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**THIRD WORKSHOP ON
THIN FILMS PHYSICS AND TECHNOLOGY
(8 - 24 MARCH 1999)**
including
**TOPICAL CONFERENCE ON
MICROSTRUCTURE AND SURFACE MORPHOLOGY
EVOLUTION IN THIN FILMS
(24 - 26 MARCH 1999)**

"Carbon Nitride Thin Films - Growth and Properties"

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Third Workshop on Microstructure and Surface Morphology Evolution in Thin Films
Trieste, Italy, 8-26 March 1999

Carbon Nitride Thin Films - Growth and Properties

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Carbon Nitride Thin Films
- Growth and Properties

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Thin Film Physics
Linköping University

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et al....

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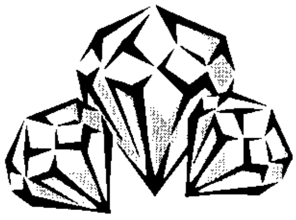
Outline

- Background
  - Hard Materials
  - Carbon Nitrides, β-C_3N_4
- Thin Film Deposition - Magnetron Sputtering
- Structure & Mechanical Properties of CN_x Thin Films
- Influence of Deposition Conditions on the Properties of CN_x
  - Role of Nitrogen
  - Influence of Plasma Parameters
- Multilayers & Nanostructured CN_x films
- Applications of CN_x
- Summary

Background - Hard Materials

Hardness = A materials ability to resist plastic and elastic deformation when exposed to an external load



Hard Materials

Requirements for forming a hard solid:

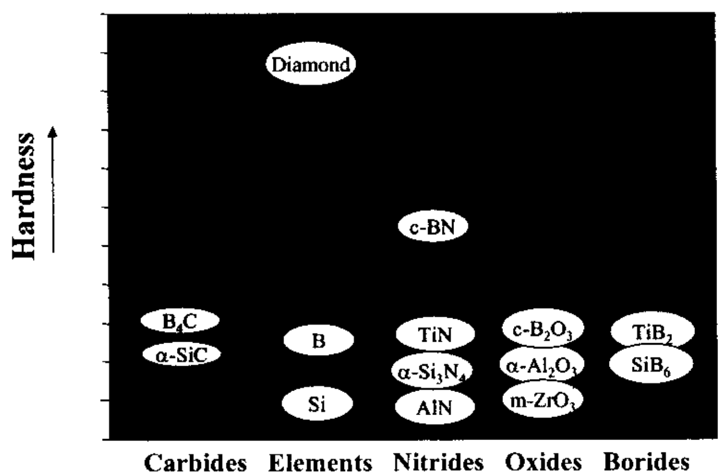
1 Small molar volume => Small atoms, closely packed

2 Strong bonds => Covalent or ionic bondings

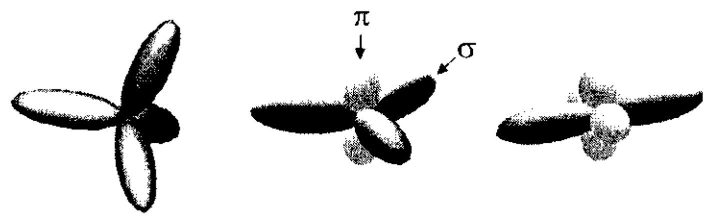
3 Crystal structure => 3-dimensional network

Suitable materials: B, C, N, ... e.g. Diamond & c-BN

Hard Materials

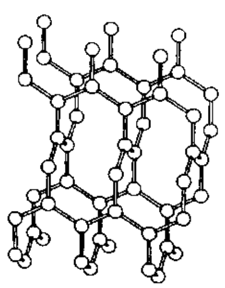


Carbon Bond Hybridization

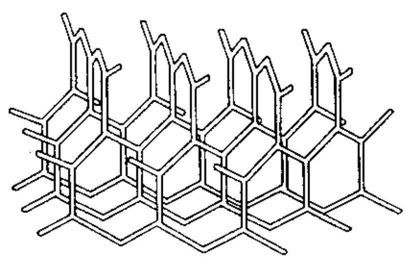


sp^3	sp^2	sp^1
Diamond (3D)	**Graphite (2D)**	**Organic compounds (1D)**

sp^2-Carbon Networks



Bct-4

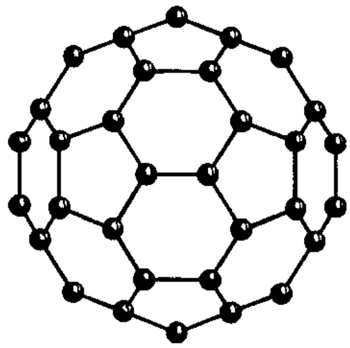


H-6

Predicted hardness comparable to c-BN

Fullerenes

C_{60}



Estimated bulk modulus of a single C_{60} molecule: 843 GPa

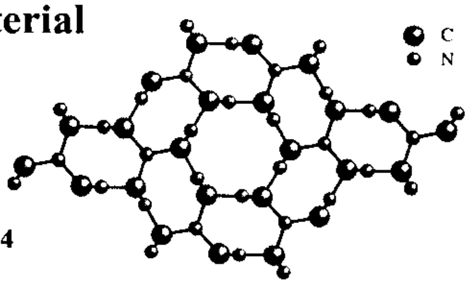
(diamond: 443 GPa)

However, crystalline C_{60}-films have weak van der Waahl-bonds between molecules => weak solid

β-C_3N_4

New predicted material

β-C_3N_4 has the hexagonal structure of β-Si_3N_4



Calculated bulk-modulus 427 GPa

Liu & Cohen, Science 245 (1989) 841

Bulk Modulus

Semi-empirical relationship:

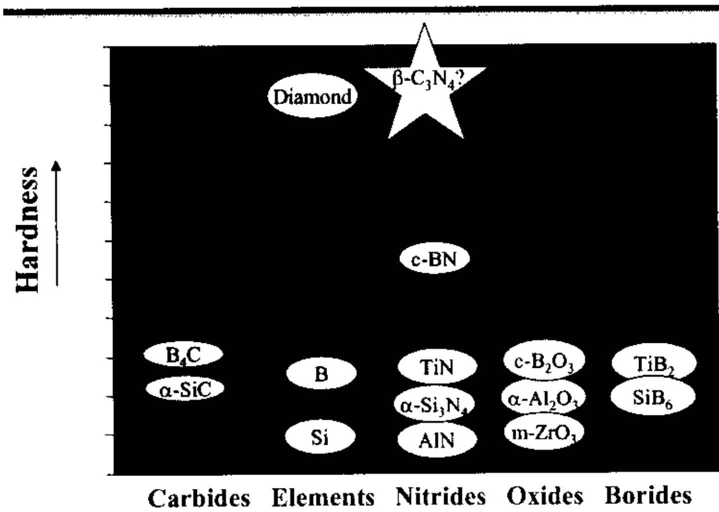
$$B = \frac{(19.71 - 2.20\lambda)}{d^{3.5}}$$

λ = ionicity (empirical parameter ranging from 0 to 2)
d = bond length (Å)

Compound	Calculated B (GPa)	Measured B (GPa)
Diamond	444	435
c-BN	367	369
β-Si_3N_4	265	256
β-C_3N_4	427	???

M.L. Cohen, J. Hard Materials, vol. 2, No. 1-2 (1991) 13-27

Hard Materials



Techniques used for CN deposition

- RF/DC Magnetron Sputtering
- Ion beam assisted deposition (IBAD)
- Arc evaporation
- Laser ablation
- Nitrogen implantation
- Chemical vapor deposition (CVD)
- Wet chemistry
-

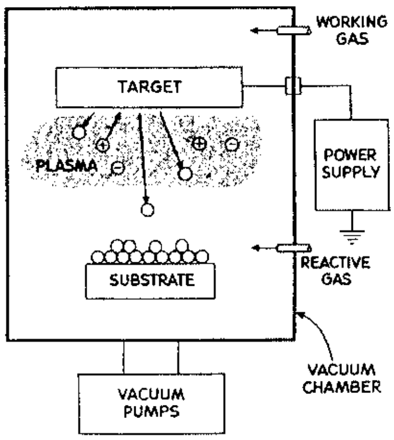
Difficult to synthesize β-C_3N_4

Thin Film Growth

- Growth occurs as a result of condensation of vapor (atoms, clusters, ions, molecules, radicals, etc.) on a surface
- The growth conditions (energy input, chemical reactions etc.) defines the microstructure of the film
- The microstructure defines the properties of the film and hence the performance of the component

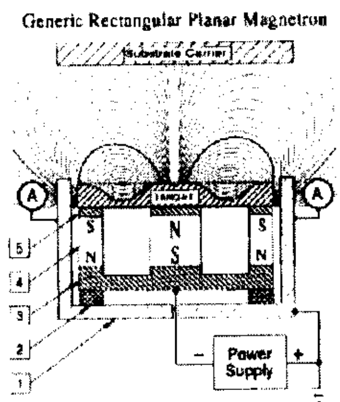
Sputtering

- Ions are accelerated to the negatively biased target
- If sufficient energy => target atoms are knocked out - Sputtering
- Atoms are transported through the vapor and condense on the substrate - Film growth



Magnetron sputtering

- Electrons are trapped in the discharge by means of a magnetic field
- Increased electron path length => electrons undergo more ionizing collisions => higher degree of ionization => Higher sputtering yield

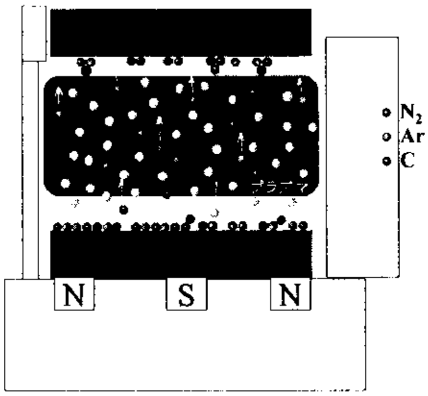


Magnetron sputtering of CN_x

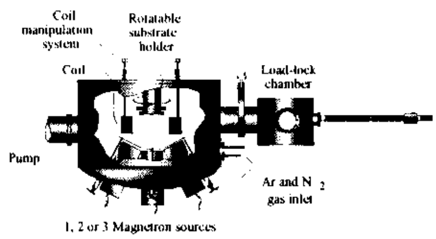
- Carbon nitride films can be grown by reactive sputtering from a graphite target in N_2 or N_2/Ar discharge

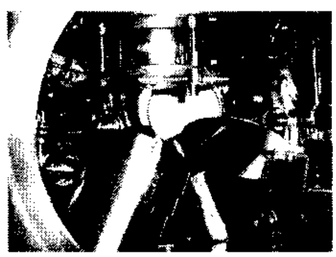
Film structure influenced by:

- Pressure and gas mixture
- Energy and flux of particles impinging on the growth surface
- Substrate temperature T_S
- ...



UHV deposition system





Film Characterization

Growth & Plasma
- Surface Profilometry
- Langmuir Probe
- Mass-spectrometry

Composition:
- RBS
- NRA

Bondings:
- XPS
- FTIR
- Raman
- EELS
- NEXAFS
- XAS

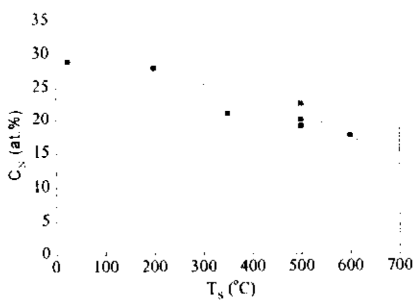
Structure & Morphology:
- SEM
- TEM
- AFM
- STM

Mechanical:
- Nanoindentation
- Pin-on-disc
- Surface Acoustic Wave
- Stress

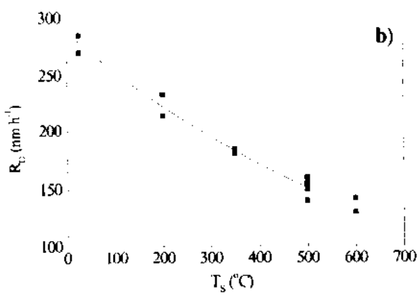
Optical & Electrical:
- Ellipsometry
- Four-point probe

Effect of Substrate Temperature

Nitrogen Concentration



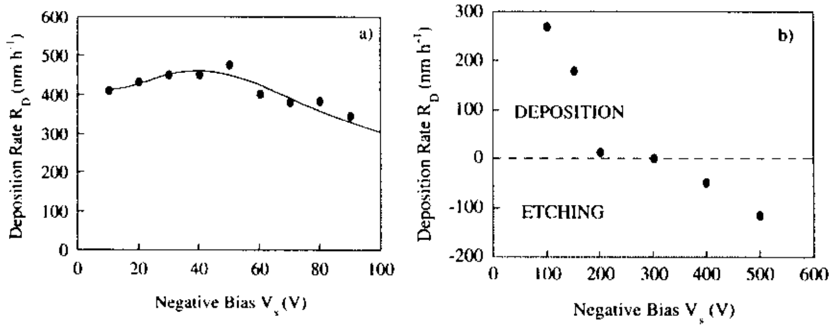
Growth Rate



Max obtained Nitrogen concentration ~ 35 at.%
57 at.% N required for C_3N_4

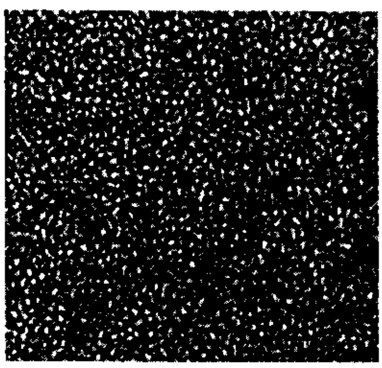
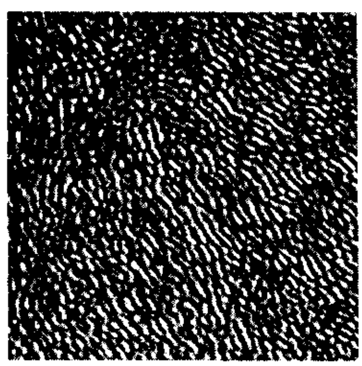
Effect of Substrate Bias

Growth Rate

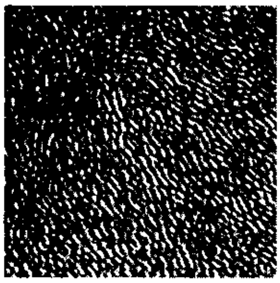


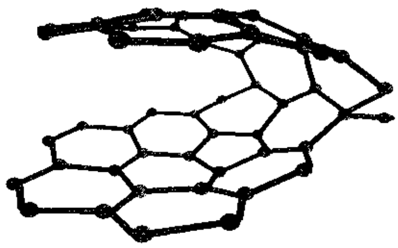
No film growth for $V_b > 200$ V

Microstructure of CN_x ($x < 1.33$)

$T_s < 150$ °C	$T_s > 200$ °C
	
Amorphous	**"Fullerene-like"**

CN_x - Proposed Microstructure

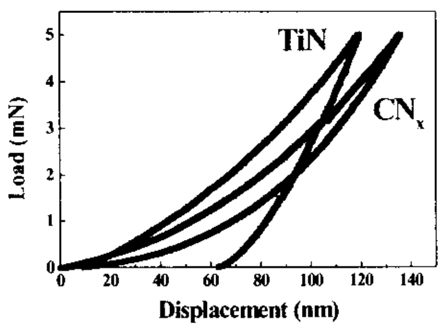


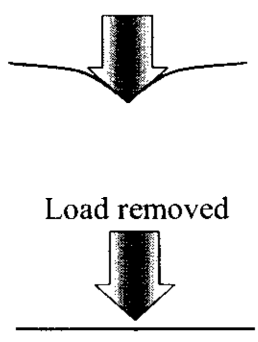


Bent and intersecting basal-planes!
The bending might be caused by the incorporation of pentagons in the otherwise hexagonal basal planes, just like in the case of fullerenes => "Fullerene-like" microstructure

Sjöström *et al.*, Phys. Rev. Lett. 75 (1995) 1336

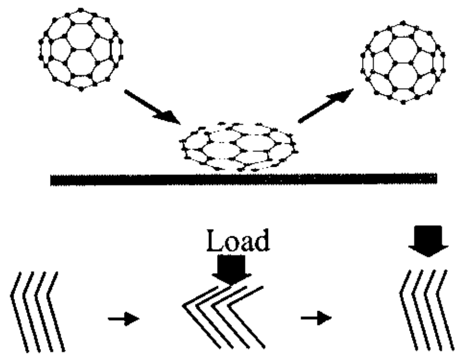
Nanoindentation





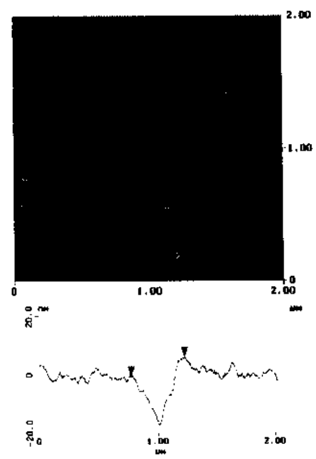
H = 40 - 60 GPa
E = ~ 200 GPa

Deformation Mechanism



Bond angle deformation - Not bond breaking

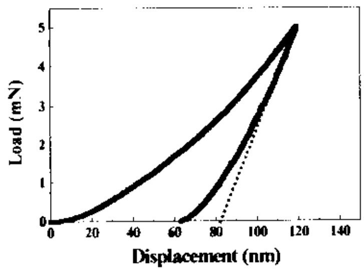
Deformation Mechanisms

Before	**After**
	

Surface structure
conserved in the indent!

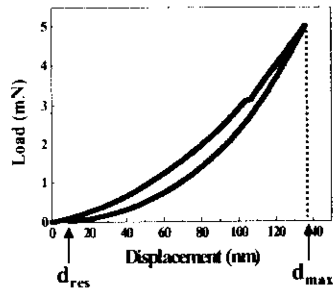
Nanoindentation

"Normal"
Elasto-plastic deformation



H & E may be deduced!

CN_x
Plastic deformation

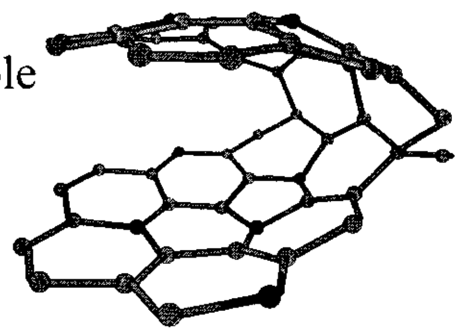


H & E = ??
Instead: d_{max} & R

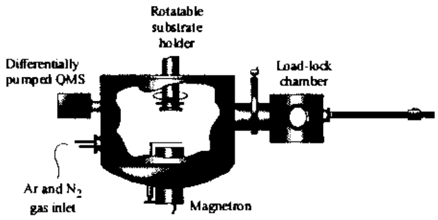
The Role of N in Hard & Elastic CN_x

Objectives:

To study which role nitrogen plays in promoting the fullerene-like microstructure to form



Film Growth



Unbalanced d.c. magnetron sputtering from graphite target

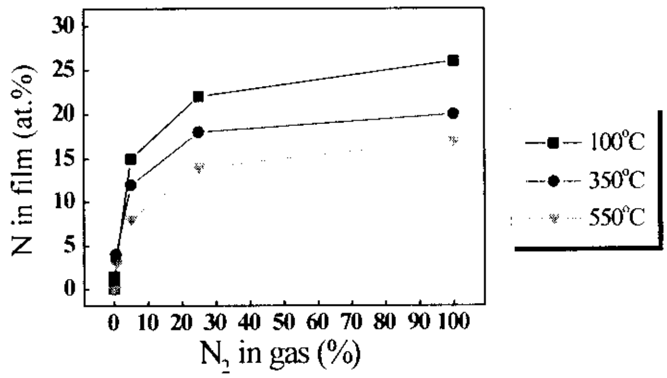
P_b = 1 x 10^{-9} Torr
P_{tot} = 3.0 mTorr (Ar+N_2)
I_t = 0.3 A
E_i ~ 10 - 15 eV
Thickness = 0.5 μm

T_s = 100, 350, 550 °C
N_2-fraction: 0 - 100%

Film Analysis

Composition:	RBS
Structure:	XPS REELS Raman spectroscopy TEM SEM
Mechanical:	Nanoindentation

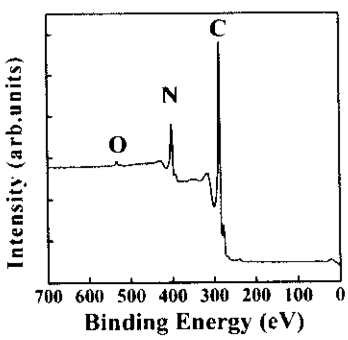
Composition



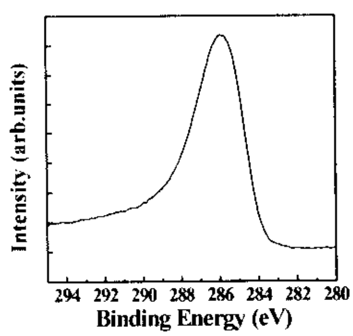
Saturation of C_N **Higher T_S => Lower C_N**

XPS

Overview



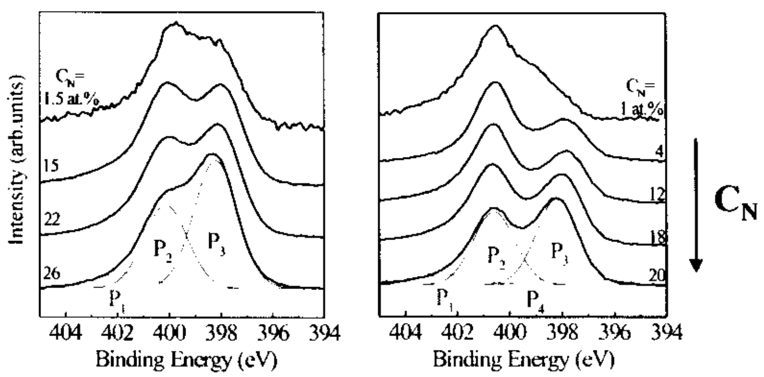
C 1s



< 2 at% Oxygen **Deconvolution difficult**

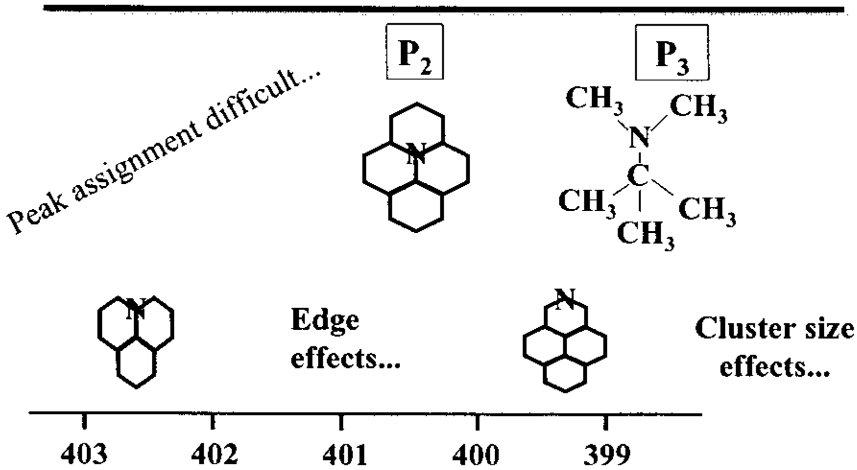
XPS N1s

$T_s = 100\ ^{\circ}C$ $T_s = 350\ ^{\circ}C$



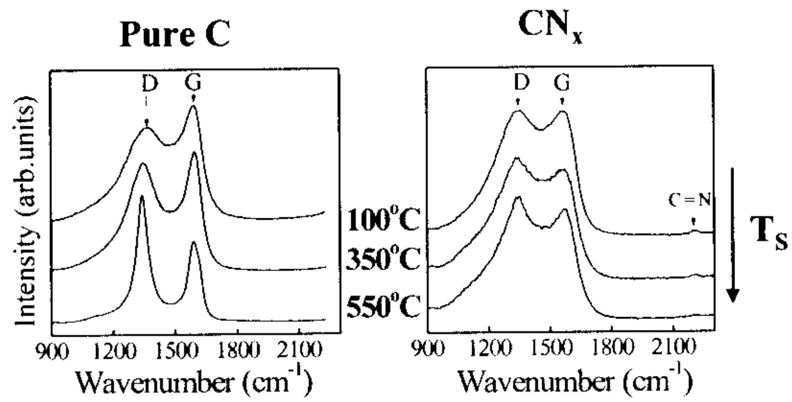
Assignments: P_2 N - sp^2 C P_3 N - sp^3 C

Calculated N1s binding energies



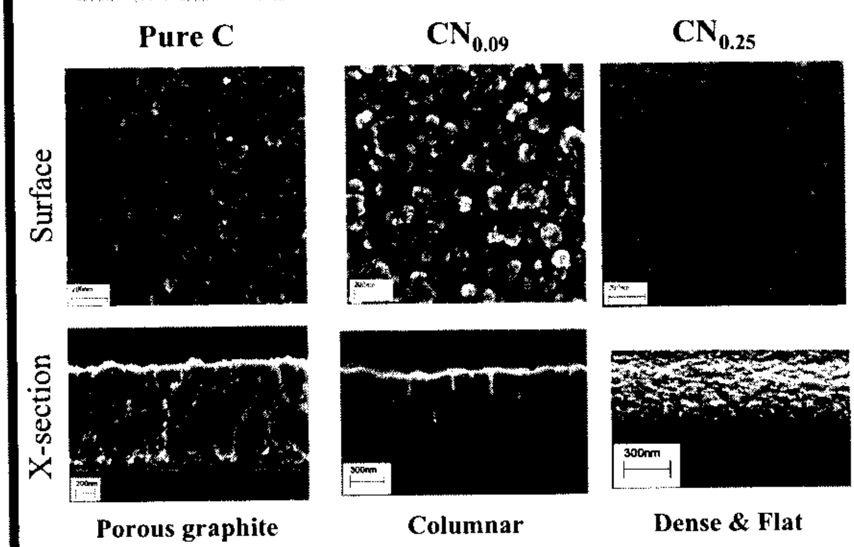
Å. Johansson & S. Stafström, *to be published*

Raman Spectroscopy



Higher T_s & Lower C_N => More ordered structure

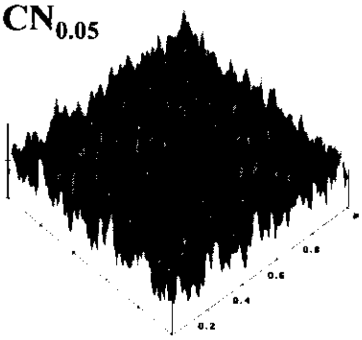
SEM



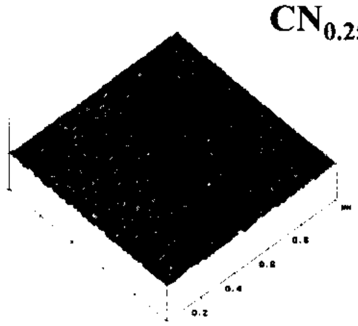
AFM
Surface roughness

T_s= 350 °C

$CN_{0.05}$

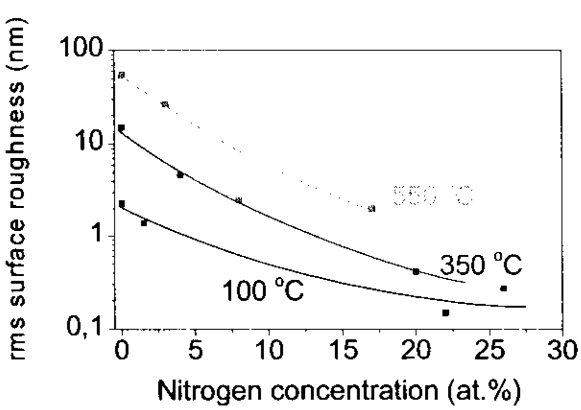


$CN_{0.25}$



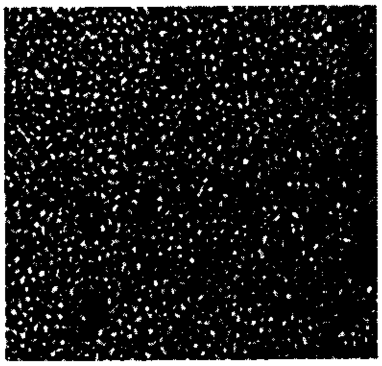
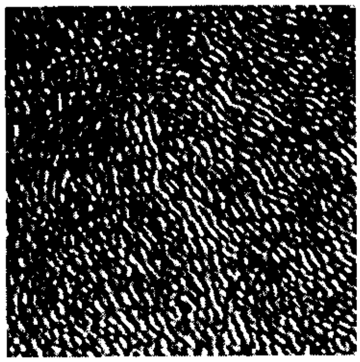
Rms roughness 4.7 nm — 0.41 nm

AFM
Surface roughness

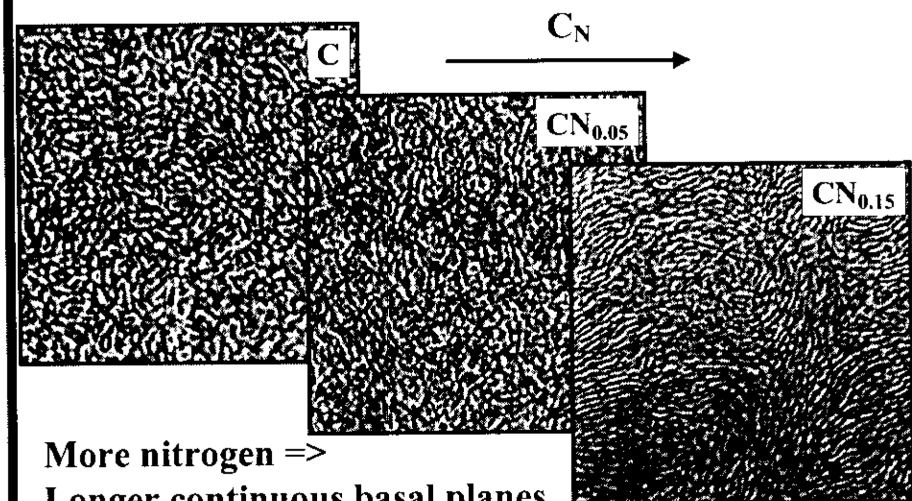


Lower T_s & More Nitrogen => Smoother film

TEM Plan-views (CN_x)

100 °C	350 °C
	
Amorphous	"Fullerene-like"

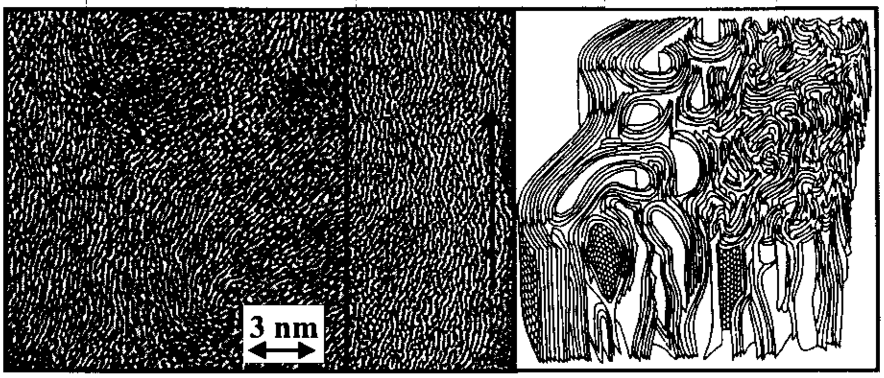
TEM Plan-views, $T_S > 200$ °C



More nitrogen =>
Longer continuous basal planes

Structure of CN_x $(0.15<x<0.3)$, $T_S > 200$ °C

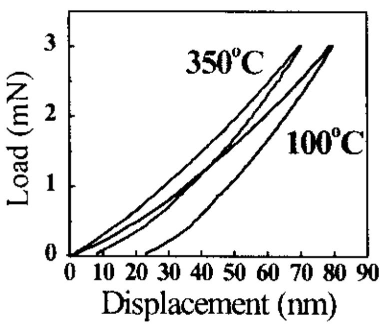
Plan-View | X-View | Schematics



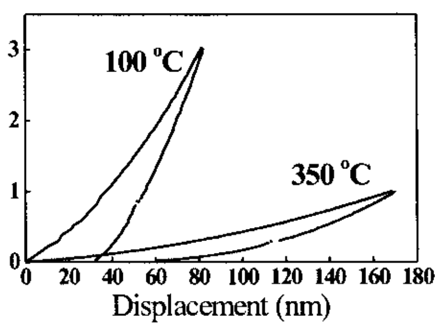
Schematic image of turbostratic carbon from S.C. Bennet and D.J. Johnson, Carbon 17 (1979) 25

Nanoindentation

CN_x



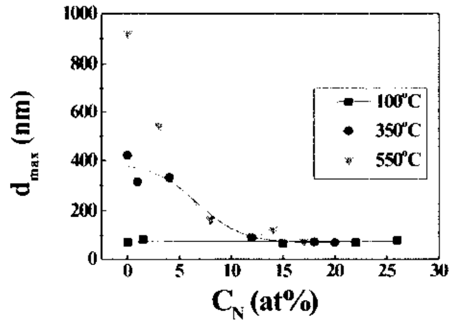
Pure C

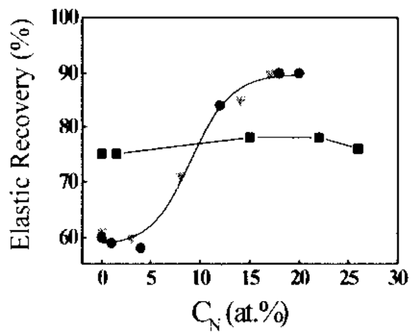


Nanoindentation

Displacement @ 3 mN

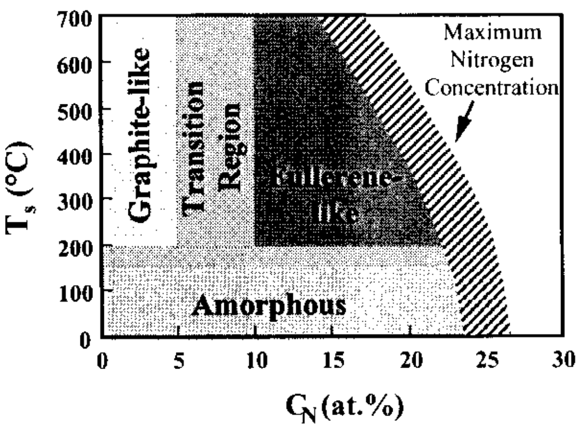
Elastic Recovery





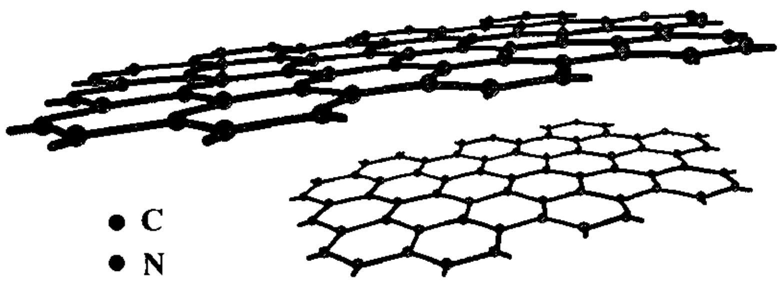
3 characteristic regions

"Phase"-diagram



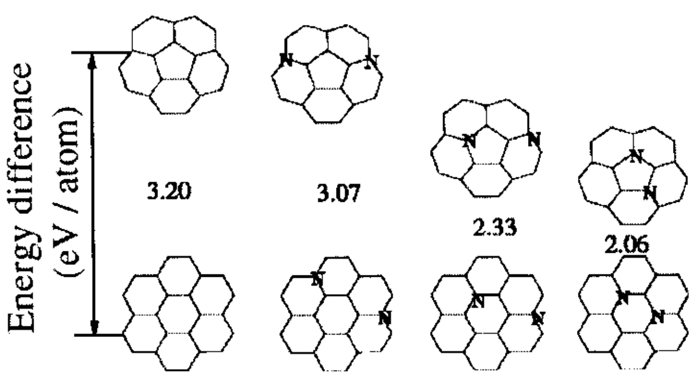
Structures ($T_s > 200$ °C)

$C_N < 5$ at.% Graphite-like domains



Nitrogen in substitutional graphite sites

Energy to form Pentagons

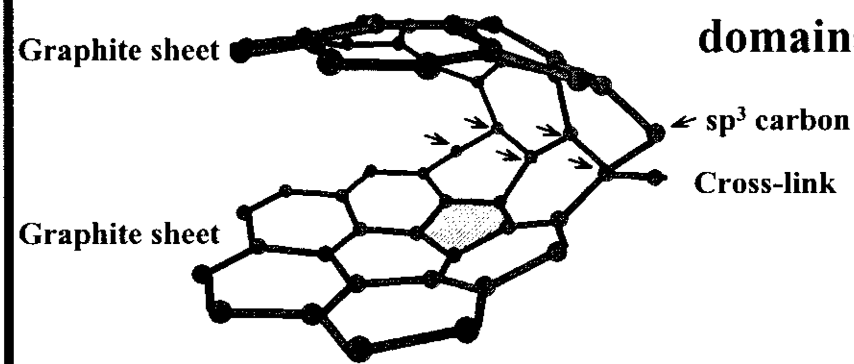


Sjöström *et al.*, Phys. Rev. Lett. 75 (1995) 1336

Structures (T_s > 200 °C)

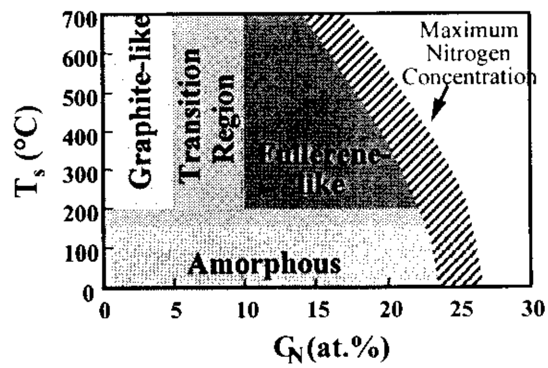
C_N > 15 at.%

"Fullerene-like" domains



Pentagons => Bending => Cross-linking

Conclusions



Nitrogen does play an important role in the formation of hard and elastic CN_x thin films !!!

Influence of plasma parameters on the growth and properties of magnetron sputtered CN_x thin films

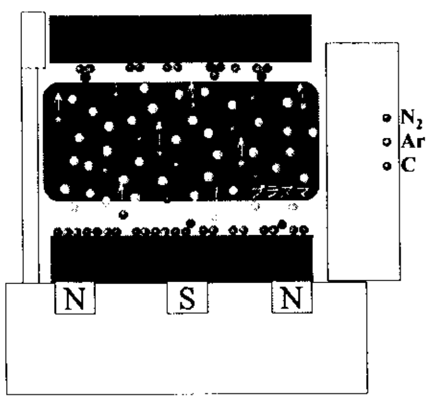
Objectives:

- Properties sensitive to process conditions => Diverging reports in the literature => Systematic study required
- Ion-assisted deposition may help to lower the critical T_S for forming the hard and elastic "fullerene-like" phase

Magnetron Sputtering

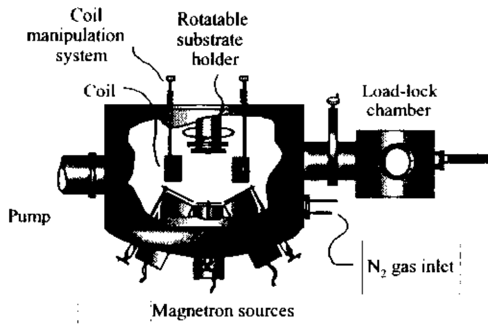
Interesting parameters:

I_i - Ion flux (mainly N_2^+)
I_n - Neutral flux (C, N_2)
E_i - Ion energy
E_n - Neutrals energy
T_s - Substrate temperature



Niklas Hellgren, MRS 1998

Sputtering conditions

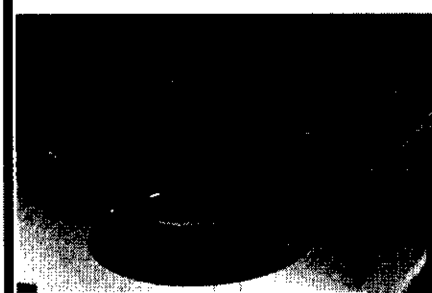


$P_b = 1 \times 10^{-9}$ mTorr

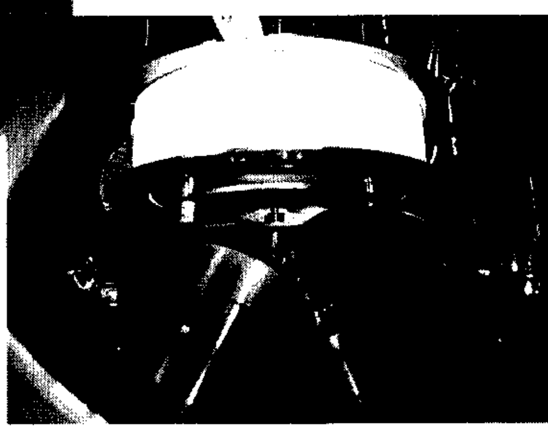
T_S = RT - 500 °C
P_{N2} = 1.5 - 10 mTorr
B_{appl} = -25 - 100 G

Interesting parameters:

I_i - Ion flux (mainly N_2^+)
I_n - Neutral flux (C, N_2)
E_i - Ion energy
E_n - Neutrals energy
T_s - Substrate temperature



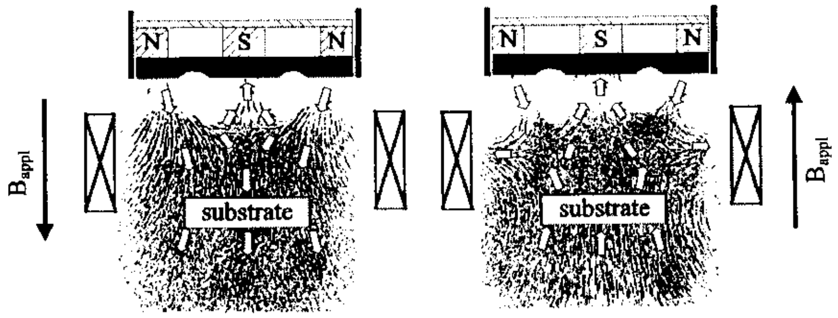
The Coil



Variable magnetic field =>

Controllably-unbalanced magnetron sputtering

Distribution of the Magnetic Field



The applied field B_{appl} supports the outer poles.

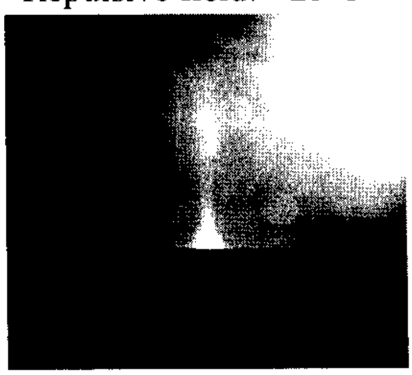
The applied field B_{appl} supports the center pole.

Controllably-Unbalanced Magnetron Sputtering

From I. Ivanov et al., J. Vac. Sci. Technol. A 12 (1994) 314

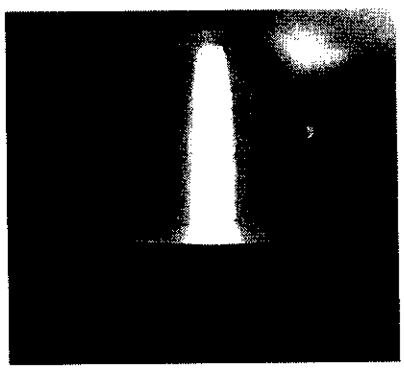
Effect on the plasma

Repulsive field: - 25 G



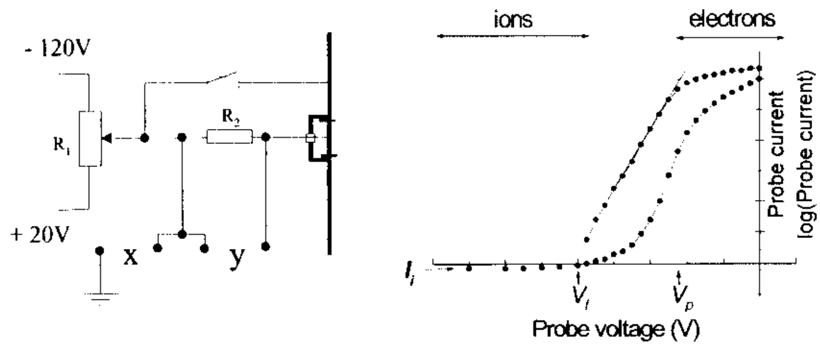
Weak diffuse plasma

Attractive field: +100 G



Strong, focused plasma

Probe Measurements

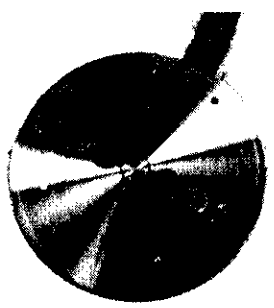


By measuring the current through a probe in the substrate position, as a function of bias voltage, the ion flux and energy can be deduced

I. Petrov *et al.*, Contrib. Plasma Phys. 28 (1988) 157

Niklas Hellgren, MRS 1998

Probe measurements



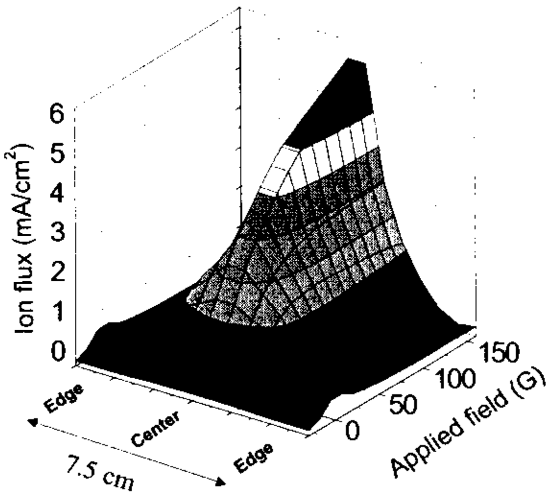
"7-point probe"

Since the conditions are not always homogenous over the substrate area, it is important to know the particle flux and energies at all positions.

Niklas Hellgren, MRS 1998

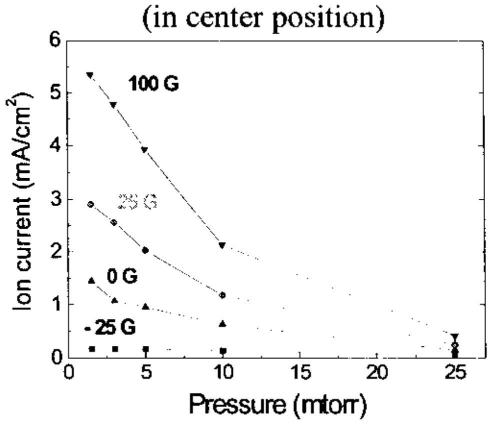
Ion flux

vs. Applied magnetic field & position



Ion flux vs. Pressure

(in center position)

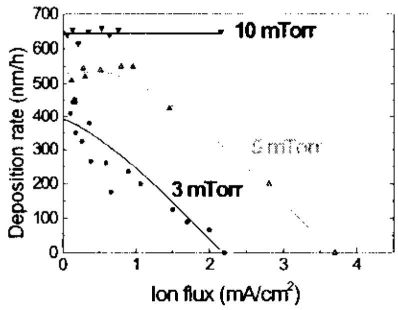


Higher pressure => Lower ion flux, due to gas scattering

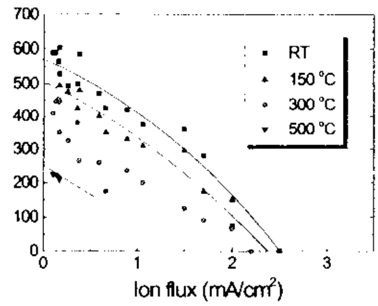
Growth rate vs. Ion flux

Ion energy E_i = 20-25 eV

@ 300 °C

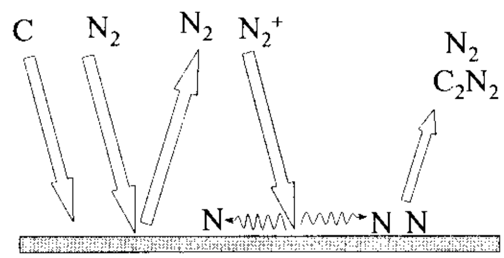


@ 3 mTorr



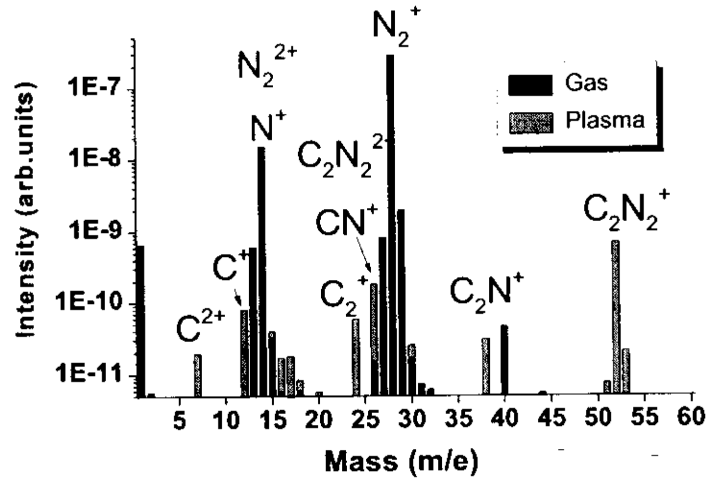
High flux, High T_S & Low pressure
=> More etching (+ densification)

Suppression of growth and N-incorporation rates

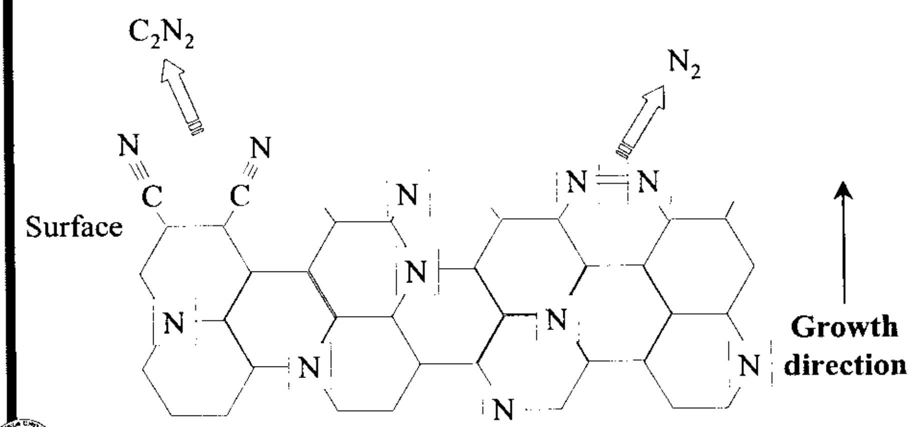


Thermal and ion-stimulated desorption of N_2 and CN-species

Mass spectra

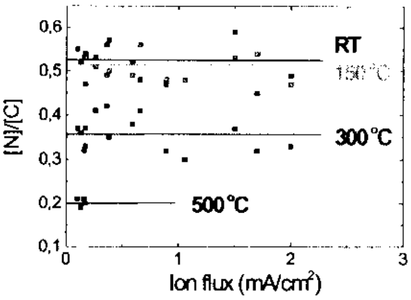


Possible mechanism for Desorption of N_2 and C_2N_2



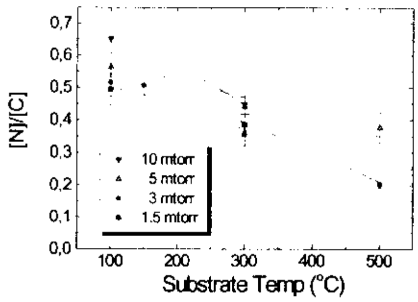
Nitrogen incorporation

vs. Ion flux
(@ 3 mTorr)



No clear effect of ion flux

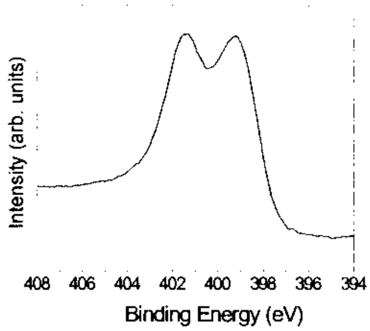
vs. Temperature
(Average over all fluxes)



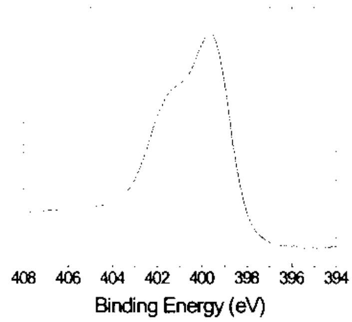
High pressure & Low T_S
=> More Nitrogen

XPS - N1s

High T_S & High flux



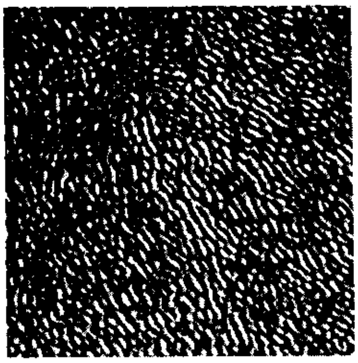
Low T_S & Low flux



Fingerprint from
"Fullerene-like" and Amorphous
microstructures

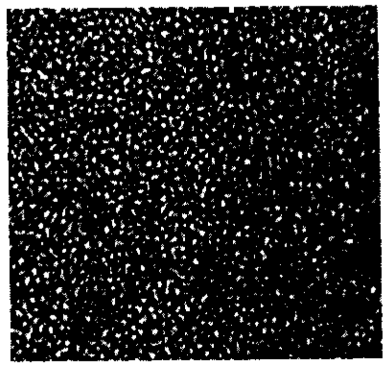
Microstructure

"Fullerene-like"



Hard & Elastic

Amorphous

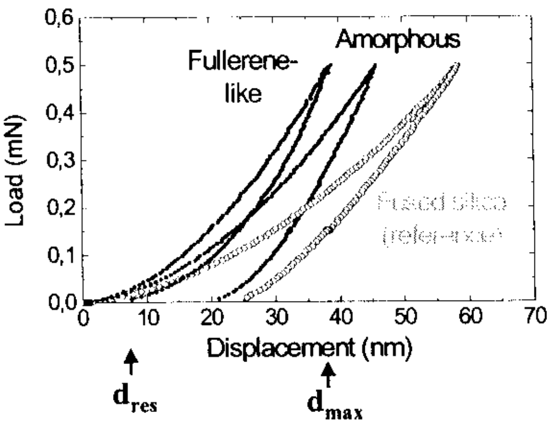


Fairly hard, but less elastic

Niklas Hellgren, MRS 1998

Nanoindentation

Load-displacement curves



High elasticity => Difficult to calculate E & H

Instead compare max displacement $\mathbf{d_{max}}$ and elastic recovery $\mathbf{R = (d_{max}-d_{res})/d_{max}}$

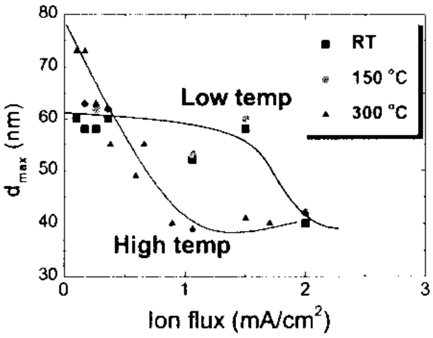
High ion flux & ~ 300 °C => High elasticity

Niklas Hellgren, MRS 1998

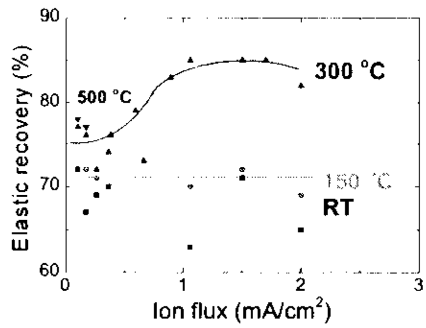
Nanoindentation

Elastic recovery @ 0.5 mN

Displacement @ 0.5 mN



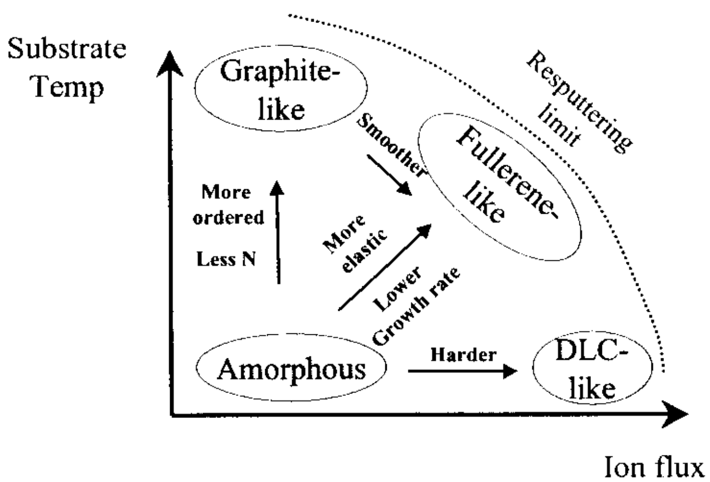
Elastic recovery



Low pressure, high T_S and high ion flux
=> Hardest and most elastic films

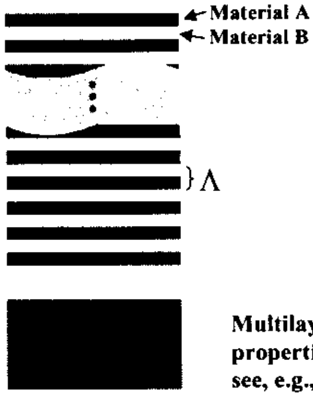
Niklas Hellgren, MRS 1998

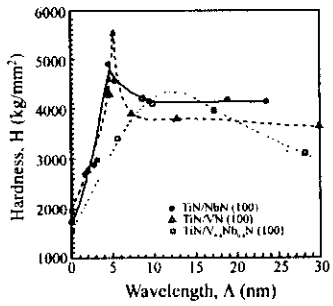
Summary - Growth of CN_x thin films



Niklas Hellgren, MRS 1998

Other ways to grow hard materials - Multilayers





Multilayered structures may have improved mechanical properties compared to the single layered films.
see, e.g., Shinn *et al.*, J. Mater. Res. 7 (1992) 901

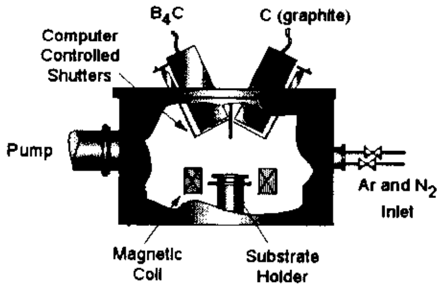
Also internal stresses may be reduced => better adhesion

CN_x/BN:C Multilayers

Objectives:

- **Grow multilayers of hard and elastic materials (fullerene-like CN_x and BN:C)**
- **Find proper growth conditions at which CN_x and BN:C can be sequentially deposited**
- **Study the structure and mechanical response of as-grown structures**

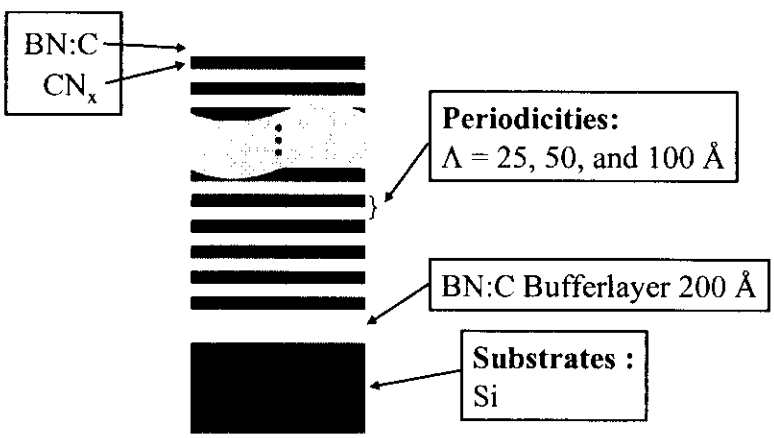
Film growth & characterization



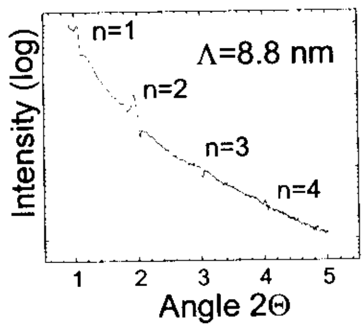
Growth conditions:
C and B_4C targets
P_b = 1 x 10^{-7} Torr
P_{tot} = 3.0 mTorr
($Ar+N_2$, 60+40%)
I_t = 0.2 A
$j_i / j_n \sim 3$, $E_i \sim 20$ eV
Thickness = 0.5 μm
T_s = 250 °C

Characterization: RBS, XRD, TEM, Nanoindentation

As-grown Structures



XRD

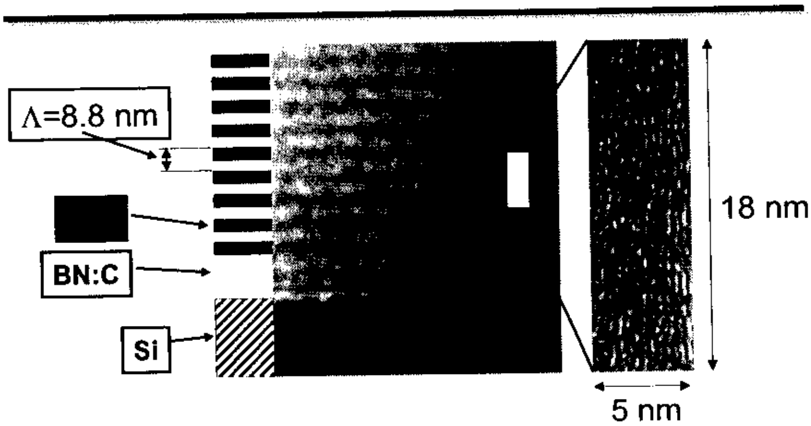


Linear regression of $\sin^2\Theta$ versus n^2

slope = $\left(\frac{\lambda}{2 \times \Lambda}\right)^2$

Well defined layer-interfaces

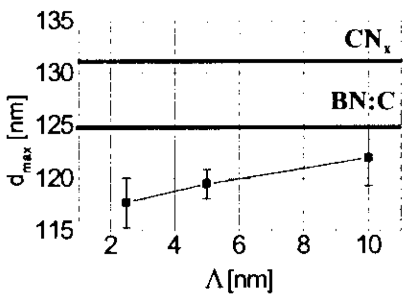
Microstructure



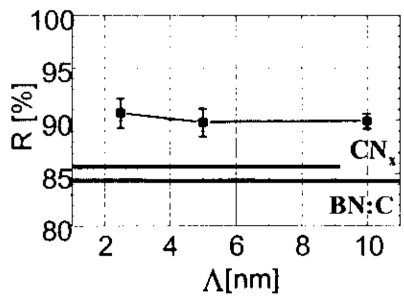
Well defined layer-interfaces, BUT continuos microstructure

Nanoindentation

Maximum Penetration Depth :



Elastic Recovery :

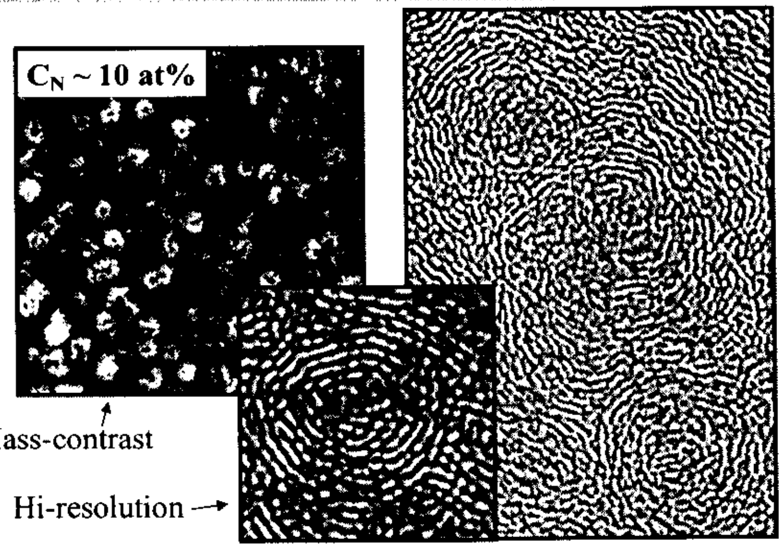


Multilayers => Slightly improved mechanical properties

Conclusions - BN/CN Multilayers

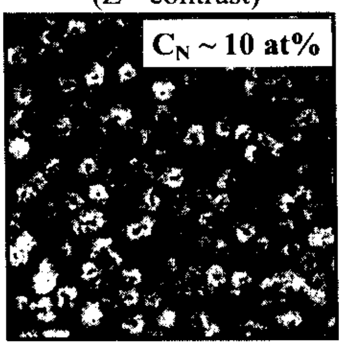
- **Possible to grow CN_x/BN:C Multilayers**
- **Well defined layer interfaces**
- **Continuos microstructure over the layer interfaces**
- **Slightly improved mechanical properties**

CN Nanotubes - HREM



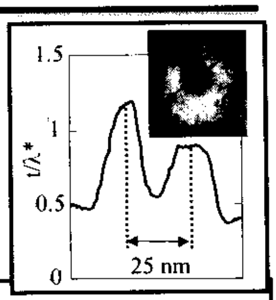
Carbon nitride "nanotubes"

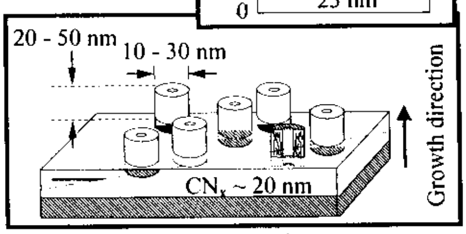
Annular Dark Field Image
(Z - contrast)



Densely packed tubules
$\sim 1 \times 10^4 \ \mu m^{-2}$

EELS
line-profile





Schematics

K. Suenaga, *et al.*, "Carbon Nitride Nanotubulite" Chem. Phys. Lett. 300 (1998) 695

Summary - magnetron sputtered CN_x

Growth and structural evolution of CN_x thin films is strongly dependent on CHEMICAL ETCHING during growth

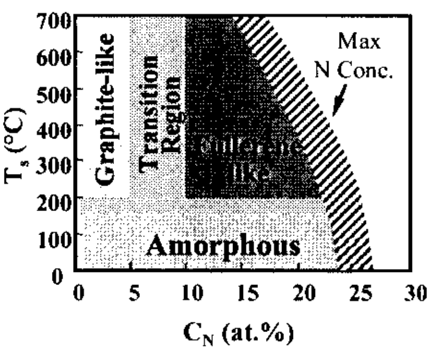
Mainly influenced by:

- Substrate Temperature
- Fluxes & energies of deposited particles
- Nitrogen concentration

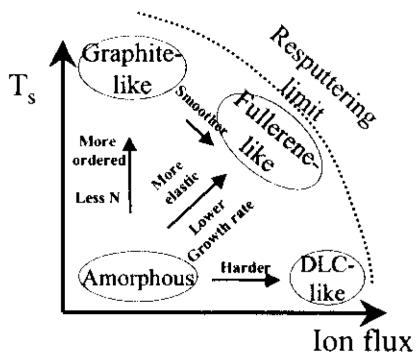
Difficult to grow homogenous films
=> be careful with interpretations

Summary - magnetron sputtered CN_x

Role of Nitrogen



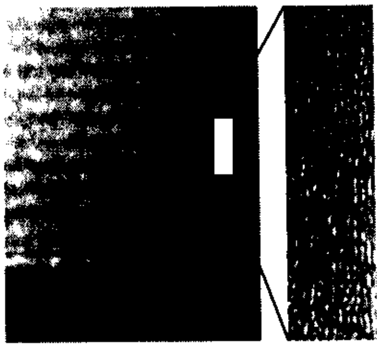
Role of Ion Flux

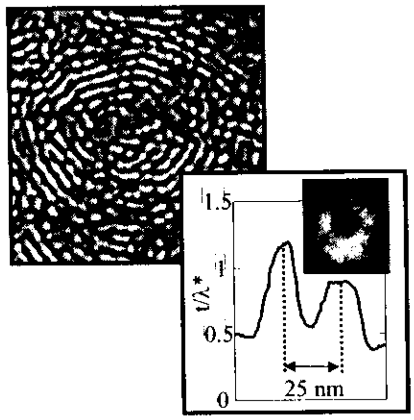


Niklas Hellgren, TMR Meeting, March 99

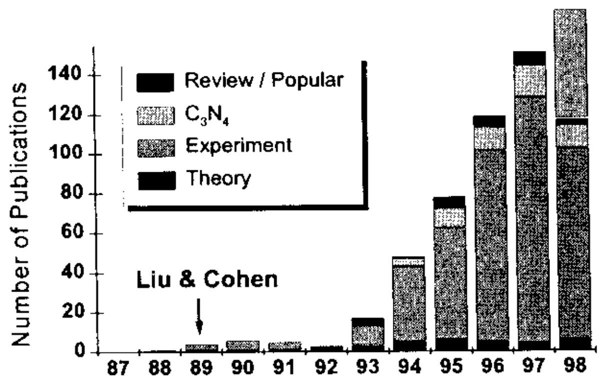
Summary - magnetron sputtered CN_x

CN_x/BN:C Multilayers | **CN nanostructures**





CN publications



Liu & Cohen started a world-wide effort to try to synthesize crystalline C_3N_4 films. However, few and incomplete reports claiming success

Difficulties in C_3N_4 synthesis

- Most efforts have resulted in nitrogen deficient (< 40 at.%) and/or amorphous films.
- Higher T_S required to grow crystalline films, BUT higher T_S => lower nitrogen concentration.
- Thus C_3N_4 growth very difficult (impossible?) by PVD techniques.
- Many claims of small C_3N_4 crystals in an amorphous, nitrogen deficient matrix. Very unlikely!!
- Most promising results from hot filament chemical vapor deposition, HFCVD. See, e.g., Chen et al., J. Crystal Growth 179 (1997) 525
- No "C_3N_4" films have shown to be superhard => Grain boundaries and other structural defects also important for the overall performance.
- BUT CN_x (x < 1.33) has very interesting properties for technological applications!

Applications of hard and elastic CN_x Films

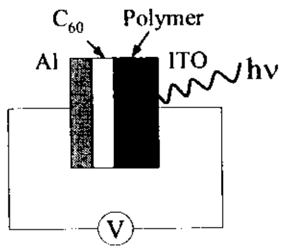
Wear Protective coatings on e.g.:

- Magnetic recording media and recording heads (already used by IBM)
- Bearings
- Ortopaedic Implants (e.g. hip joints)
- Scalpels, razor blades,...

However, problem with adhesion to metals. Can be solved by bufferlayers, graded interfaces, multilayers,...

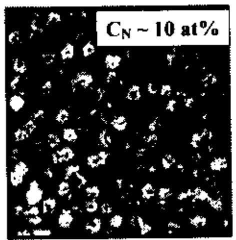
Applications of Nanostructured CN_x Films

Solar Cells/
Photovoltaic Devices

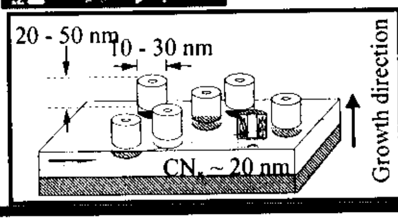


Evaporated C_{60} may be replaced by nanostructured sputtered CN_x

Electron Field Emitters



Out-standing "CN nano-tubes" may be good field emitters



Conclusions

- New predicted hard material: β-C_3N_4
- Diffucult to produce β-C_3N_4
- Non-crystalline CN_x ($x < 1.33$) has many interesting properties
- Many possible applications of CN_x
- Deposition conditions need to be controlled!