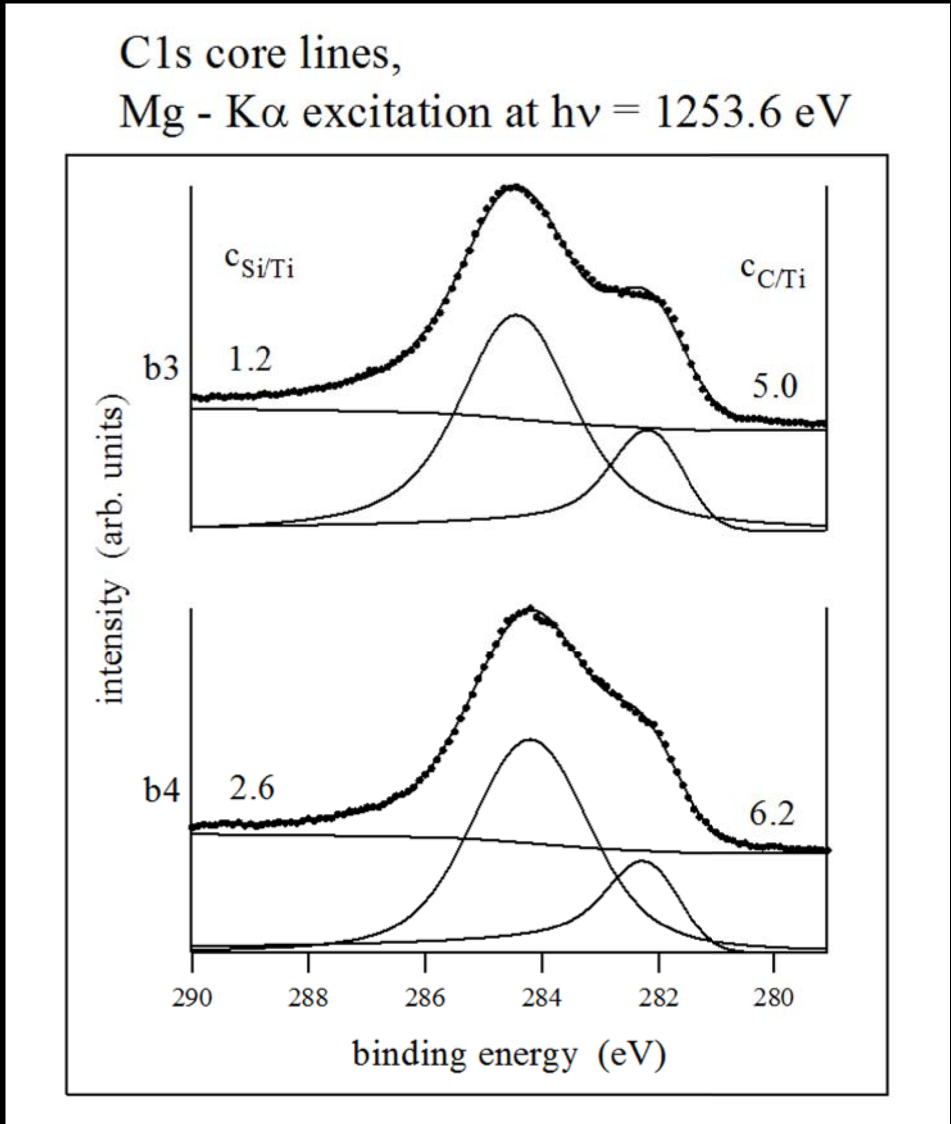
or to the dielectric matrix?

C1s core lines



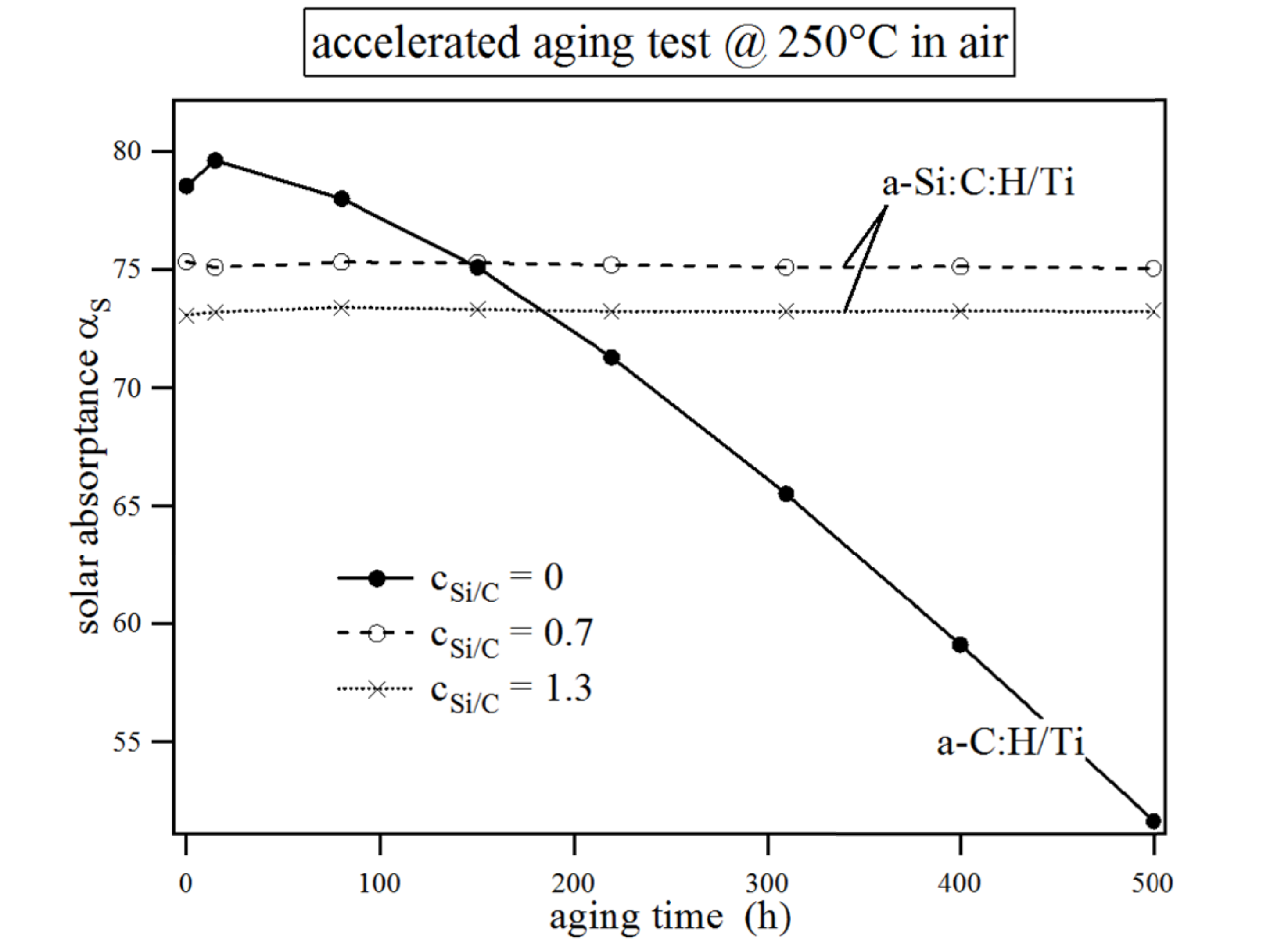
A. Schüler , P. Oelhafen, Appl. Phys. A 73, 237 (2001)

Deconvolution of C1s core lines



A. Schüler , P. Oelhafen, Appl. Phys. A 73, 237 (2001)

Heat resistance by introduction of Si
a-Si:C:H/Ti on Al substrates

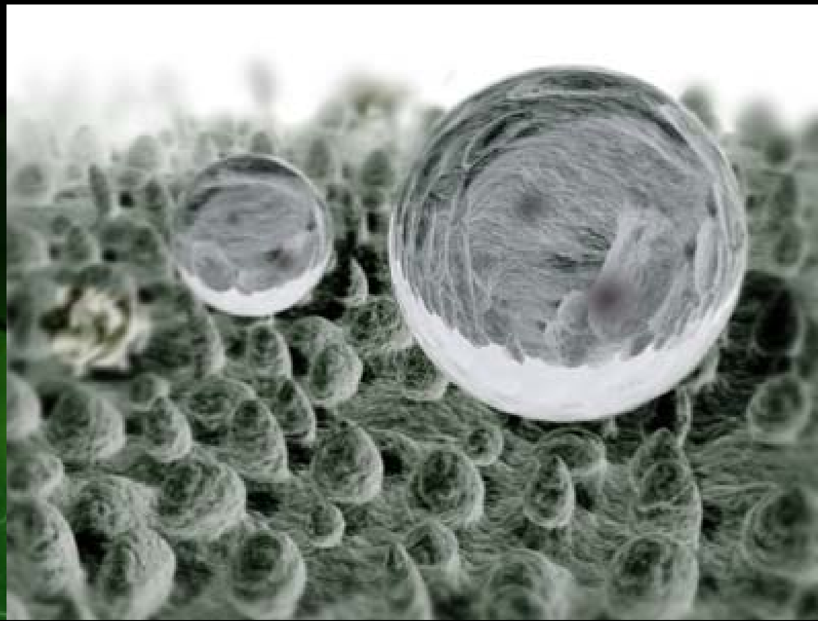


A.Schüler et al., Sol. Energy Mater. and Sol. Cells 69, 271 (2001)

possible explanations
for the improved durability:

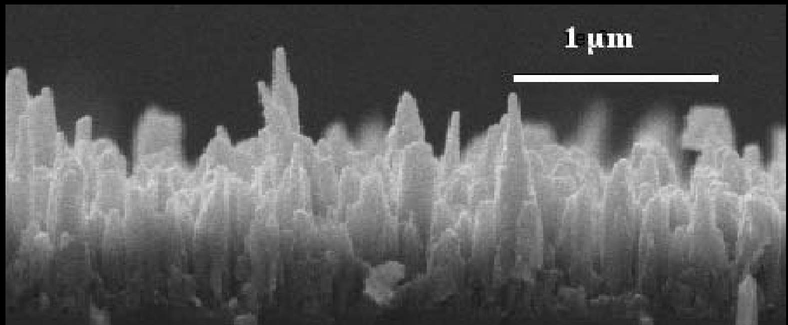
- formation of passivating oxide
- stabilization of amorphous matrix
- enhanced adhesion
- smaller hydrogen concentration
- better tightness regarding Cu diffusion
  (films on Cu substrates)

Micro/Nano- structures in Nature:
The Lotus Effect

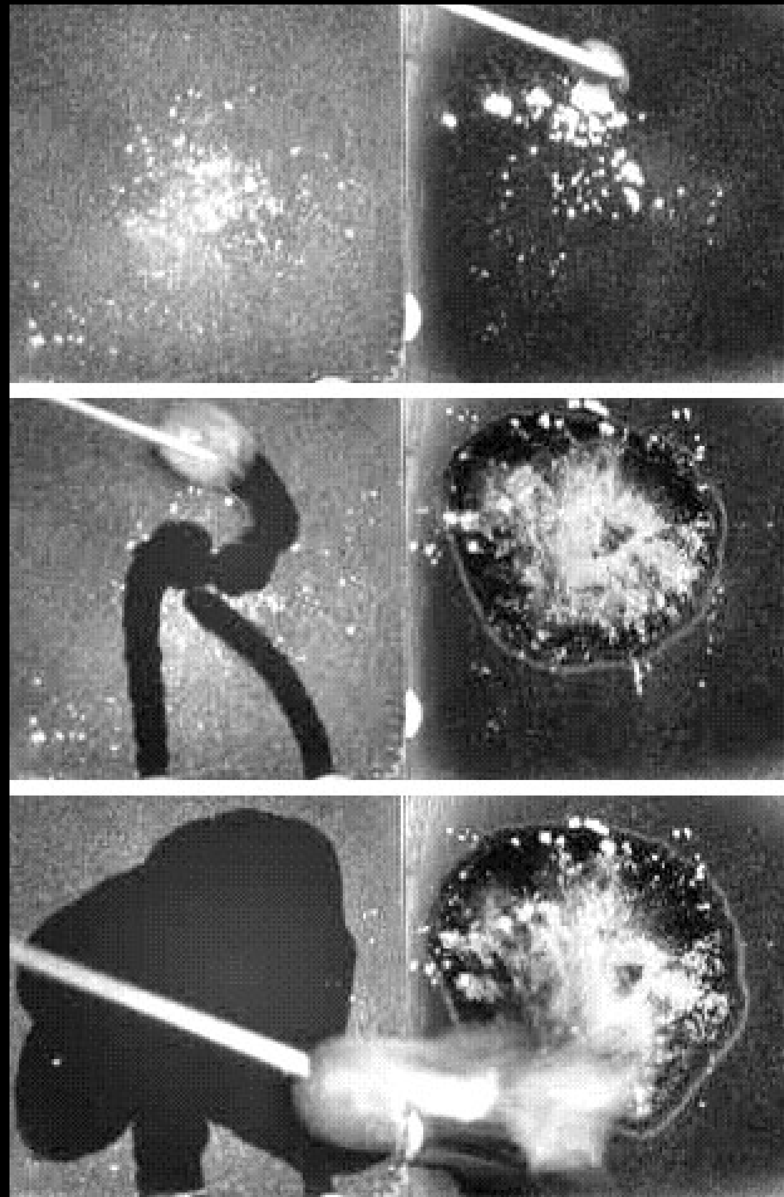


water-repellent, self-cleaning leaves

Bioinspired nanomaterials:
Self-cleaning surfaces



micro/nano structure



self-cleaning coating *conventional coating*

J. Geng, PhD thesis Uni Basel 2000

Conclusions (I)

- PVD/PECVD of nanocomposite thin films
  a-C:H/Me

- Characterisation of nanostructure
  HRTEM, GISAXS

- Determination of optical constants n & k
  spectrophotometry, laser-reflectometry

- Comparison with effective medium theories
  Ping Sheng, Bruggeman

- Solar selective absorber coatings
  multilayered a-C:H/Me

Conclusions (II)

- Accelerated aging tests
  performance criterion, aging mechanisms

- Novel nanocomposite material a-Si:C:H/Me
  structure model from PES

- Breakthrough in durability

- Preparation of self-cleaning surfaces:
  Lotus-effect

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University of Basel

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SPF Rapperswil

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Swiss National Science Foundation SNF

Industry:

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Thank you for your attention !