Instituto de Física
Universidade Federal Fluminense

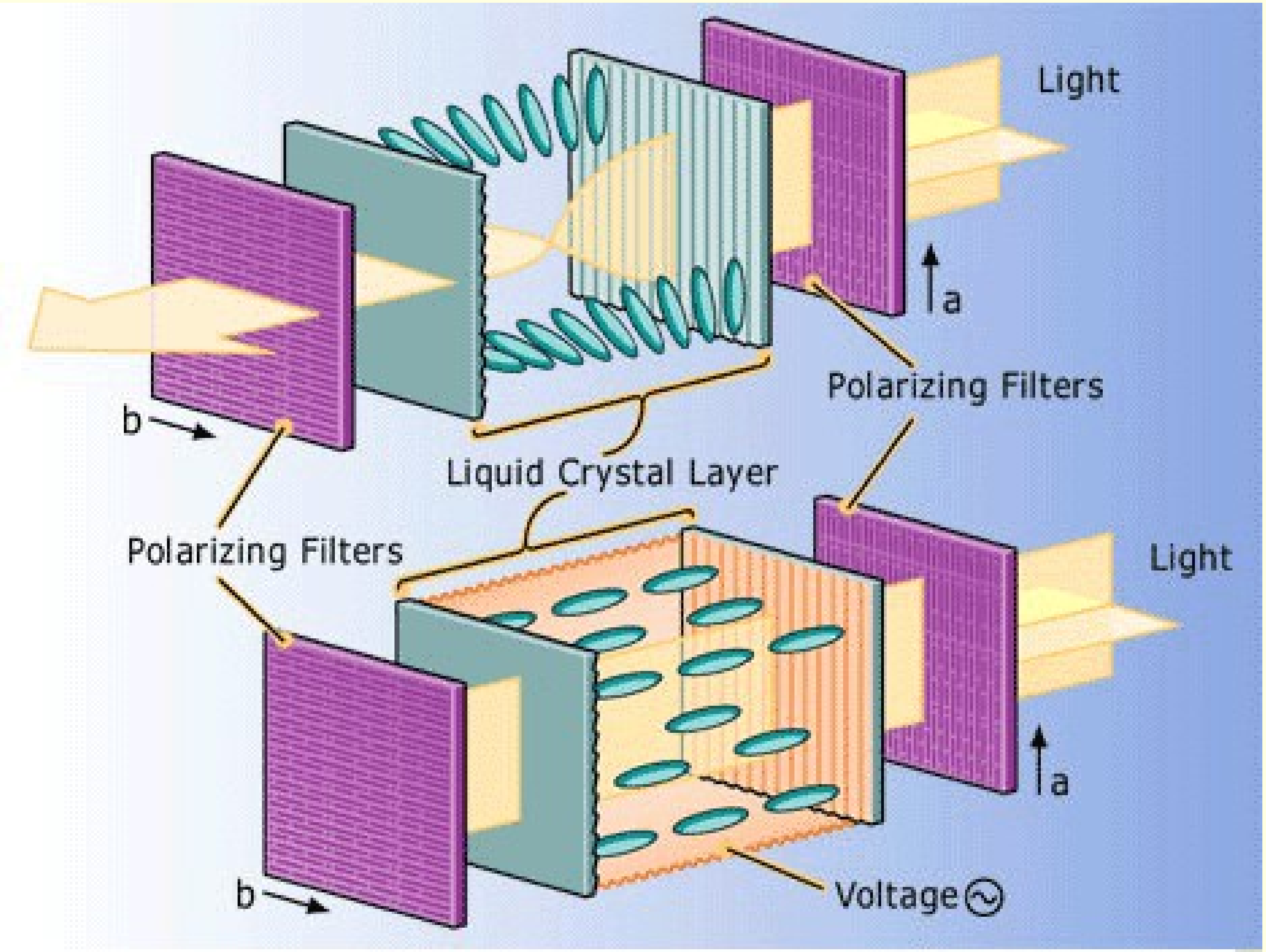
Novos materiais como requisito para novas tecnologias

Prof. Dante F. Franceschini Filho
Laboratório de Filmes Finos

Visão geral

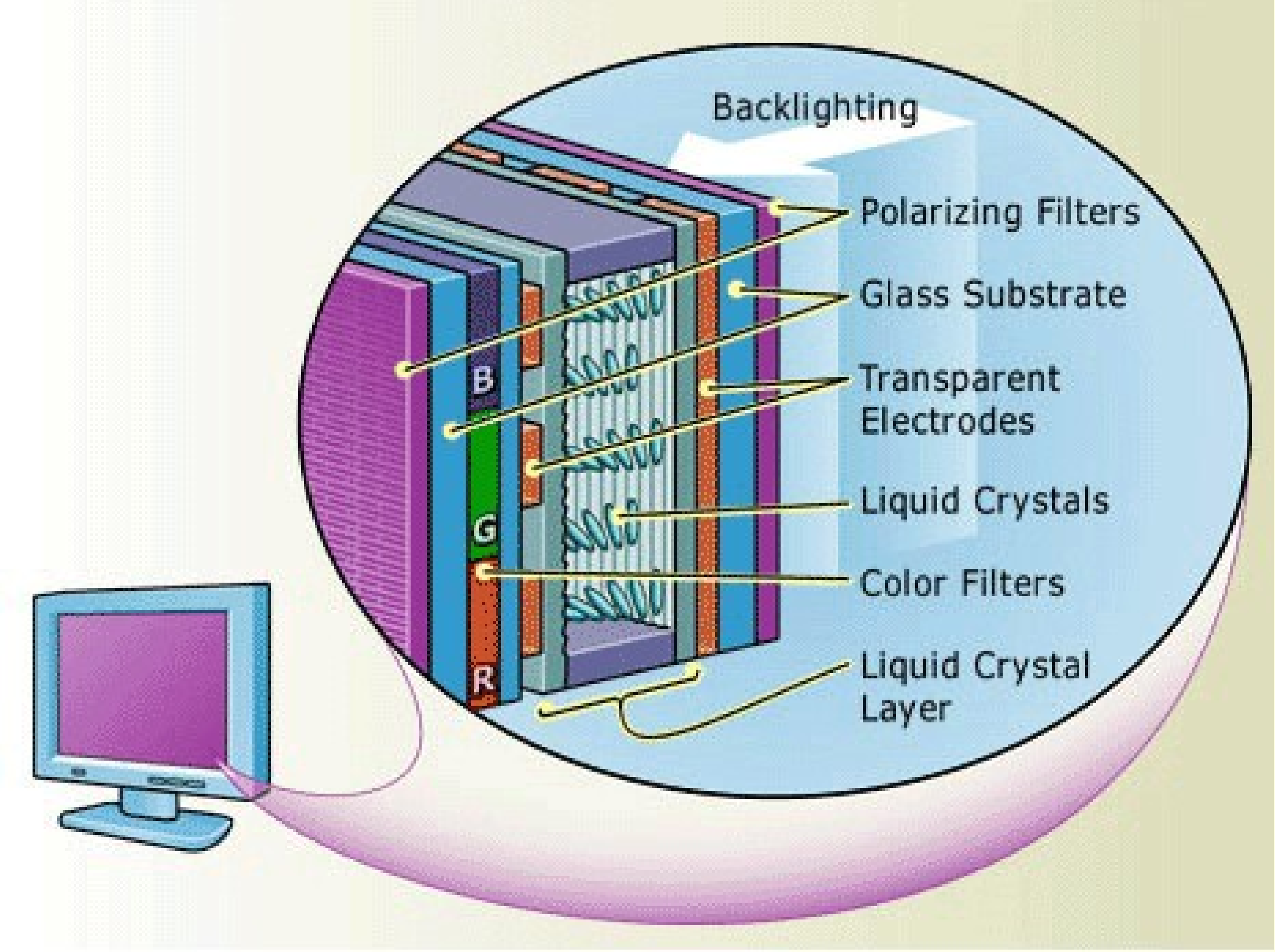
- Monitor LCD
- Condutores Transparentes
- Materiais superduros
- Carbono amorfo hidrogenado: resultados recentes
- Ablação por laser: Filmes finos e nanoestruturas.
- Nanotubos de Carbono
- Conclusões

LCD



Light
a
Polarizing Filters
b
Liquid Crystal Layer
Polarizing Filters
Light
a
b
Voltage

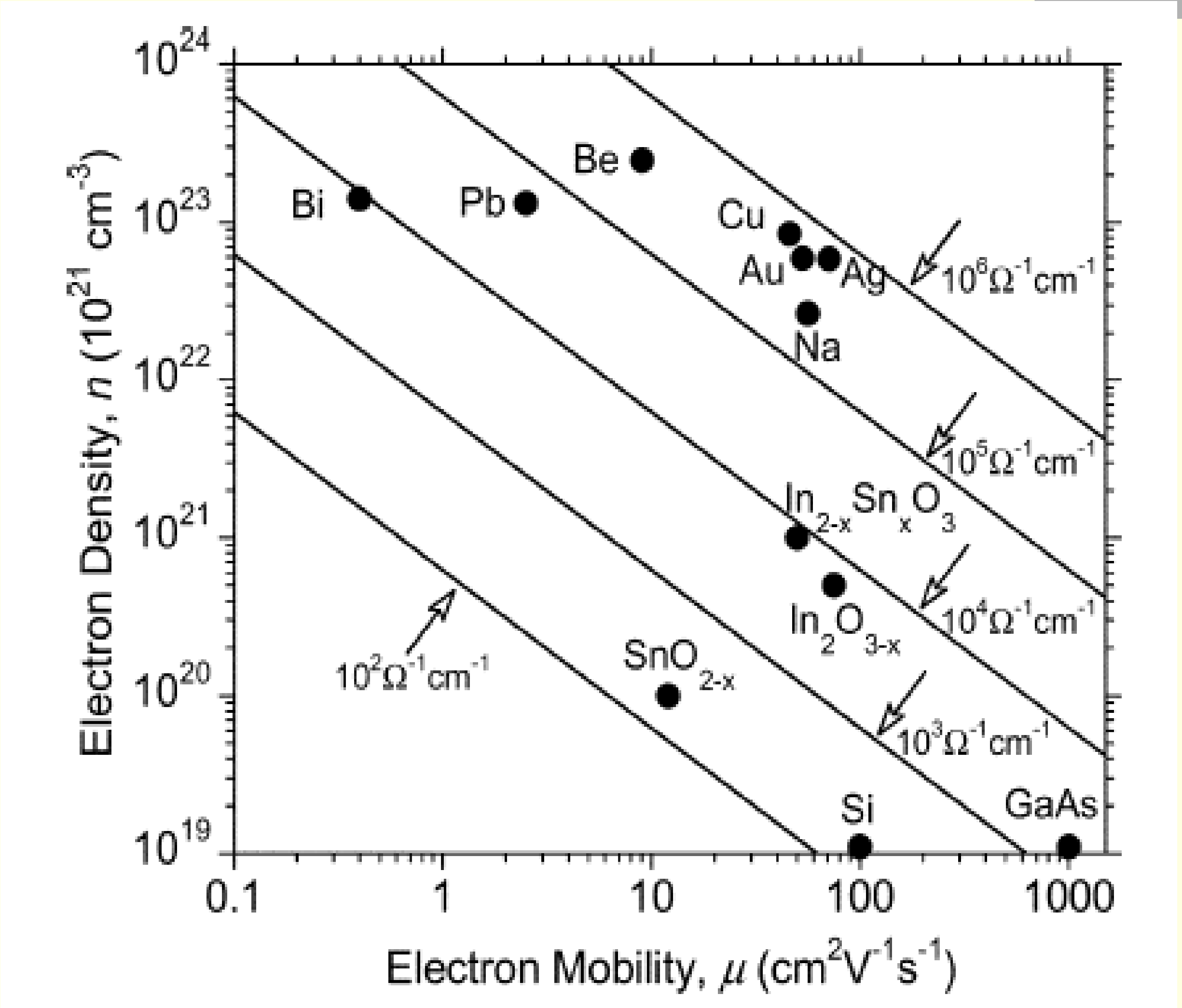
LCD


Backlighting
Polarizing Filters
Glass Substrate
Transparent Electrodes
Liquid Crystals
Color Filters
Liquid Crystal Layer
B
G
R

Condutores transparentes

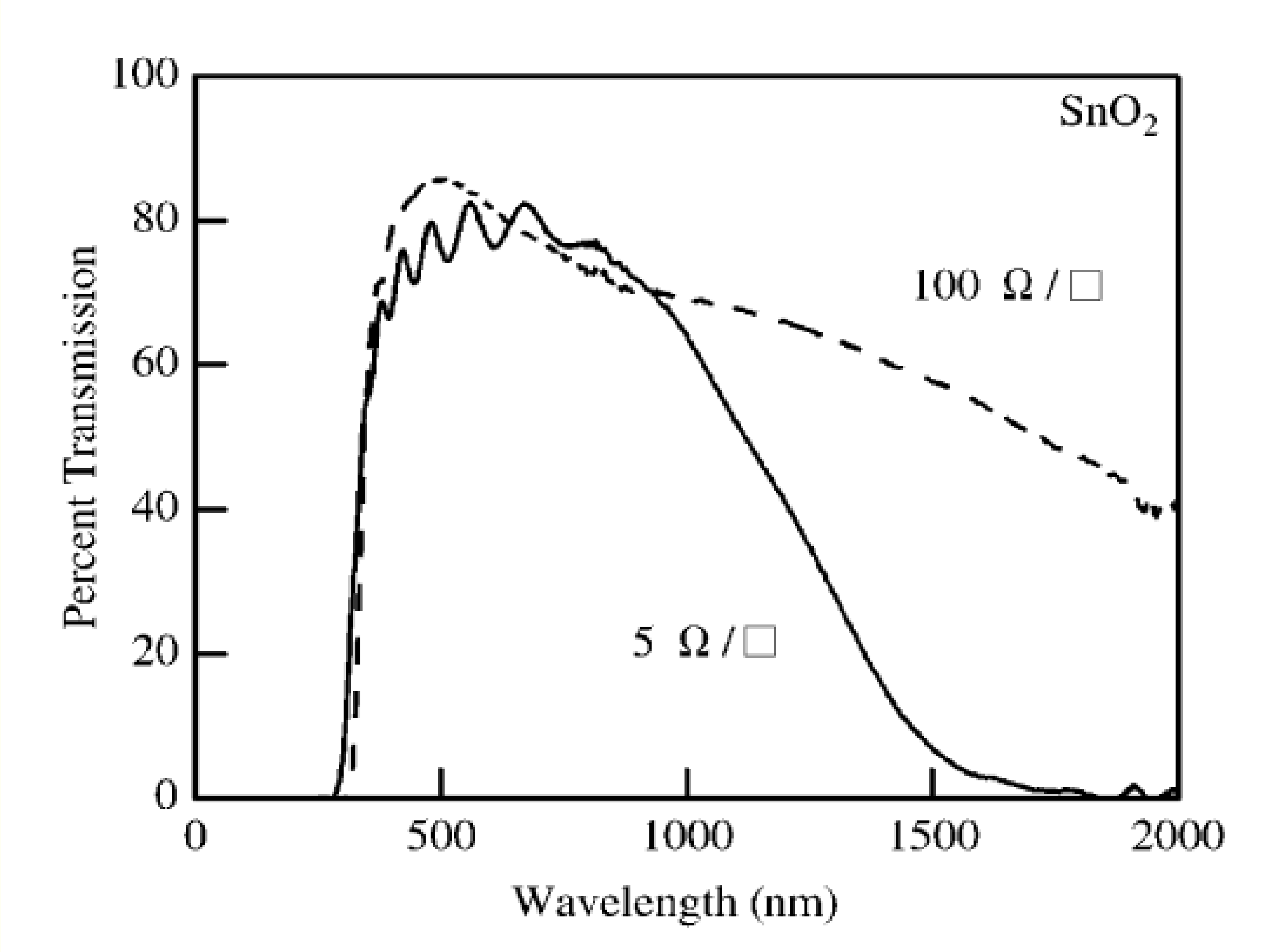
- **MRS Buletin vol. 25 no.8 (2000)**
- Transparent Conducting Oxides – D.S. Ginley and Clark Beight
- Criteria for Choosing Transparent Conductors – R.G. Gordon
- Characterization of Transparent |Conducting Oxides – T.J. Coutts, D.L. Young and X. Li

Condutores transparentes



$\mu = v/E$

Condutividade vs.transparência



Teoria de Drude – elétrons livres

$$\sigma = \frac{ne^2\tau}{m_c^*}$$

$$\mu = \frac{e\tau}{m_c^*}$$

$$\varepsilon_1 = \varepsilon_\infty\left(1 - \frac{\omega_p^2}{\omega^2}\right)$$

$$\varepsilon_2 = \left(\frac{\varepsilon_\infty \omega_p^2}{\omega^3 \tau}\right)$$

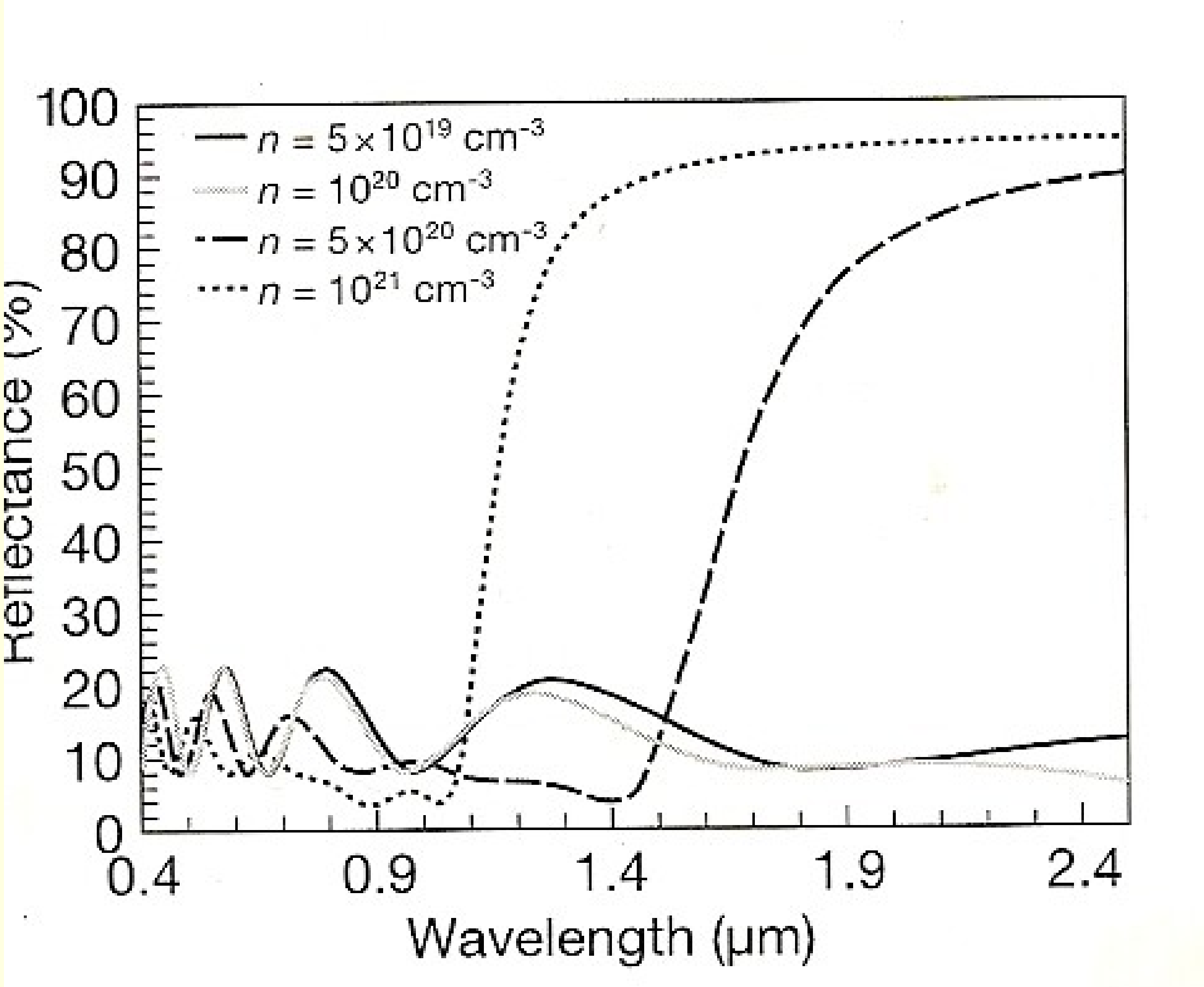
$$\omega_p = \left(\frac{ne^2}{\varepsilon_0 \varepsilon_\infty m_c^*}\right)^{\frac{1}{2}}$$

$$\frac{1}{\tau} << \omega$$

$$\varepsilon_1, \varepsilon_2 \rightarrow N, k + coef.Fresnel \rightarrow$$

reflectância
absorbância

Reflectância

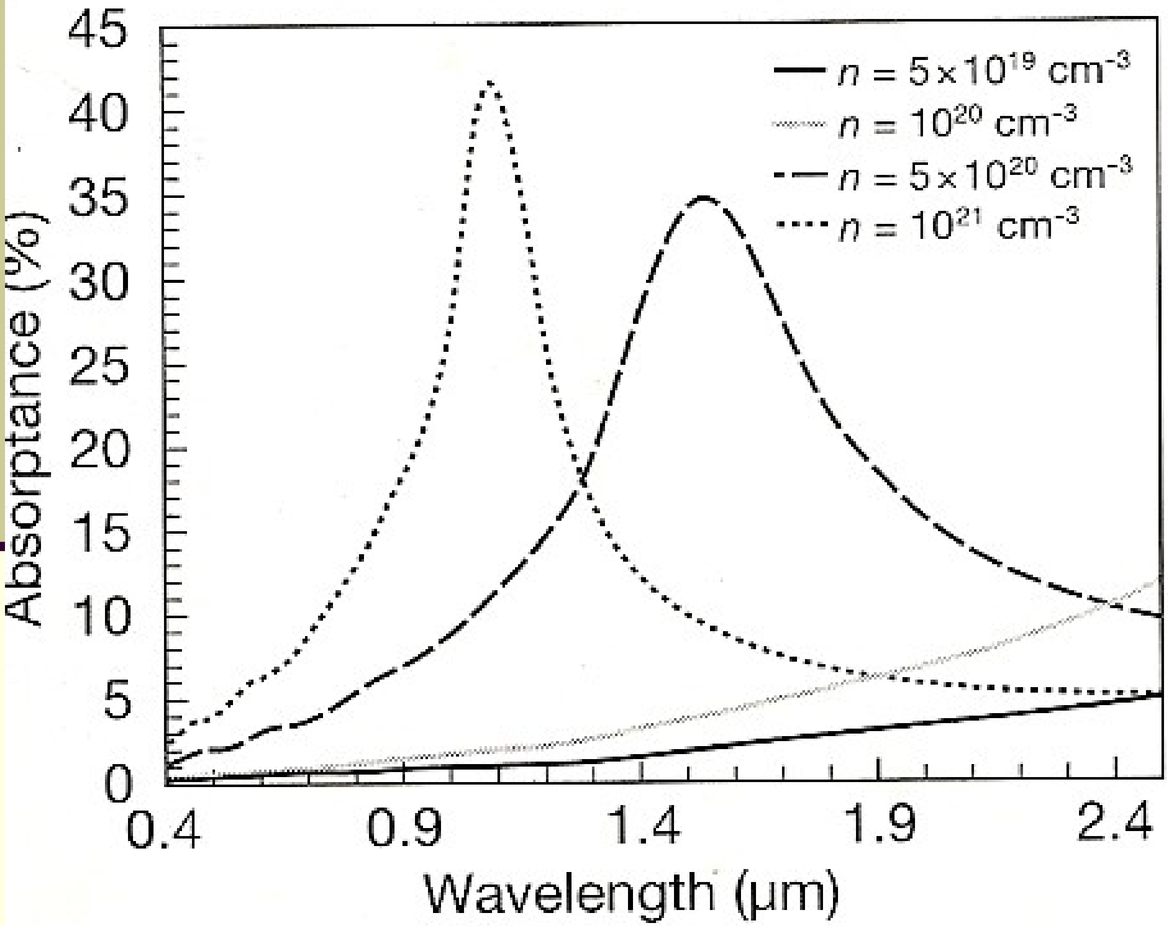


$\mu = 1000\ cm^2V^{-1}s^{-1}$

$m^*_c = 0.3\ m_e$

$t = 0.5\ \mu m$

Absorbância



$\mu = 1000\ cm^2V^{-1}s^{-1}$

$m^*_c = 0.3\ m_e$

$t = 0.5\ \mu m$

Teoria de Drude – elétrons livres

$$\sigma = \frac{ne^2\tau}{m_c^*} \qquad \mu = \frac{e\tau}{m_c^*}$$

$$\varepsilon_1 = \varepsilon_\infty\left(1 - \frac{\omega_p^2}{\omega^2}\right) \qquad \varepsilon_{٢} = \left(\frac{\varepsilon_\infty \omega_p^{٢}}{\omega^{٣}\tau}\right) \qquad \omega_p = \left(\frac{ne^{٢}}{\varepsilon_{٠}\varepsilon_\infty m_c^*}\right)^{\frac{١}{٢}}$$

$$\frac{١}{\tau} << \omega$$

$$\varepsilon_{١}, \varepsilon_{٢} \rightarrow N, k + coef.Fresnel \rightarrow$$

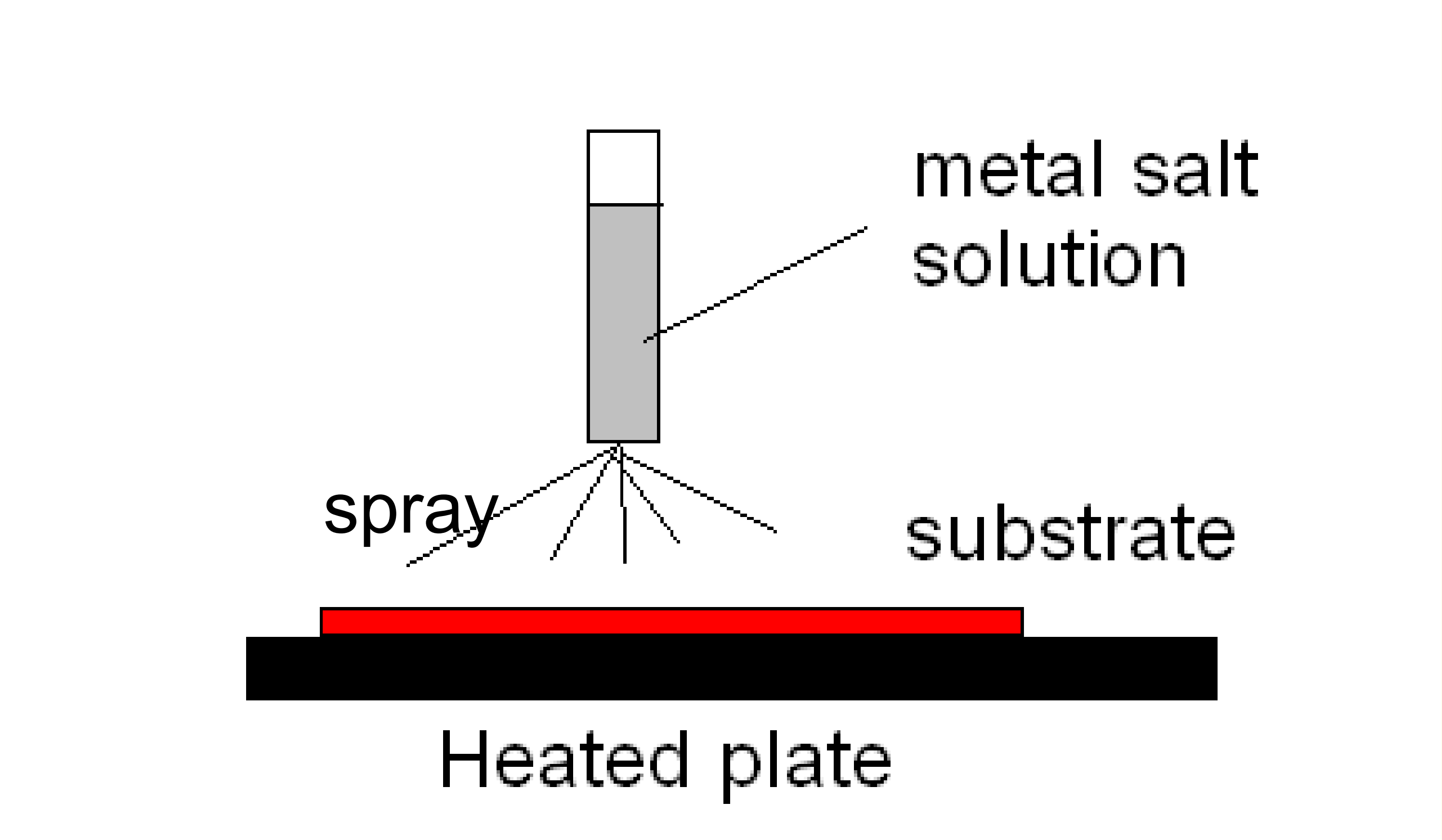
reflectância
absorbância

Table I: History of Processes for Making Transparent Conductors.

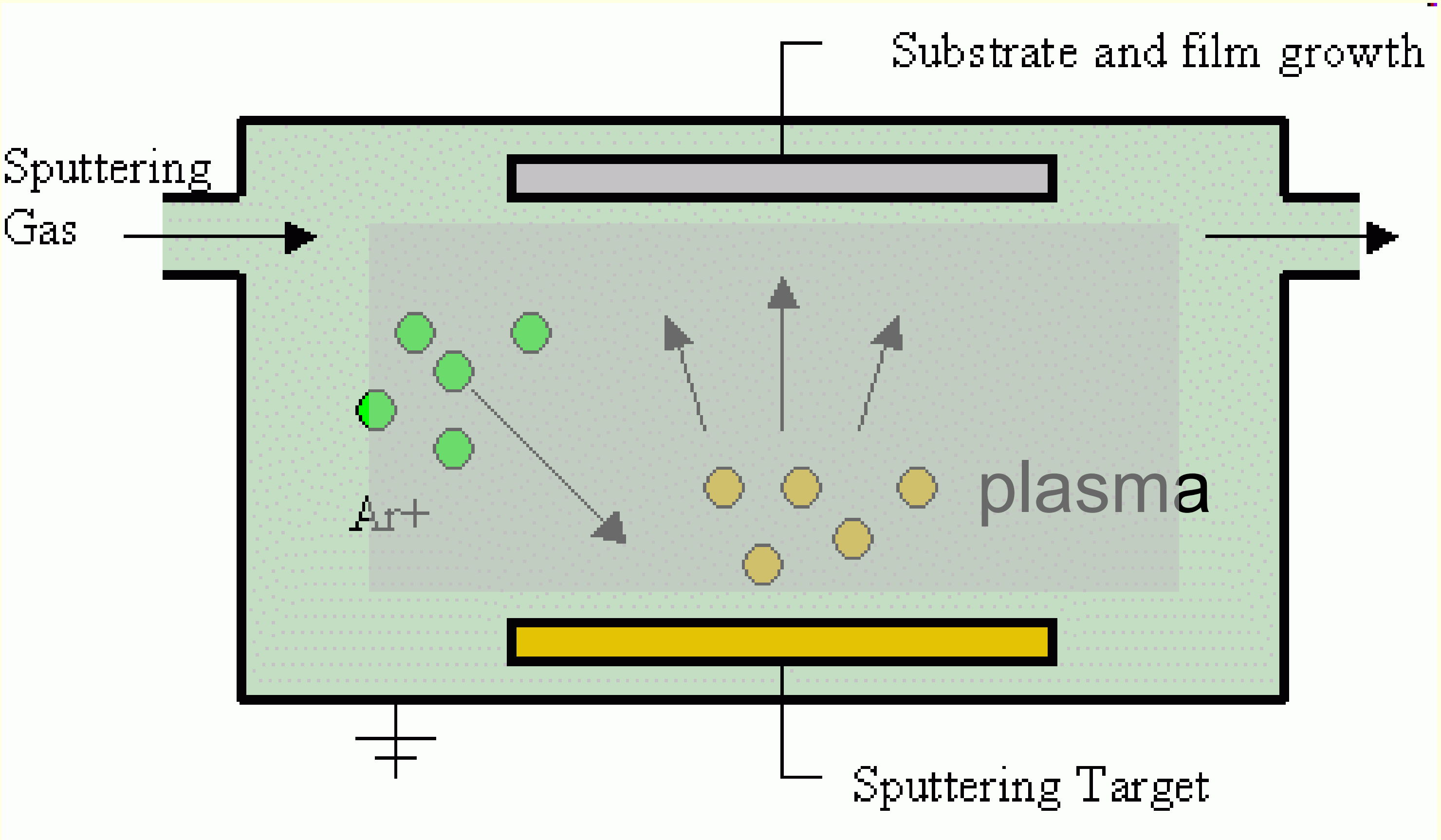
Materials and Process	Reference
Ag by chemical-bath deposition	Unknown Venetian
SnO_2:Sb by spray pyrolysis	J.M. Mochel (Corning), 1947[1]
SnO_2:Cl by spray pyrolysis	H.A. McMaster (Libbey-Owens-Ford), 1947[2]
SnO_2:F by spray pyrolysis	W.O. Lytle and A.E. Junge (PPG), 1951[3]
In_2O_3:Sn by spray pyrolysis	J.M. Mochel (Corning), 1951[4]
In_2O_3:Sn by sputtering	L. Holland and G. Siddall, 1955[5]
SnO_2:Sb by CVD	H.F. Dates and J.K. Davis (Corning), 1967[6]
Cd_2SnO_4 by sputtering	A.J. Nozik (American Cyanamid), 1974[7]
Cd_2SnO_4 by spray pyrolysis	A.J. Nozik and G. Haacke (American Cyanamid), 1978[8]
SnO_2:F by CVD	R.G. Gordon (Harvard), 1979[9]
TiN by CVD	S.R. Kurtz and R.G. Gordon (Harvard), 1986[10]
ZnO:In by spray pyrolysis	S. Major et al. (Ind. Inst. Tech.), 1984[11]
ZnO:Al by sputtering	T. Minami et al. (Kanazawa), 1984[12]
ZnO:In by sputtering	S.N. Qiu et al. (McGill), 1987[13]
ZnO:B by CVD	P.S. Vijayakumar et al. (Arco Solar), 1988[14]
ZnO:Ga by sputtering	B.H. Choi et al. (KAIST), 1990[15]
ZnO:F by CVD	J. Hu and R.G. Gordon (Harvard), 1991[16]
ZnO:Al by CVD	J. Hu and R.G. Gordon (Harvard), 1992[17]
ZnO:Ga by CVD	J. Hu and R.G. Gordon (Harvard), 1992[18]
ZnO:In by CVD	J. Hu and R.G. Gordon (Harvard), 1993[19]
Zn_2SnO_4 by sputtering	H. Enoki et al. (Tohoku), 1992[20]
$ZnSnO_3$ by sputtering	T. Minami et al. (Kanazawa), 1994[21]
Cd_2SnO_4 by pulsed laser deposition	J.M. McGraw et al. (Colorado School of Mines and NREL), 1995[22]

spray-pyrolysis (SnO_2)

Janelas – Revestimentos Funcionais



Sputtering



Indium Tim Oxide - FPD

Table VI: Etchants for Transparent Conductors.

Material	Etchant
ZnO	Dilute acids
ZnO	Ammonium chloride
TiN	$H_2O_2 + NH_3$
In_2O_3	$HCl + HNO_3$ or $FeCl_3$
SnO_2	Zn + HCl
SnO_2	$CrCl_2$

Table VII: Hardness of Some Transparent Conductors.

Material	Mohs Hardness
TiN	9
SnO_2	6.5
Soda-lime glass	6
In_2O_3	~5
ZnO	4
Ag	low

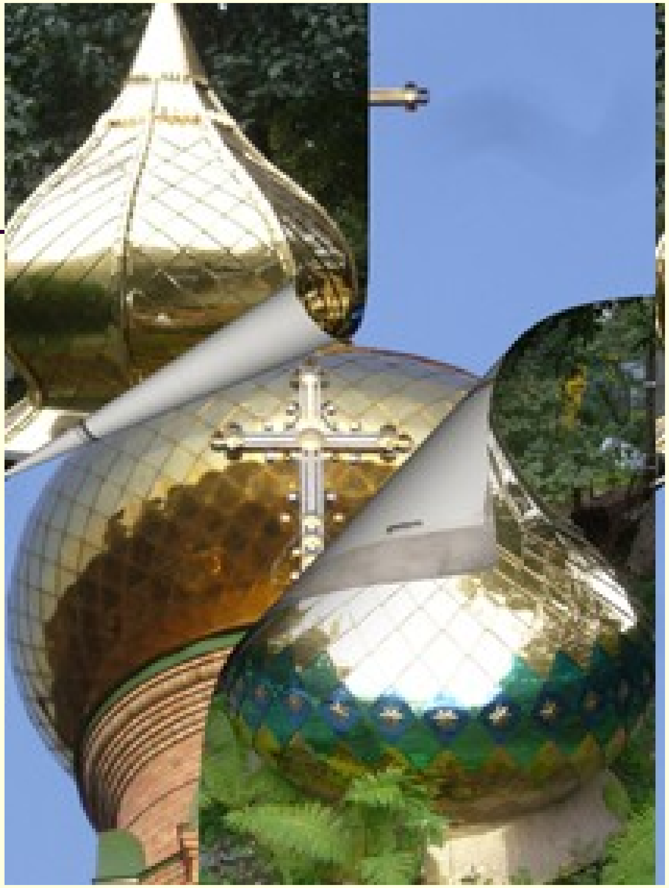
Table III: Approximate Minimum Resistivities and Plasma Wavelengths for Some Transparent Conductors.

Material	Resistivity ($\mu\Omega$ cm)	Plasma Wavelength (μm)
Ag	1.6	0.4
TiN	20	0.7
In_2O_3:Sn	100	>1.0
Cd_2SnO_4	130	>1.3
ZnO:Al	150	>1.3
SnO_2:F	200	>1.6
ZnO:F	400	>2.0

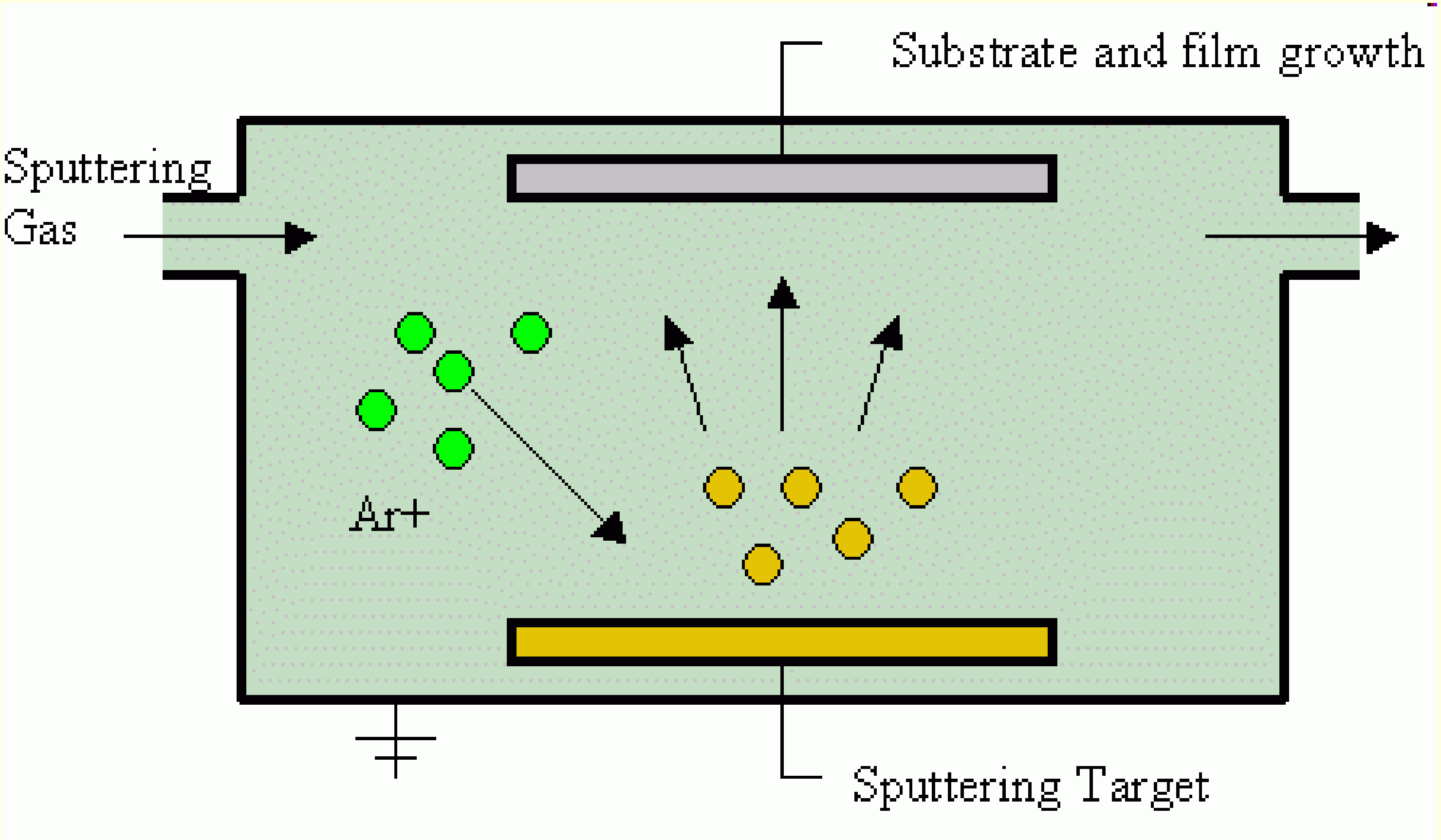
Table VIII: Choice of Transparent Conductors.

Property	Material
Highest transparency	$ZnO:F$, Cd_2SnO_4
Highest conductivity	$In_2O_3:Sn$
Lowest plasma frequency	$SnO_2:F$, $ZnO:F$
Highest plasma frequency	Ag, TiN, $In_2O_3:Sn$
Highest work function, best contact to *p*-Si	$SnO_2:F$, $ZnSnO_3$
Lowest work function, best contact to *n*-Si	$ZnO:F$
Best thermal stability	$SnO_2:F$, TiN, Cd_2SnO_4
Best mechanical durability	TiN, $SnO_2:F$
Best chemical durability	$SnO_2:F$
Easiest to etch	$ZnO:F$, TiN
Best resistance to H plasmas	$ZnO:F$
Lowest deposition temperature	$In_2O_3:Sn$, $ZnO:B$, Ag
Least toxic	$ZnO:F$, $SnO_2:F$
Lowest cost	$SnO_2:F$

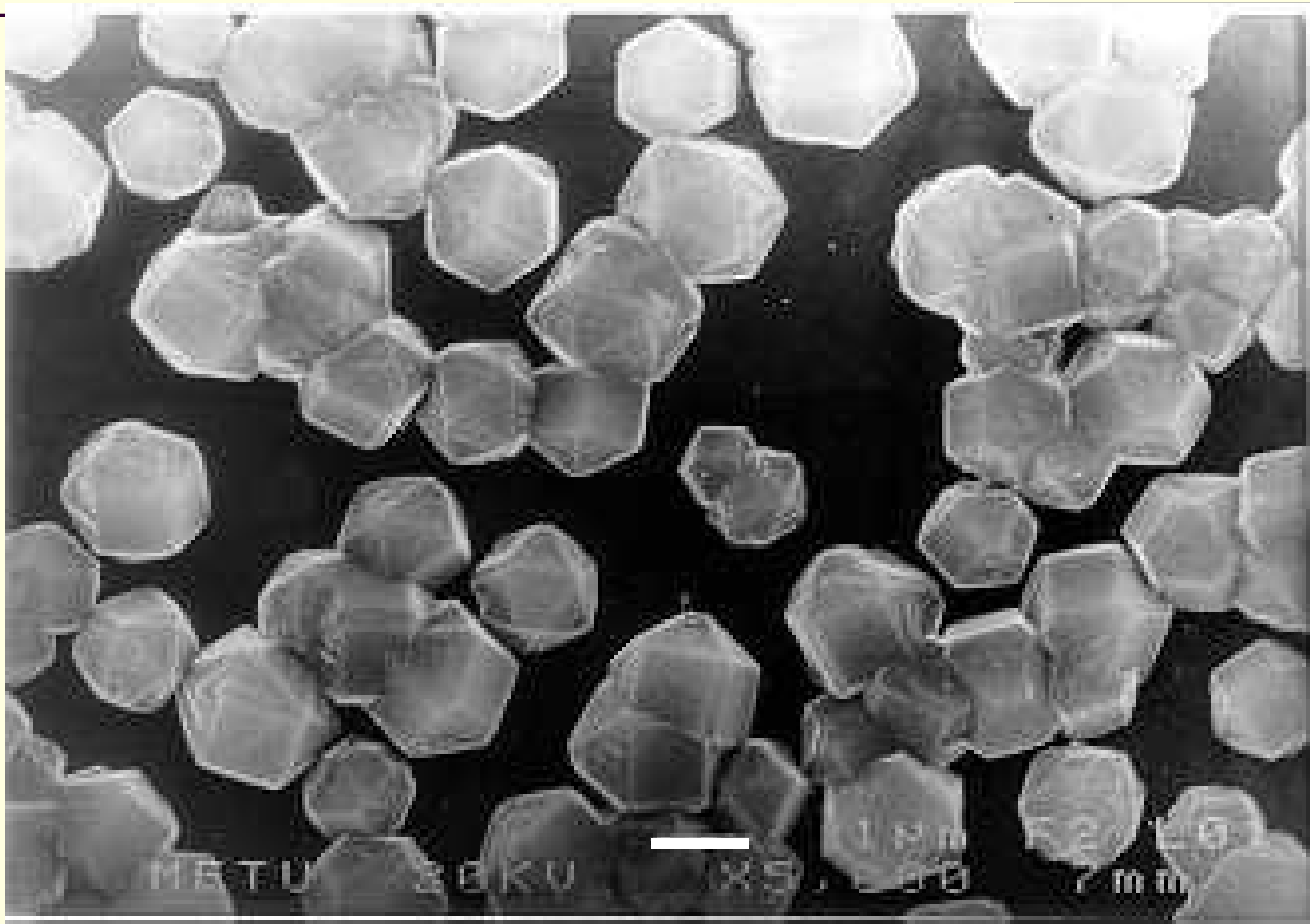
TiN



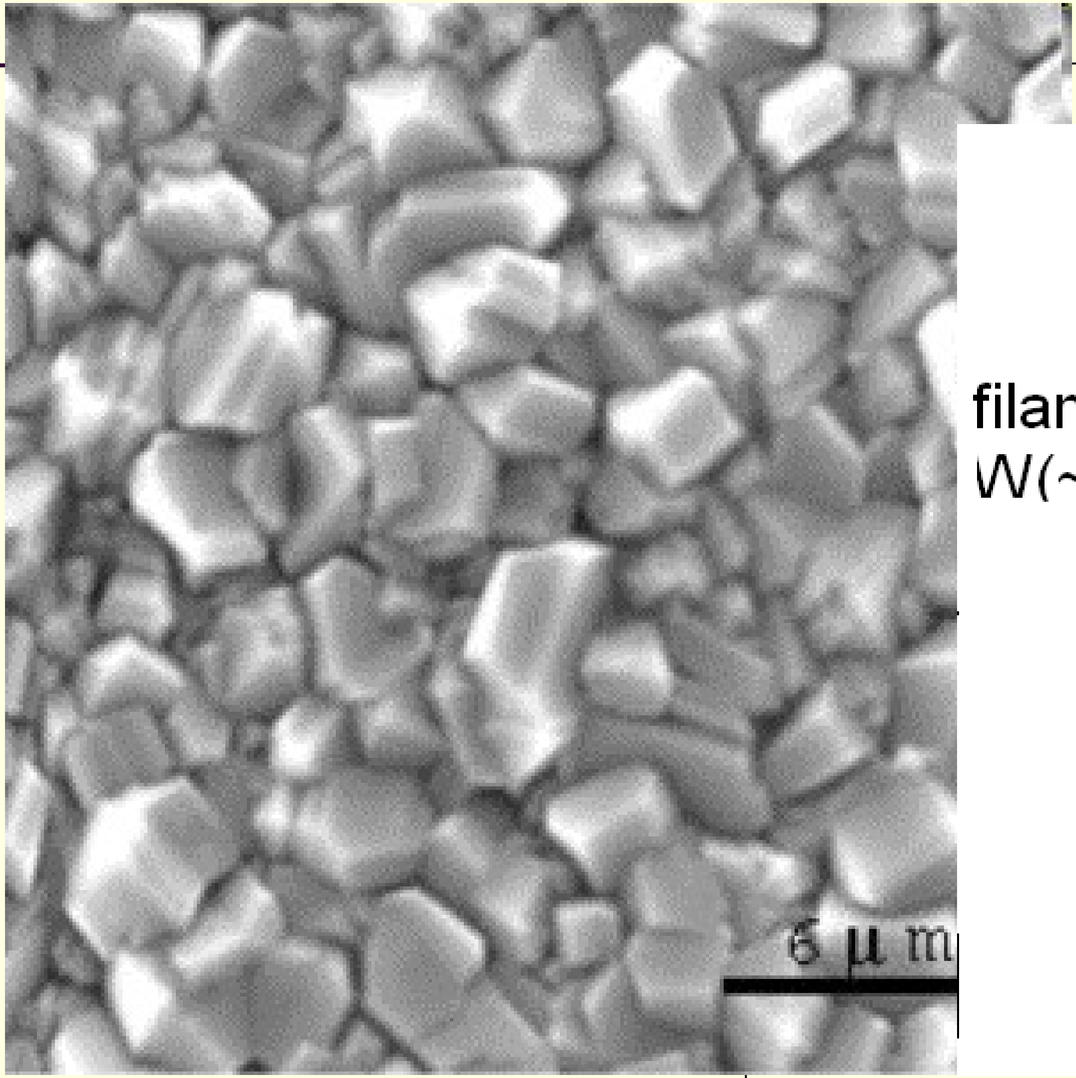
Adição de N_2

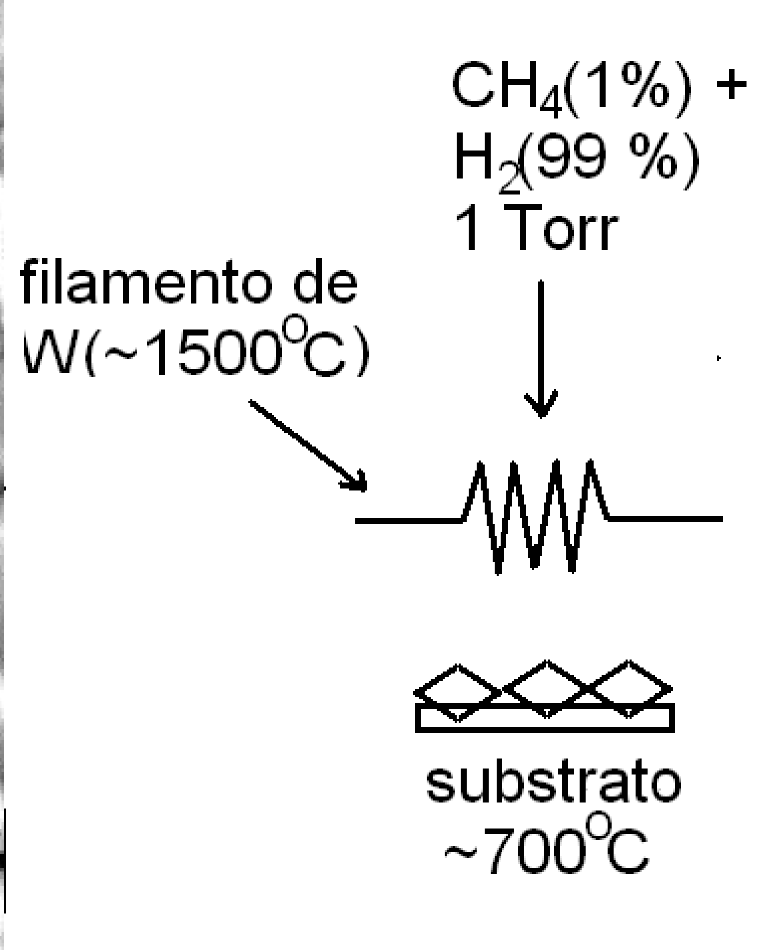

Substrate and film growth
Sputtering
Gas
Ar+
Sputtering Target

Diamante CVD



Filamento Quente





Aplicações

- Brocas odontológicas
- Janelas resistentes à radiação
- Ferramentas de corte para metais não ferrosos
- ~~Revestimentos anti-desgaste e anti-atrito~~

ALTA RUGOSIDADE (CRISTAIS DE ~1μ m)

Amorphous Hydrogenated Carbon a-C:H

	sp^3 (%)	H (% at.)	Density (g / cm^3)	Gap (eV)	Hardness (GPa)
Diamond	100	0	3.515	5.5	100
Graphite	0	0	2.267	0	
ta-C	80-88	0	3.1	2.5	80
Hard a-C:H	40	30-40	1.6-2.2	1.1-1.7	10-20
Soft a-C:H	60	40-50	1.2-1.6	1.7-4	<10
ta-C:H	70	30	2.4	2-2.5	50
polyethylene	100	67	0.92	6	0.01

DLC

Applications

- Mechanical protective coatings

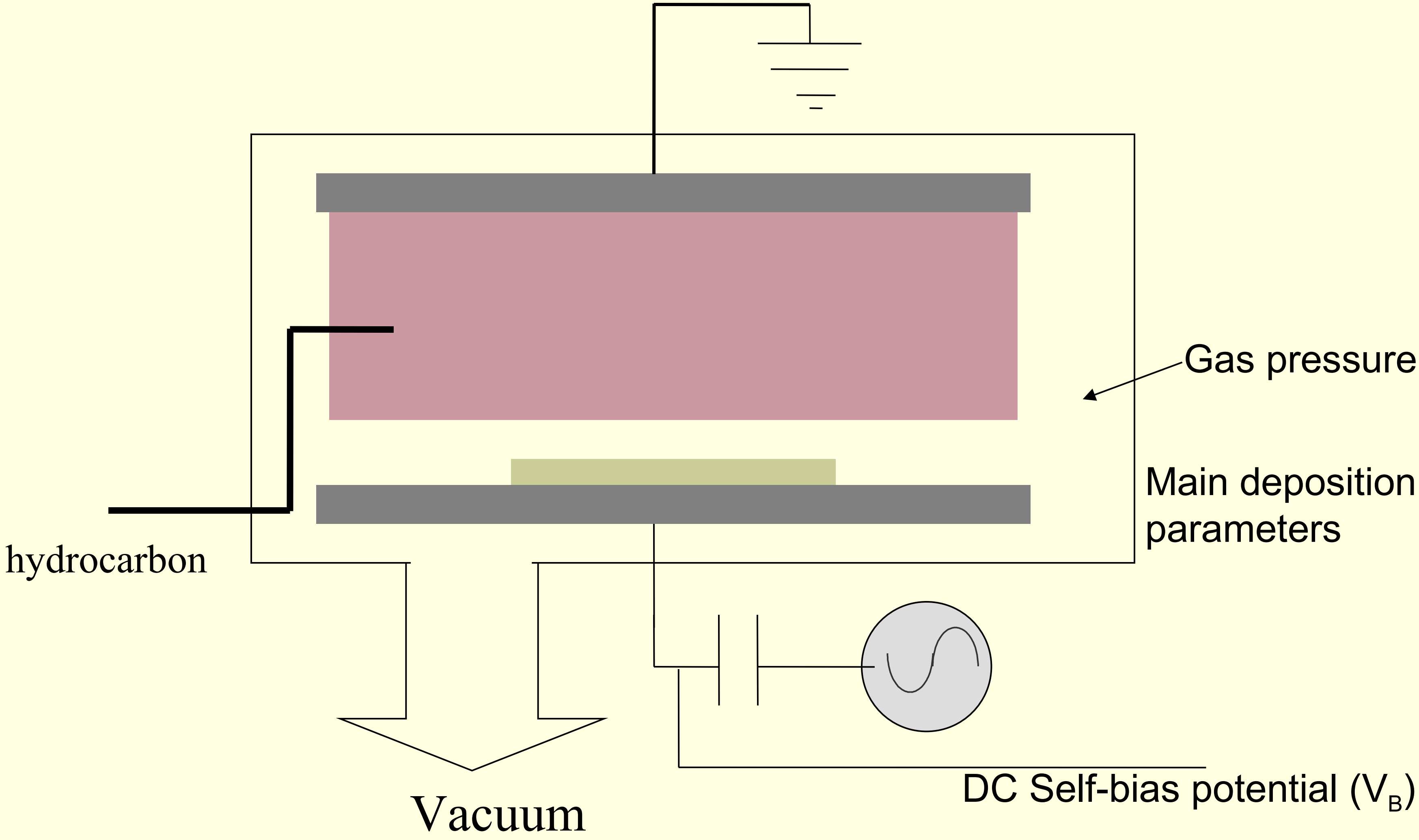
Friction reduction

Wear Protection

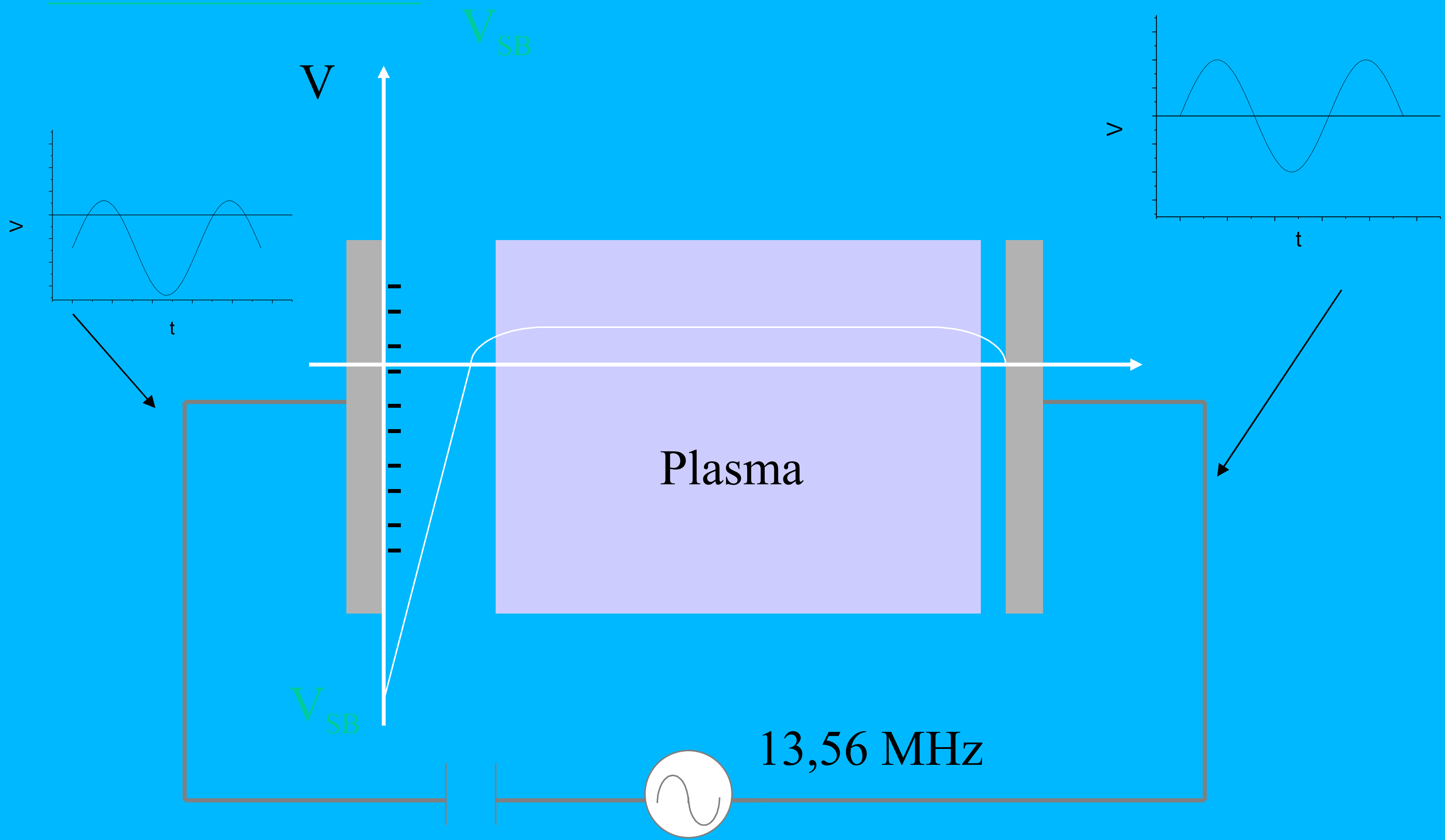
Hydrophobic anti-adhesion coatings

- Gas Barrier Coatings
- IR antireflective coatings
- Dielectric in ULSI ICs

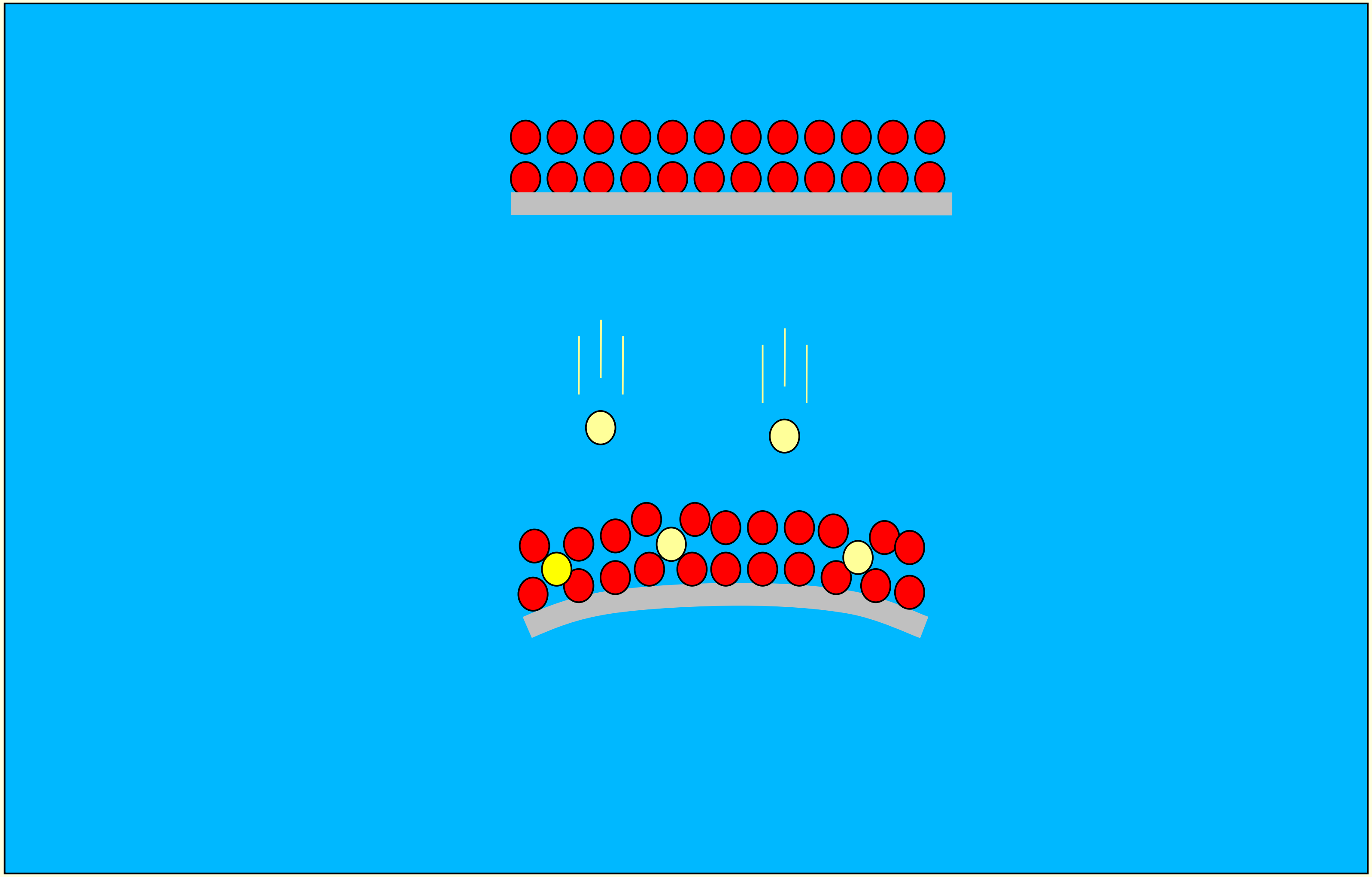
a-C:H film deposition - PECVD



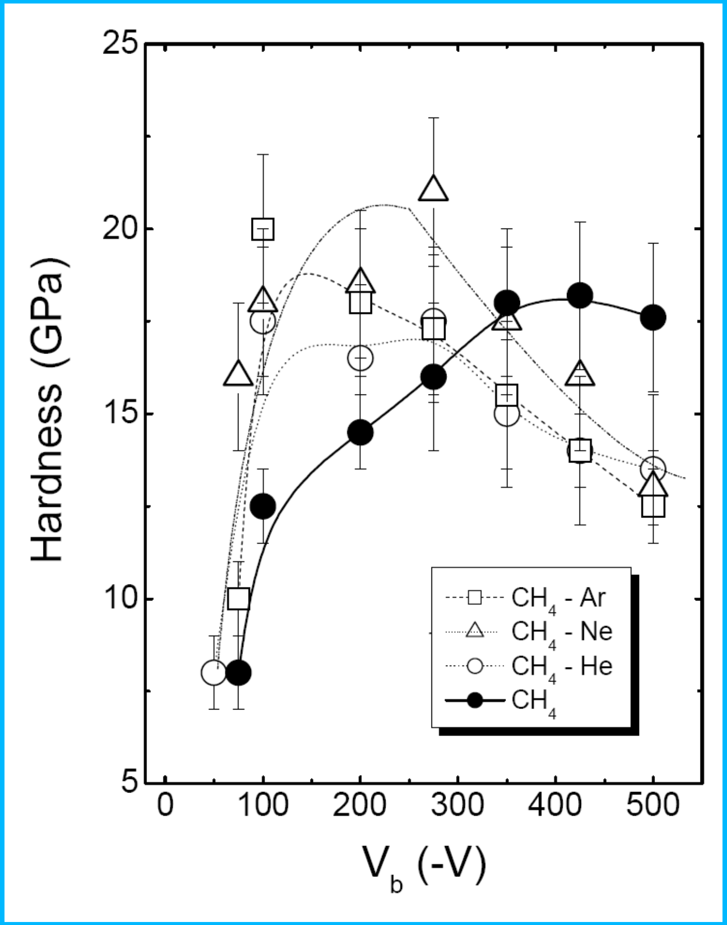
RF-Plasma Enhanced Chemical Vapor Deposition

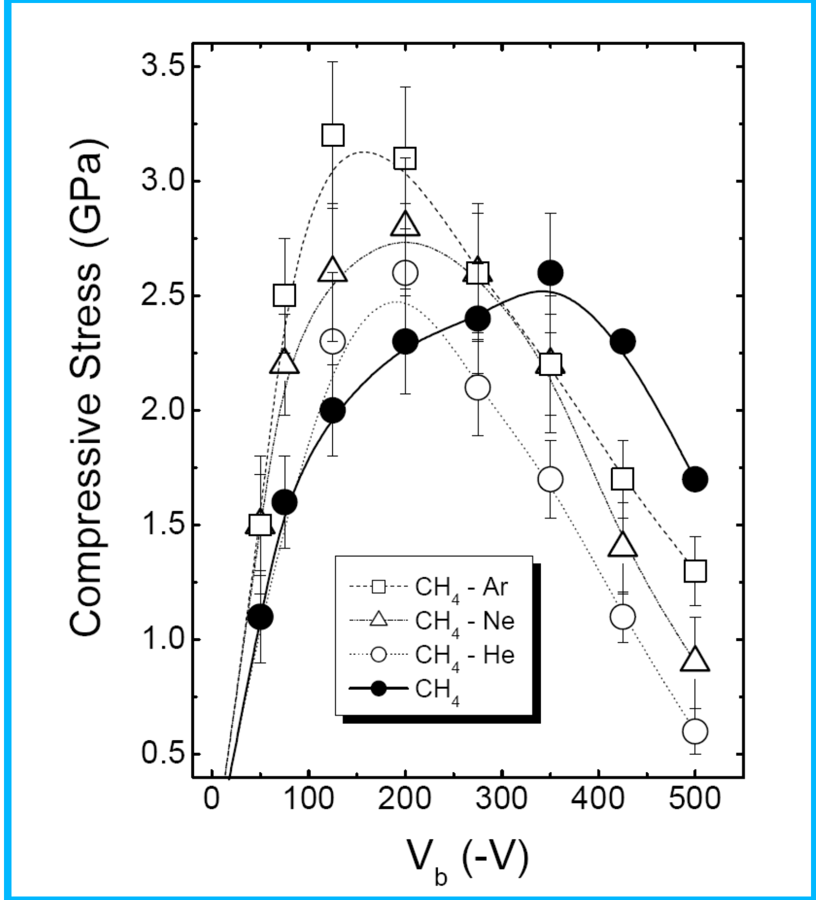


Ion Impact
Hardness and Stress



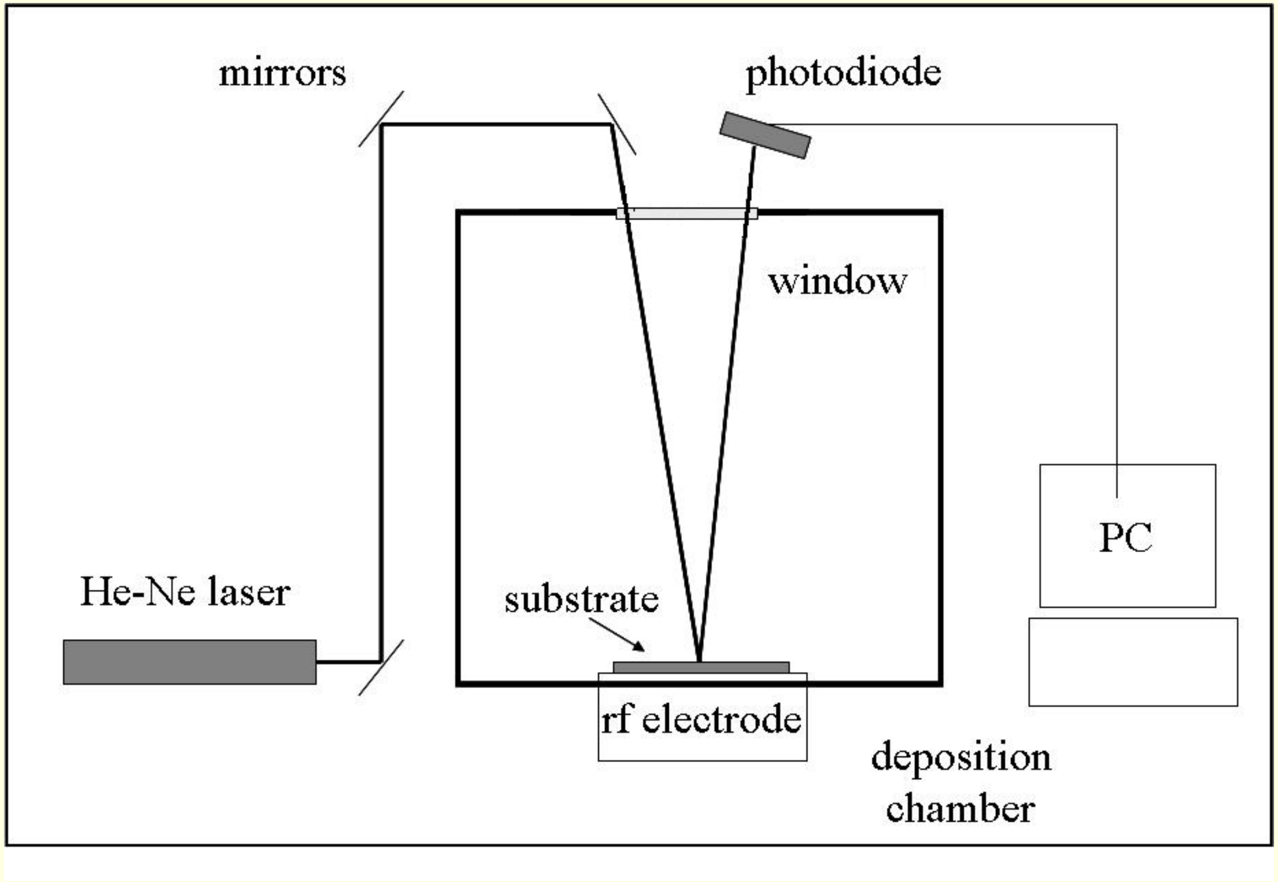
a-C:H from noble gas diluted CH_4 plasmas.



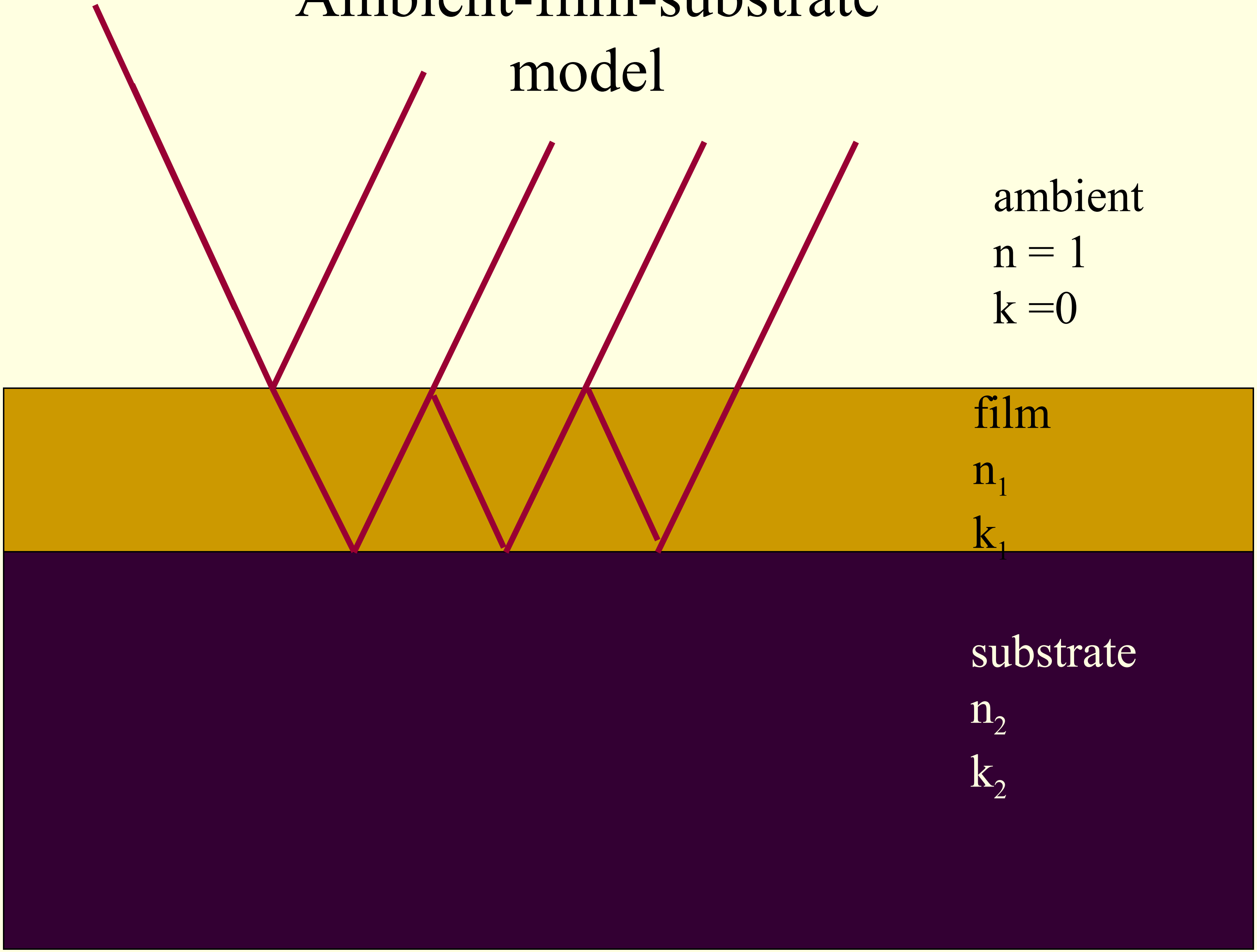


Capote and Freire Mater. Sci. Eng. B (2004)

Caracterização das constantes ópticas in-situ



Ambient-film-substrate model



$$R(d) = A\frac{r_1^{\ 2} + r_2^{\ 2} \cdot e^{-4\,\mathrm{Im}(\beta)} + 2 \cdot r_1 \cdot r_2 \cdot e^{-2\,\mathrm{Im}(\beta)} \cdot \cos[2 \cdot \mathrm{Re}(\beta) + \delta_2 - \delta_1]}{1 + r_1^{\ 2} \cdot r_2^{\ 2} \cdot e^{-4\,\mathrm{Im}(\beta)} + 2 \cdot r_1 \cdot r_2 \cdot e^{-2\,\mathrm{Im}(\beta)} \cdot \cos[2 \cdot \mathrm{Re}(\beta) + \delta_2 + \delta_1]}$$

$$r_2^{\ 2} = R_2 = \frac{(n_1 + n_2)^2 + (k_1 - k_2)^2}{(n_1 + n_2)^2 + (k_1 + k_2)^2}$$

$$r_1^{\ 2} = R_1 = \frac{(1 - n_1)^2 + k_1^{\ 2}}{(1 + n_1)^2 + k_1^{\ 2}}$$

reflectâncias das duas interfaces

$$R(d) = A\frac{r_1^{\,2} + r_2^{\,2}\cdot e^{-4\,\mathrm{Im}(\beta)} + 2\cdot r_1\cdot r_2\cdot e^{-2\,\mathrm{Im}(\beta)}\cdot\cos[2\cdot\mathrm{Re}(\beta)+\delta_2-\delta_1]}{1 + r_1^{\,2}\cdot r_2^{\,2}\cdot e^{-4\,\mathrm{Im}(\beta)} + 2\cdot r_1\cdot r_2\cdot e^{-2\,\mathrm{Im}(\beta)}\cdot\cos[2\cdot\mathrm{Re}(\beta)+\delta_2+\delta_1]}$$

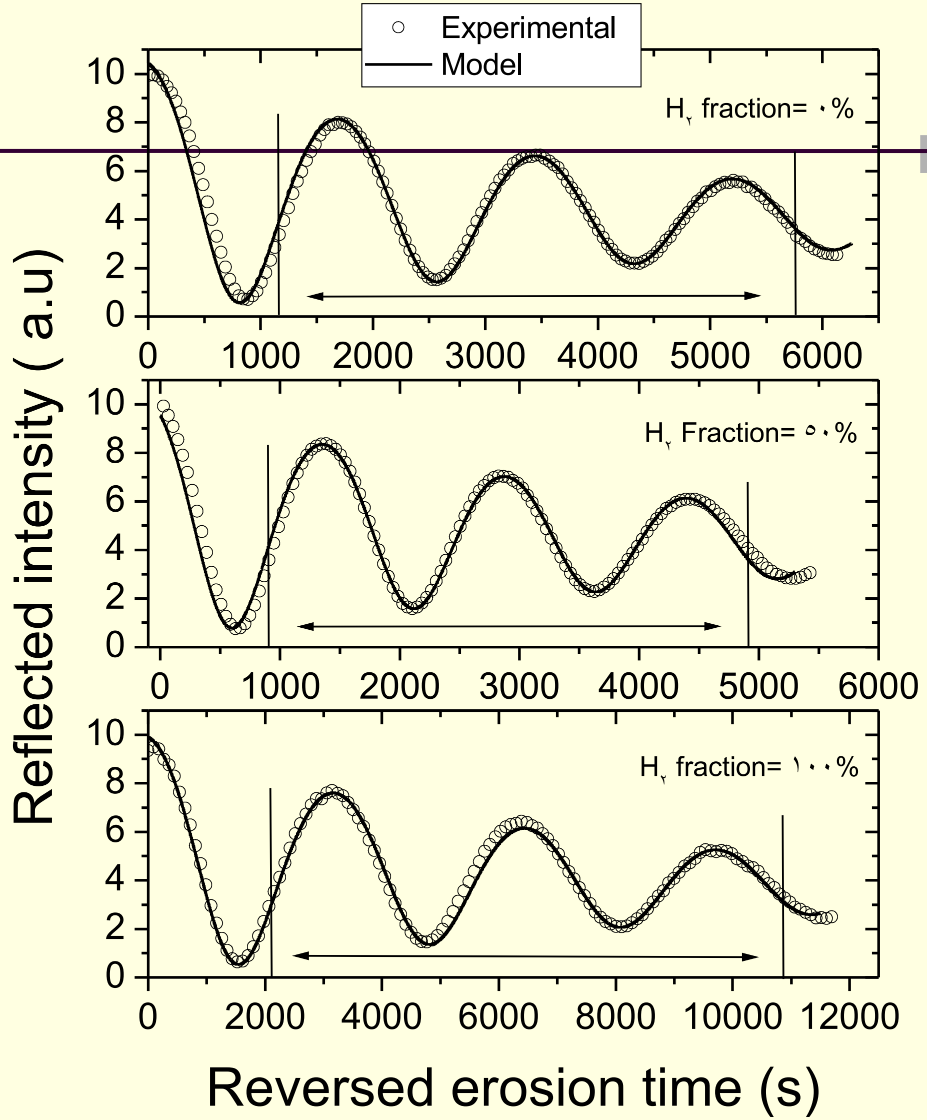
$$r_{٢}^{\;٢} = R_{٢} = \frac{(n_{١}+n_{٢})^{٢} + (k_{١}-k_{٢})^{٢}}{(n_{١}+n_{٢})^{٢} + (k_{١}+k_{٢})^{٢}}$$

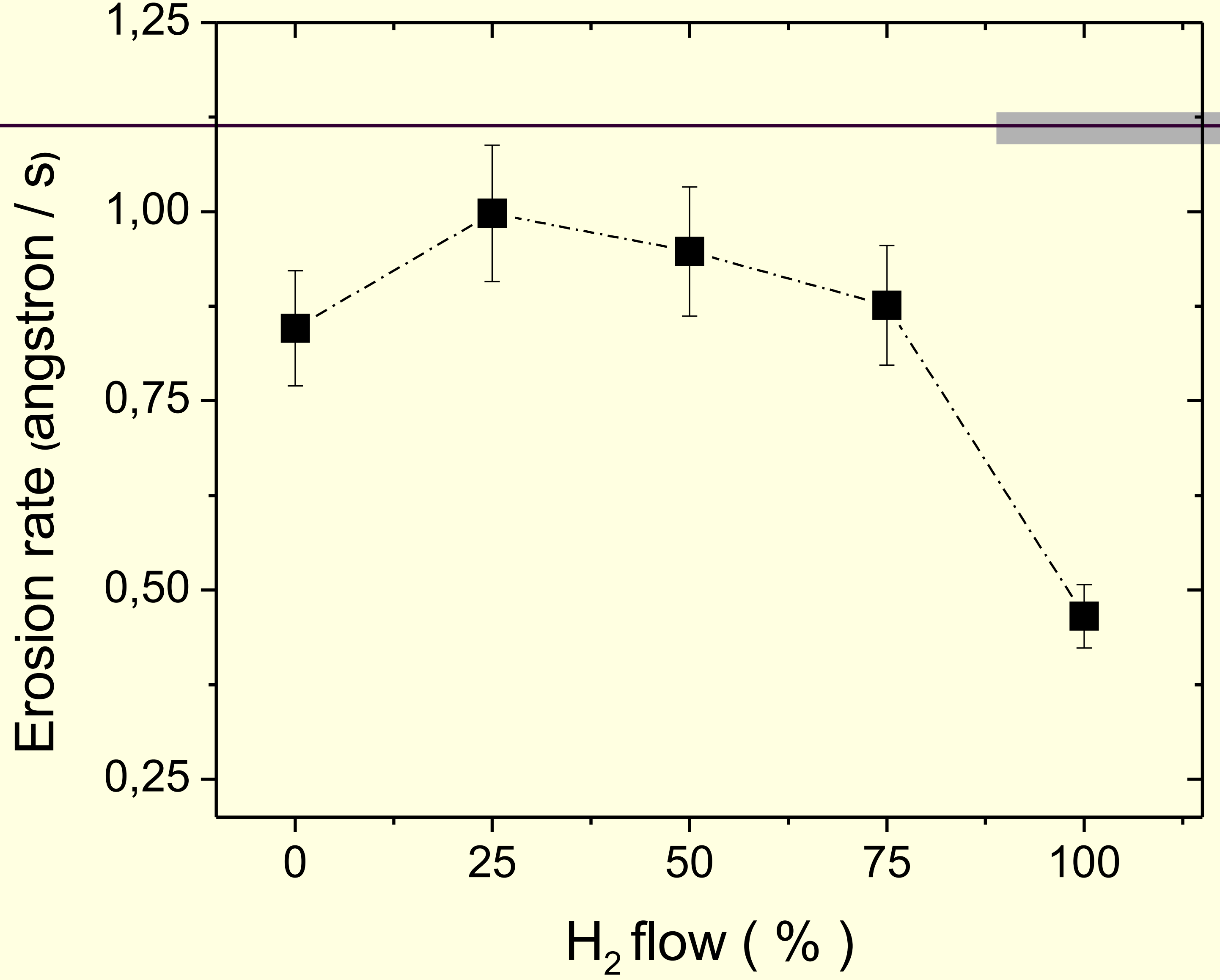
$$r_{١}^{\;٢} = R_{١} = \frac{(١-n_{١})^{٢} + k_{١}^{\;٢}}{(١+n_{١})^{٢} + k_{١}^{\;٢}}$$

reflectâncias das duas interfaces

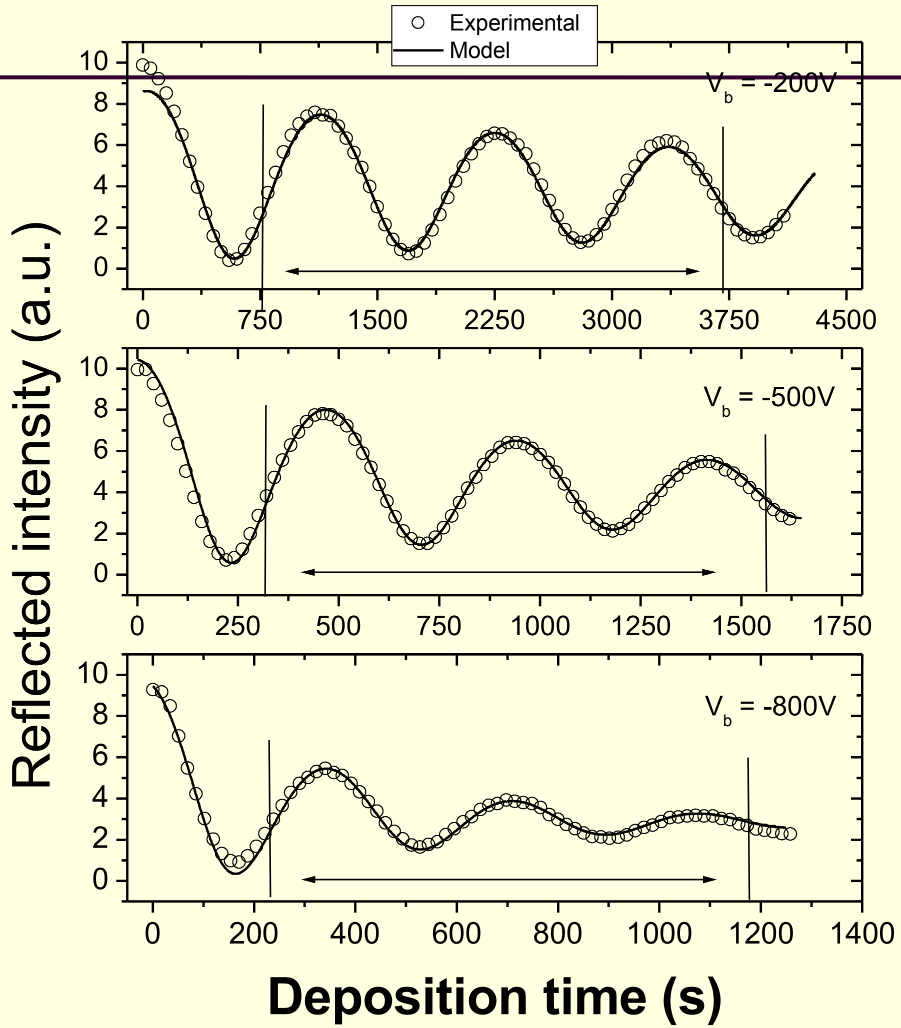
In-situ optical characterization of plasma deposited a-C:H films during deposition by CH4 plasmas and erosion by N2-H2 plasmas.

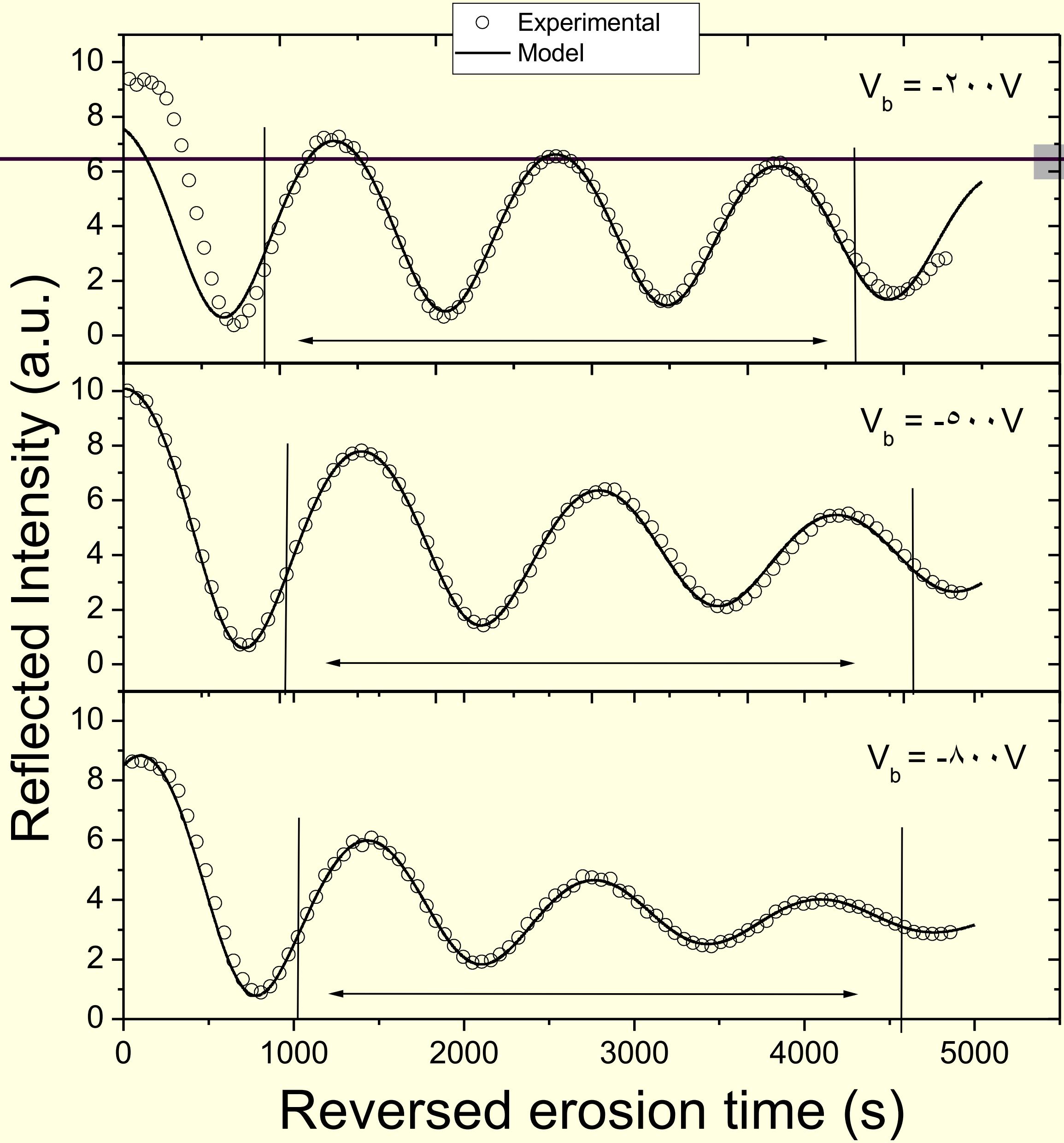
Fabiano Pereira (dout.), Dácio Souza (IC)


Experimental
Model
H₂ fraction= ٠%
H₂ Fraction= ٥٠%
H₂ fraction= ١٠٠%
Reflected intensity (a.u)
Reversed erosion time (s)

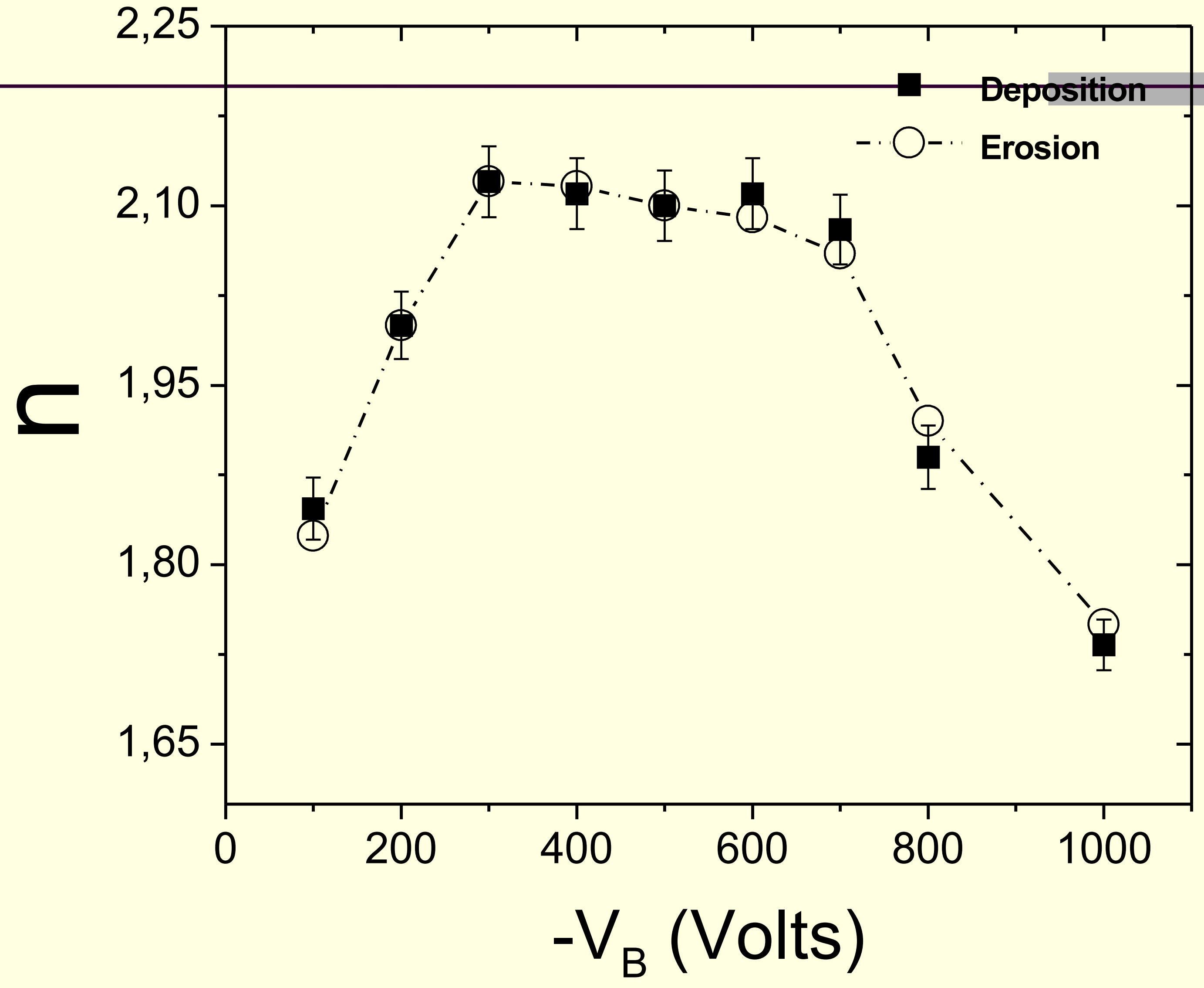


1,25
1,00
0,75
0,50
0,25
Erosion rate (angstron / s)
0
25
50
75
100
H$_2$ flow (%)

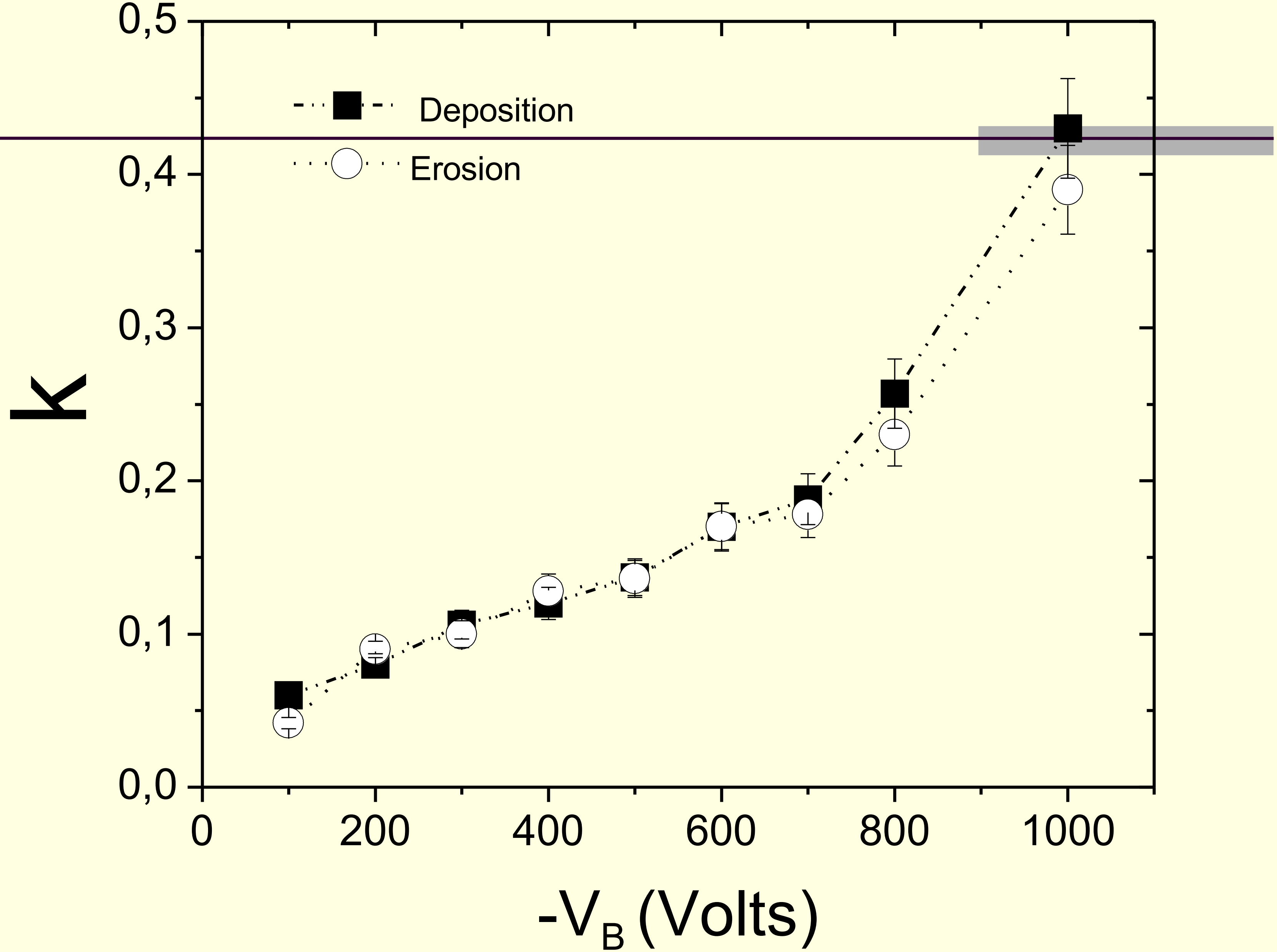

Experimental
Model
V_b = -200V
V_b = -500V
V_b = -800V
Reflected intensity (a.u.)
Deposition time (s)



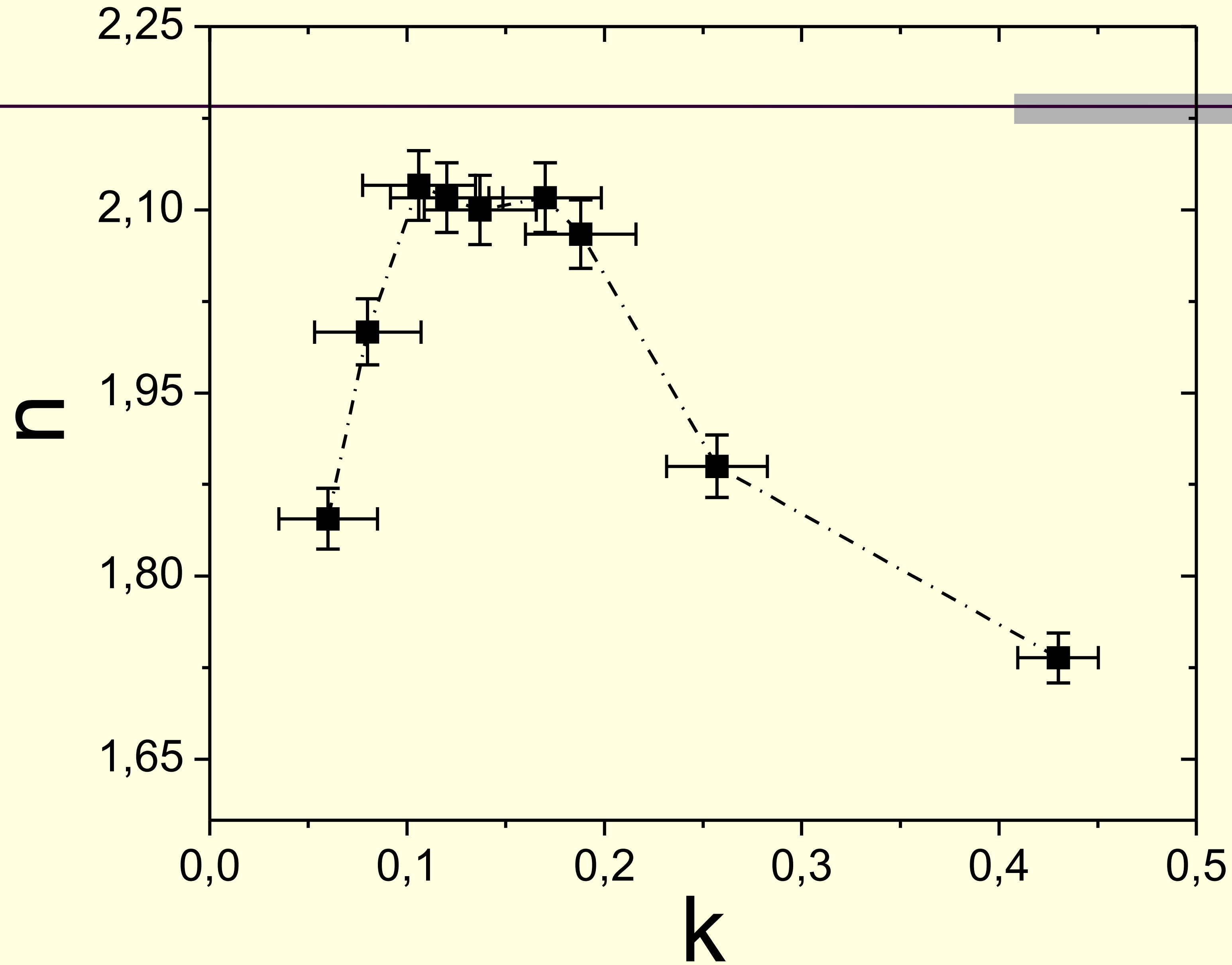
Experimental
Model
V_b = -٢٠٠V
V_b = -٥٠٠V
V_b = -٨٠٠V
Reflected Intensity (a.u.)
Reversed erosion time (s)
0
1000
2000
3000
4000
5000
0
2
4
6
8
10

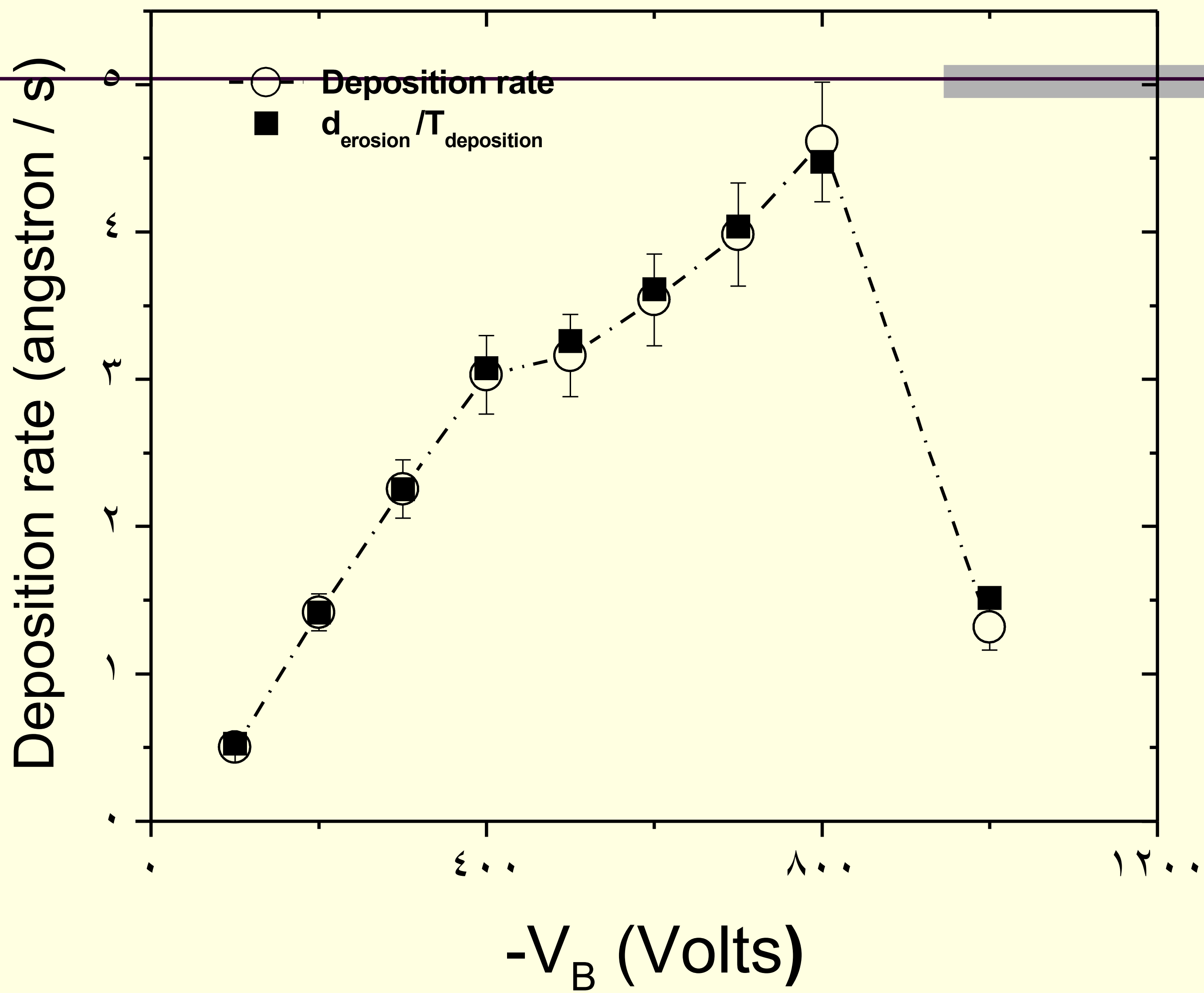


2,25
2,10
1,95
1,80
1,65
n
Deposition
Erosion
0
200
400
600
800
1000
-V_B (Volts)

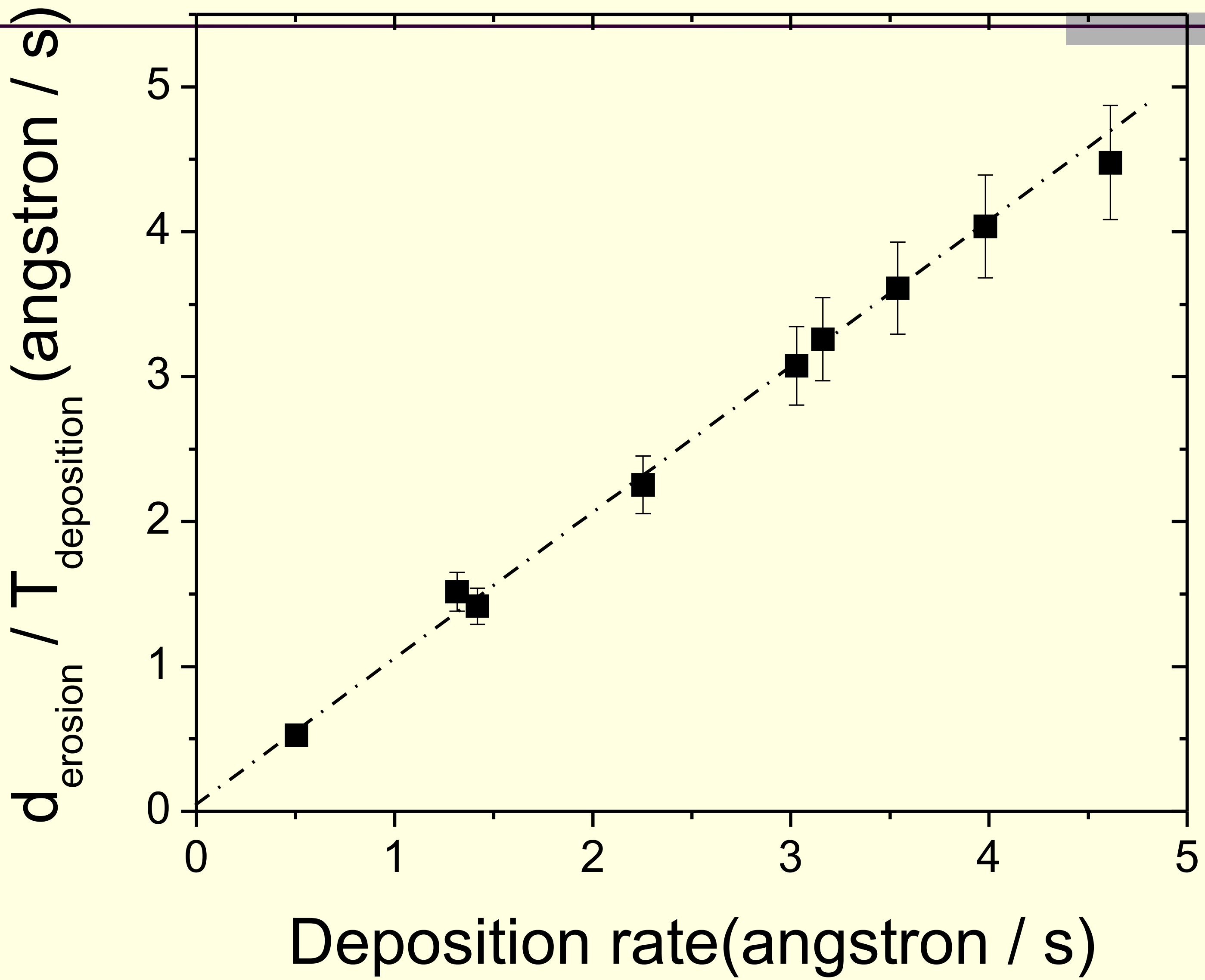


k
0,0
0,1
0,2
0,3
0,4
0,5
0
200
400
600
800
1000
Deposition
Erosion
$-V_B$ (Volts)

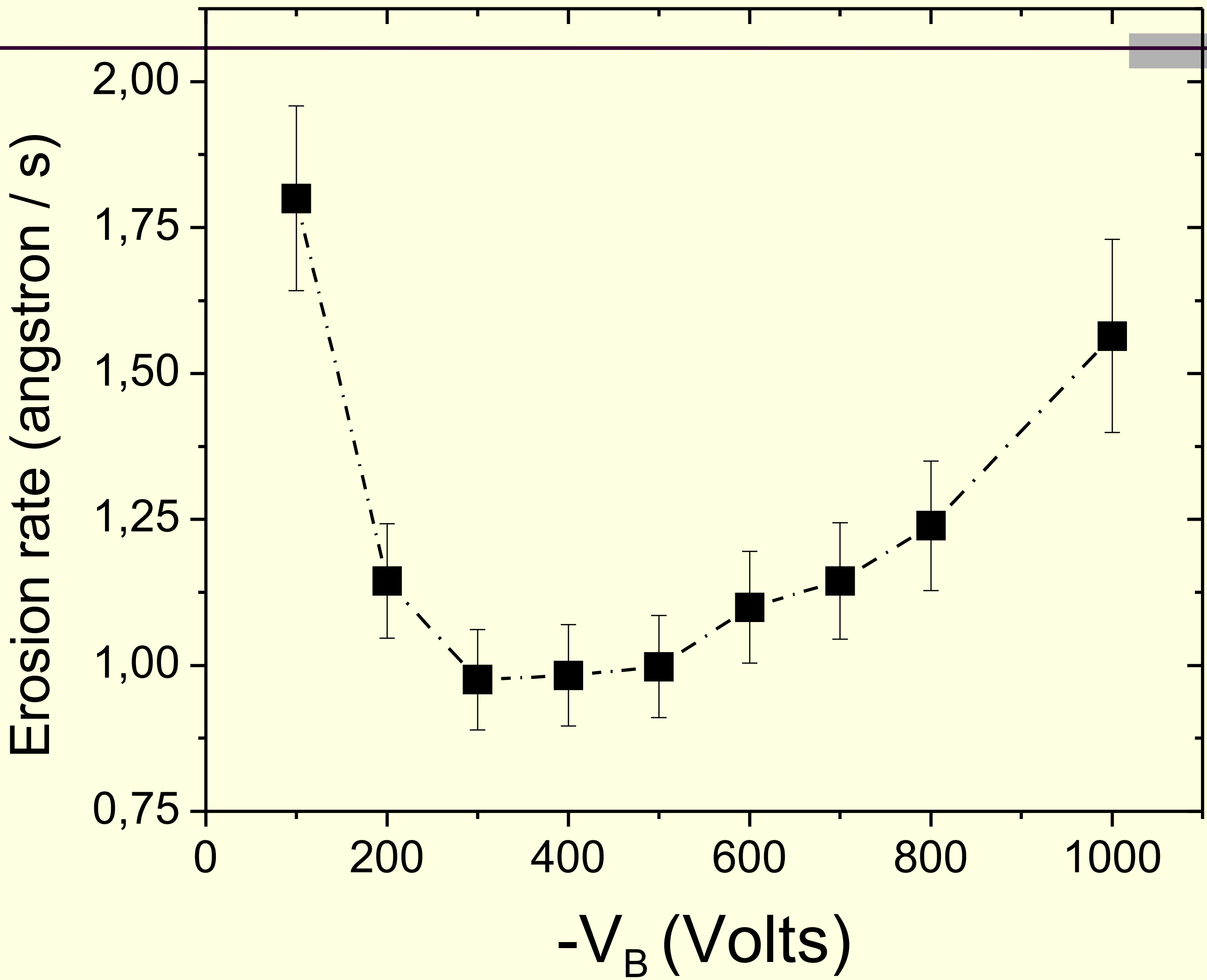

2,25
2,10
1,95
1,80
1,65
n
0,0
0,1
0,2
0,3
0,4
0,5
k



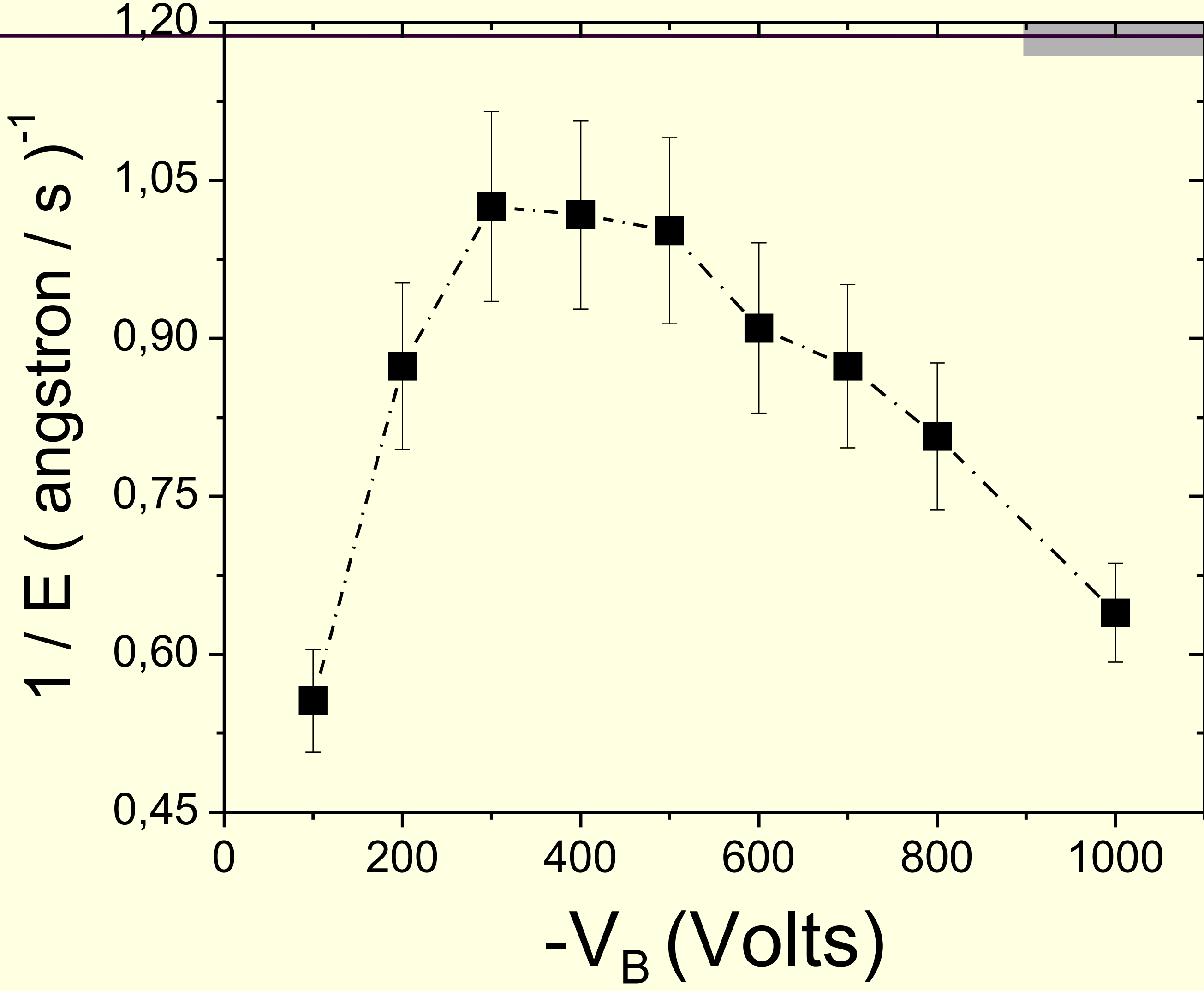
Deposition rate
$d_{erosion}/T_{deposition}$
Deposition rate (angstron / s)
٠
١
٢
٣
٤
٥
٠
٤٠٠
٨٠٠
١٢٠٠
$-V_B$ (Volts)



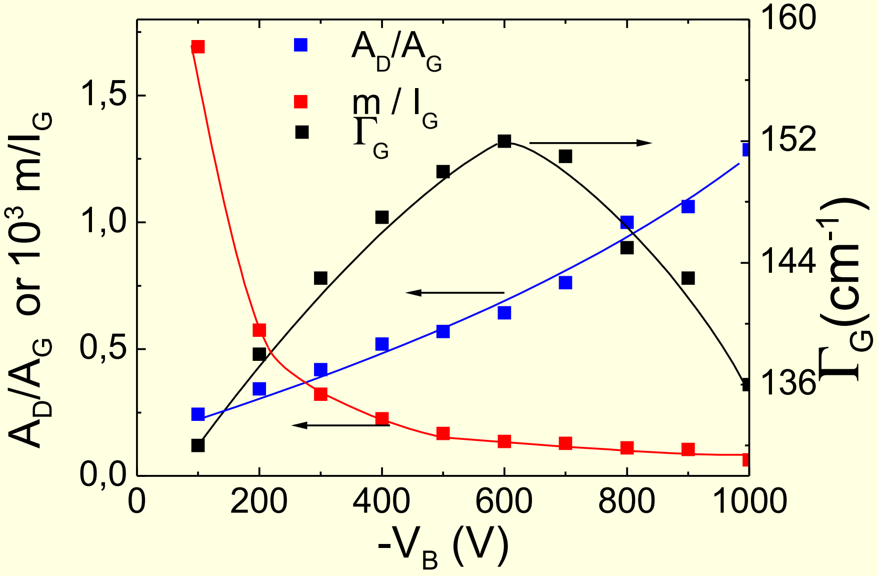
$d_{erosion}$ / $T_{deposition}$(angstron / s)
0
1
2
3
4
5
0
1
2
3
4
5
Deposition rate(angstron / s)



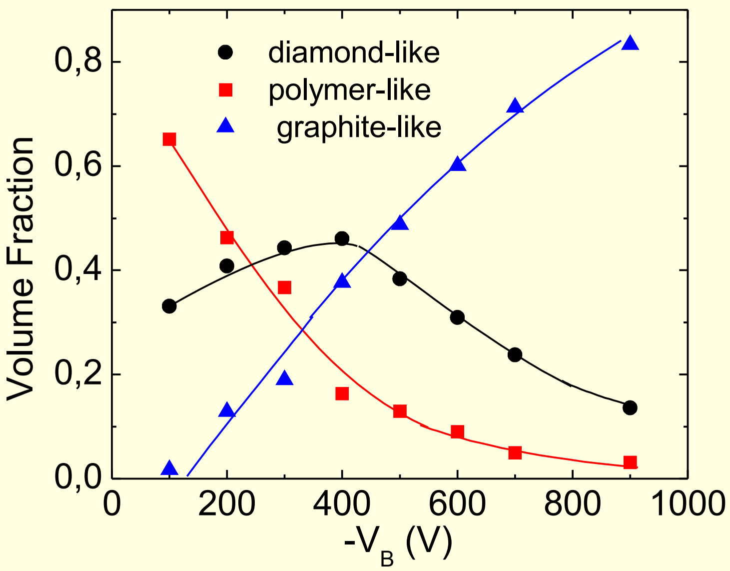
2,00
1,75
1,50
1,25
1,00
0,75
Erosion rate (angstron / s)
0
200
400
600
800
1000
$-V_B$ (Volts)



1,20
1,05
0,90
0,75
0,60
0,45
1 / E (angstron / s)-1
0
200
400
600
800
1000
-VB (Volts)



A_D/A_G
m / I_G
Γ_G
A_D/A_G or 10^3 m/I_G
$\Gamma_G(cm^{-1})$
$-V_B$ (V)

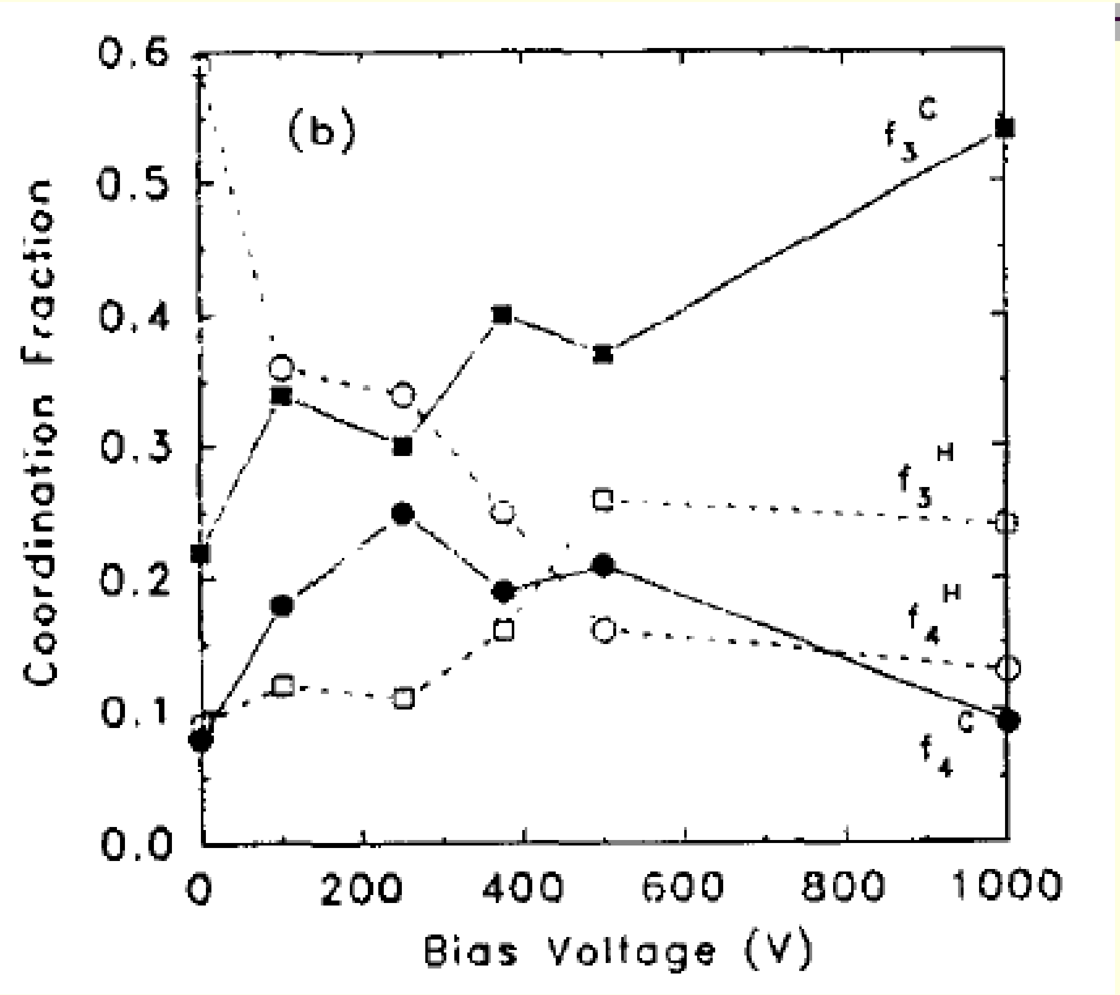


diamond-like
polymer-like
graphite-like
Volume Fraction
$-V_B$ (V)

Framework for analysis of optical constants of a-C:H films

- Fabiano Pereira (dout.), Alexandre P. Silva (ex-dout)

^{13}C NMR



M.A. Tamor et al, Appl. Phys. Lett. 1990

Fingerprinting of a-C:H films by optical constants

- a-C:H films taken as an inhomogeneous mixture of three fases:
- Diamond-like: clustered sp^3 carbon, dense transparent. n = 2.41 , k = 0
- Polymer-like: hydrogenated carbon, low density, transparent n = 1.5, k=0
- Graphite-like: clustered sp^2 carbon, dense, absorbing n=2.47 , k=0.41

Efective Medium – three components

A.M. Jayannavar, N.Kumar – Phys. Rev. 44 (1991), 12014

$$\left(\frac{\varepsilon_0}{\varepsilon}\right)^{1/2}\left(\frac{\varepsilon - A}{\varepsilon_0 - A}\right)^{\alpha}\left(\frac{\varepsilon - B}{\varepsilon_0 - B}\right)^{\beta} = (1-C)^{3/2}$$

$$A = A(x_1, x_2, \varepsilon_1, \varepsilon_2)$$

$$B = B(x_1, x_2, \varepsilon_1, \varepsilon_2)$$

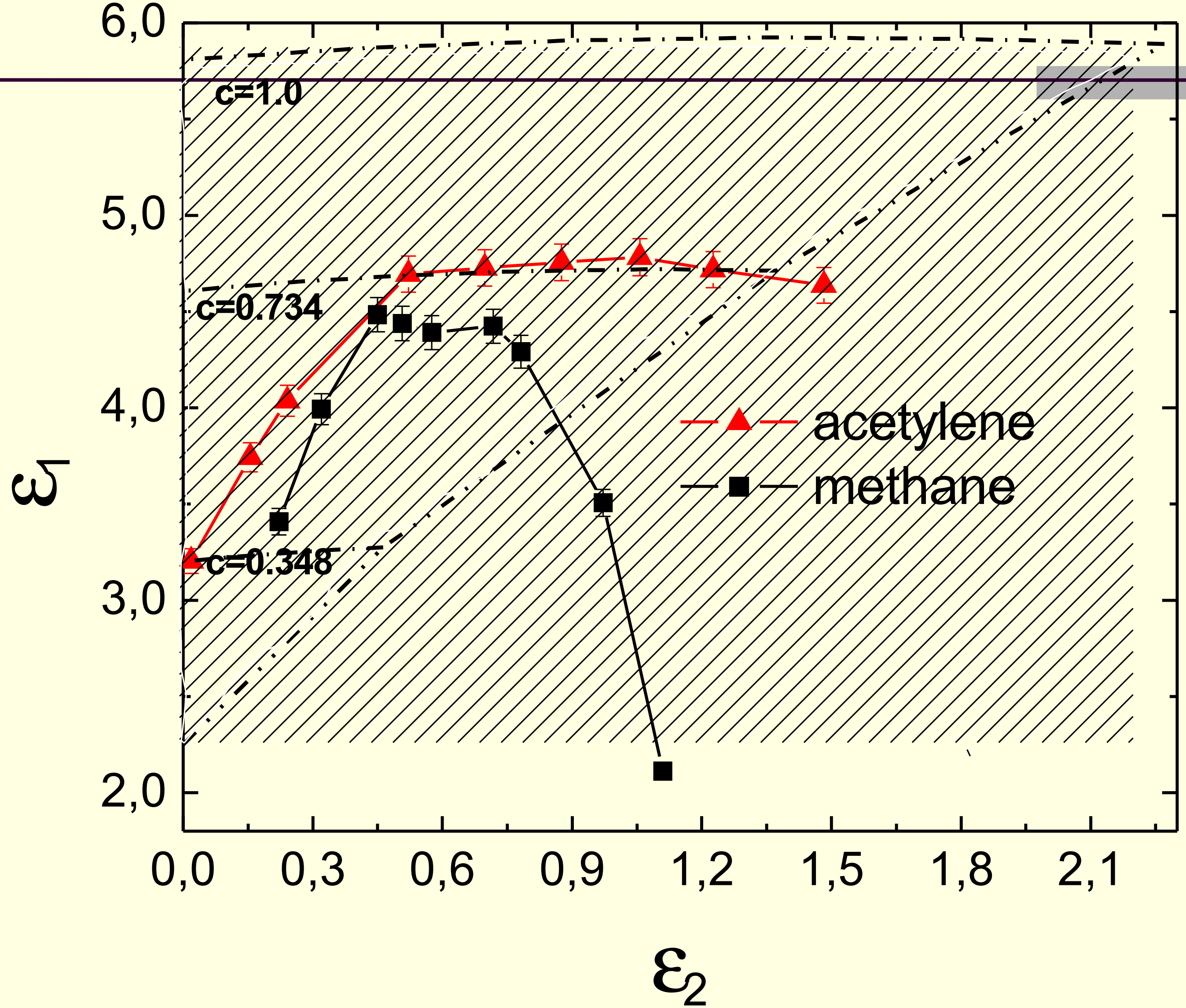
$$\alpha = \alpha(A, B, \varepsilon_1, \varepsilon_2)$$

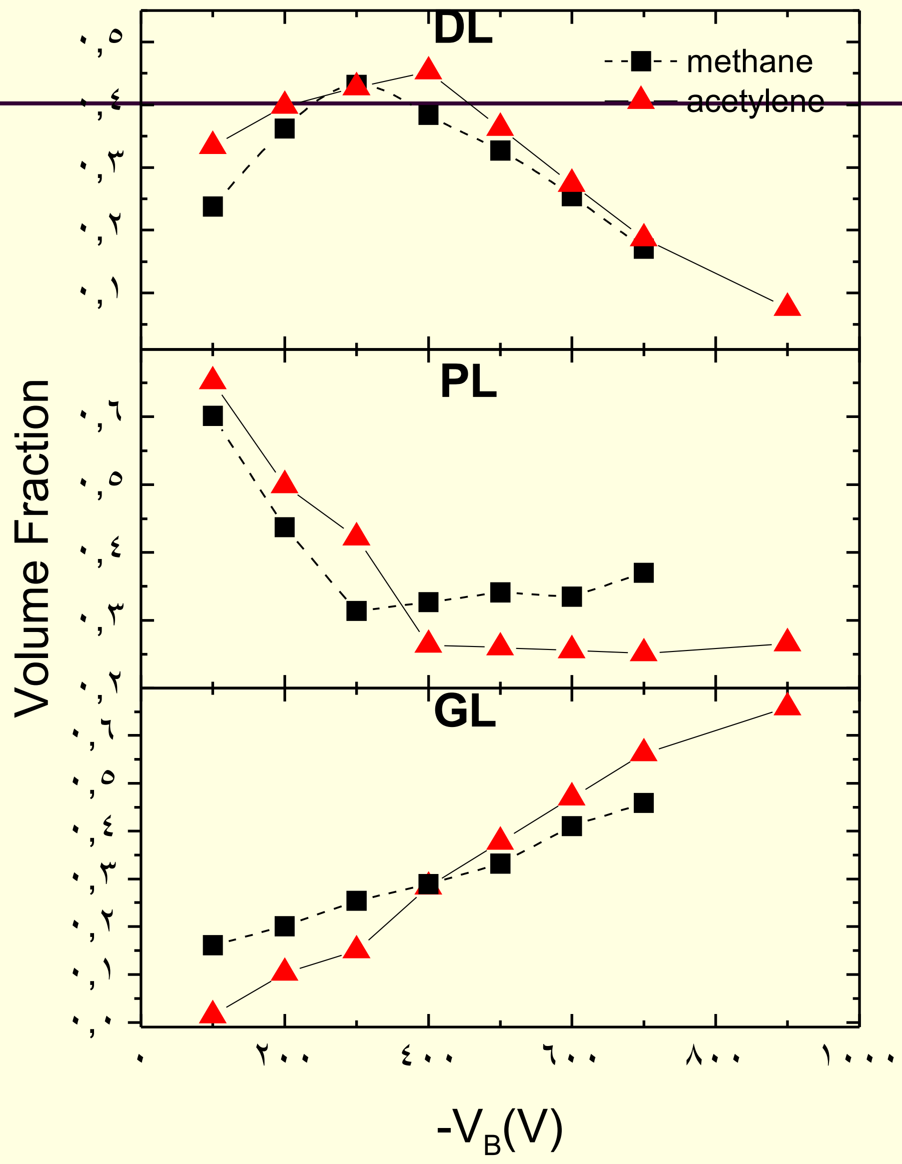
$$\beta = \beta(A, B, \varepsilon_1, \varepsilon_2)$$

(1-C) – volume fraction of the polymer-like fraction

x_1C – volume fraction of sp^3 clustered phase

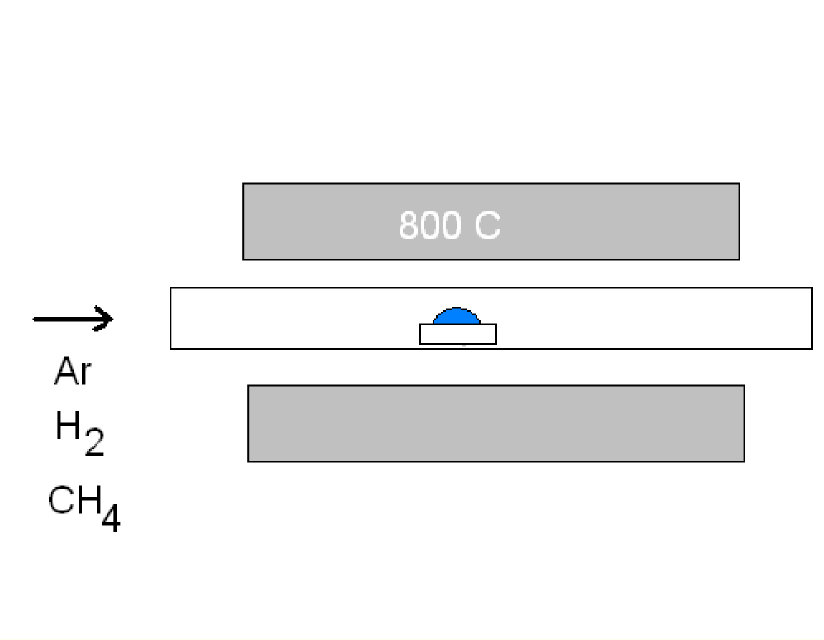
x_2 C = (1-x_1) C – volume fraction of sp^2clustered phase

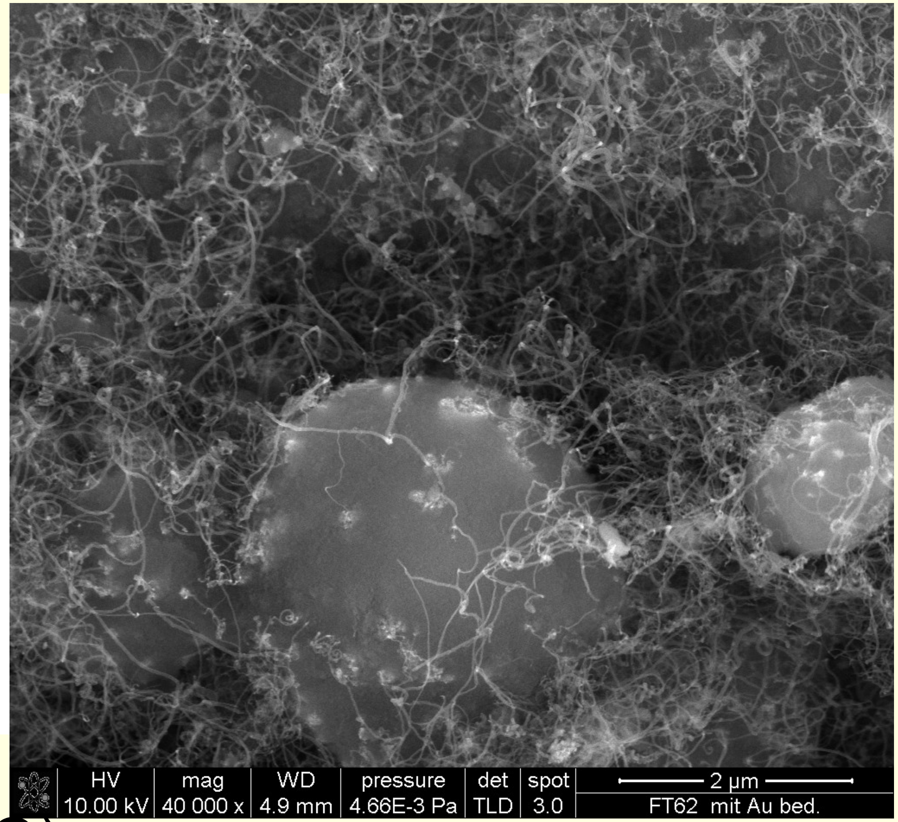

6,0
5,0
4,0
3,0
2,0
0,0
0,3
0,6
0,9
1,2
1,5
1,8
2,1
ε1
ε2
c=1.0
c=0.734
c=0.348
acetylene
methane



DL
PL
GL
methane
acetylene
Volume Fraction
-V_B(V)
٠,١
٠,٢
٠,٣
٠,٤
٠,٥
٠,٦
٠
٢٠٠
٤٠٠
٦٠٠
٨٠٠
١٠٠٠

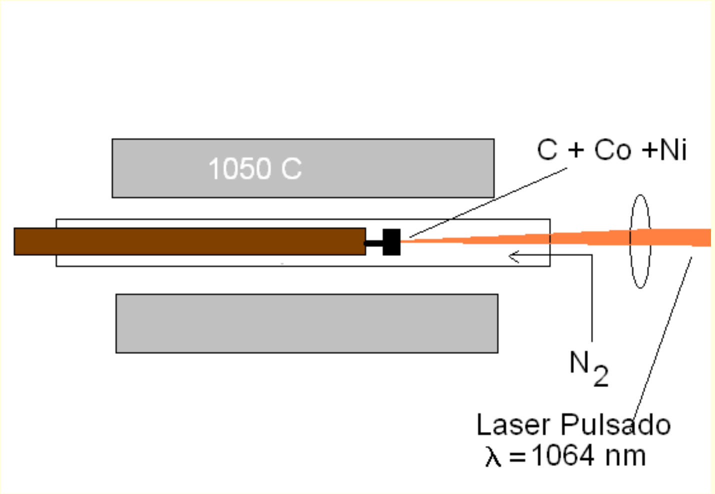
MWNT

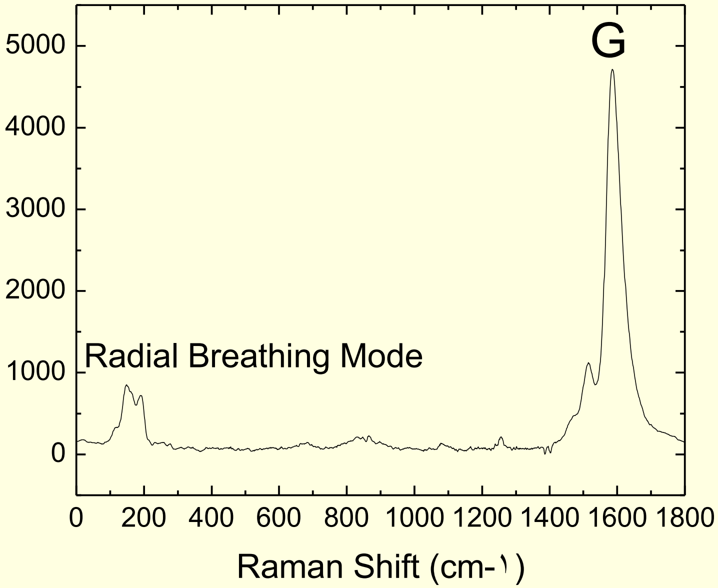




Prof. F.B. Passos (EQ)
Hugo Alvarenga (dout, EQ)
Dácio Souza (IC, UFF)

SWNT





Dr. Carlos Sanchez (pós-doc)
Dacio Souza (IC),, Ingrid Hames (mestr)

Planos

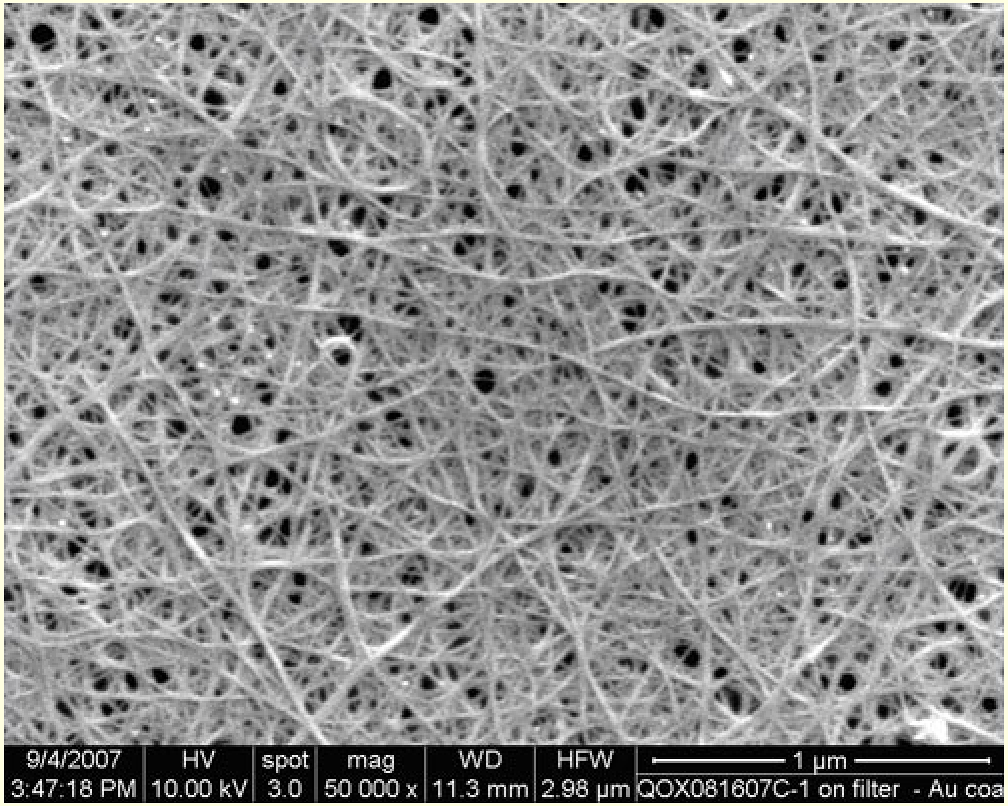
- Dispersão de nanotubos (Prof. E. Ponzio Quim)
- Filmes finos para determinação de propriedades ópticas [prof. A.Latge, Ingrid Hames (mestrado)]
- formação de compósitos nanotubos-a-C:H
- condutores transparentes (Prof. E. Ponzio – QUI)

Filmes Finos por ablação por laser

- Filmes de carbono duro – 32 GPa!   Dr. C. Sanchez (Pós-doc uff), Prof. M. Maia da Costa (PUC)
- Nanopartículas de Óxido de Eu –

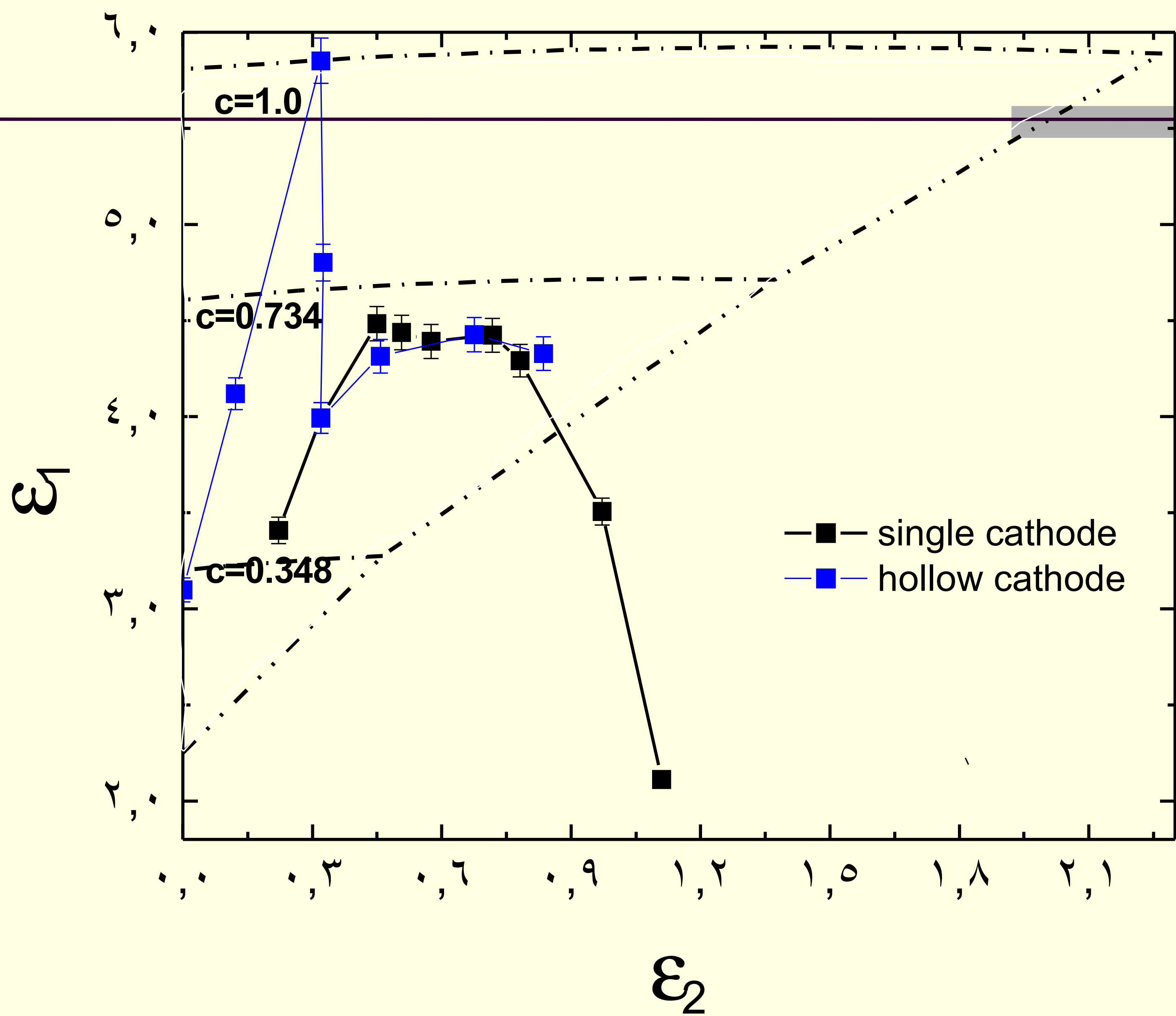
C. Sanches, prof. Glauco Maciel (UFF), prof Hugo Luna (UFRJ), prof. C. Fellows (UFF), prof. Dalber Candela (UFF), prof. Renato Guimarães (UFF)

condutor transparente comercial

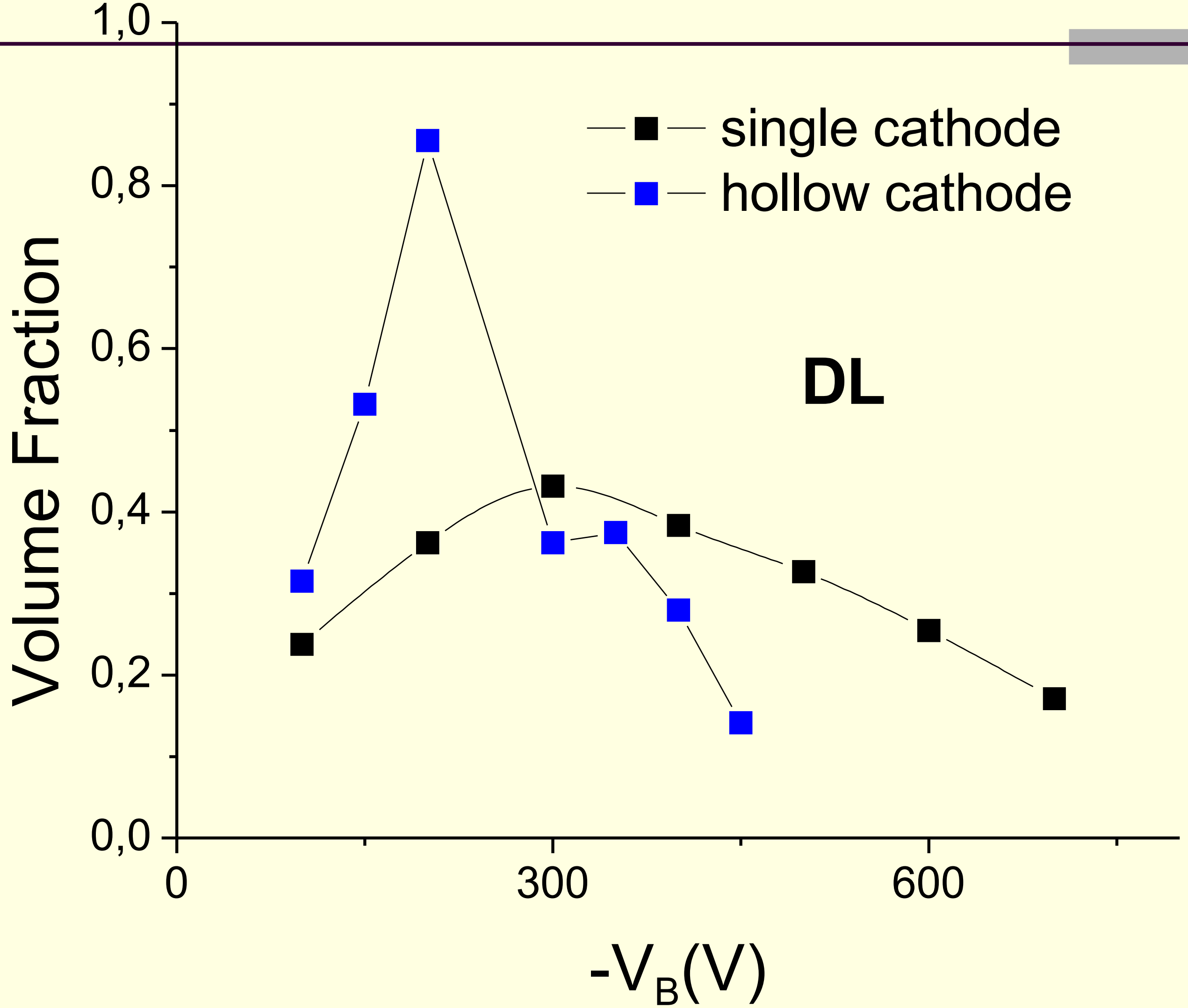


Conclusões

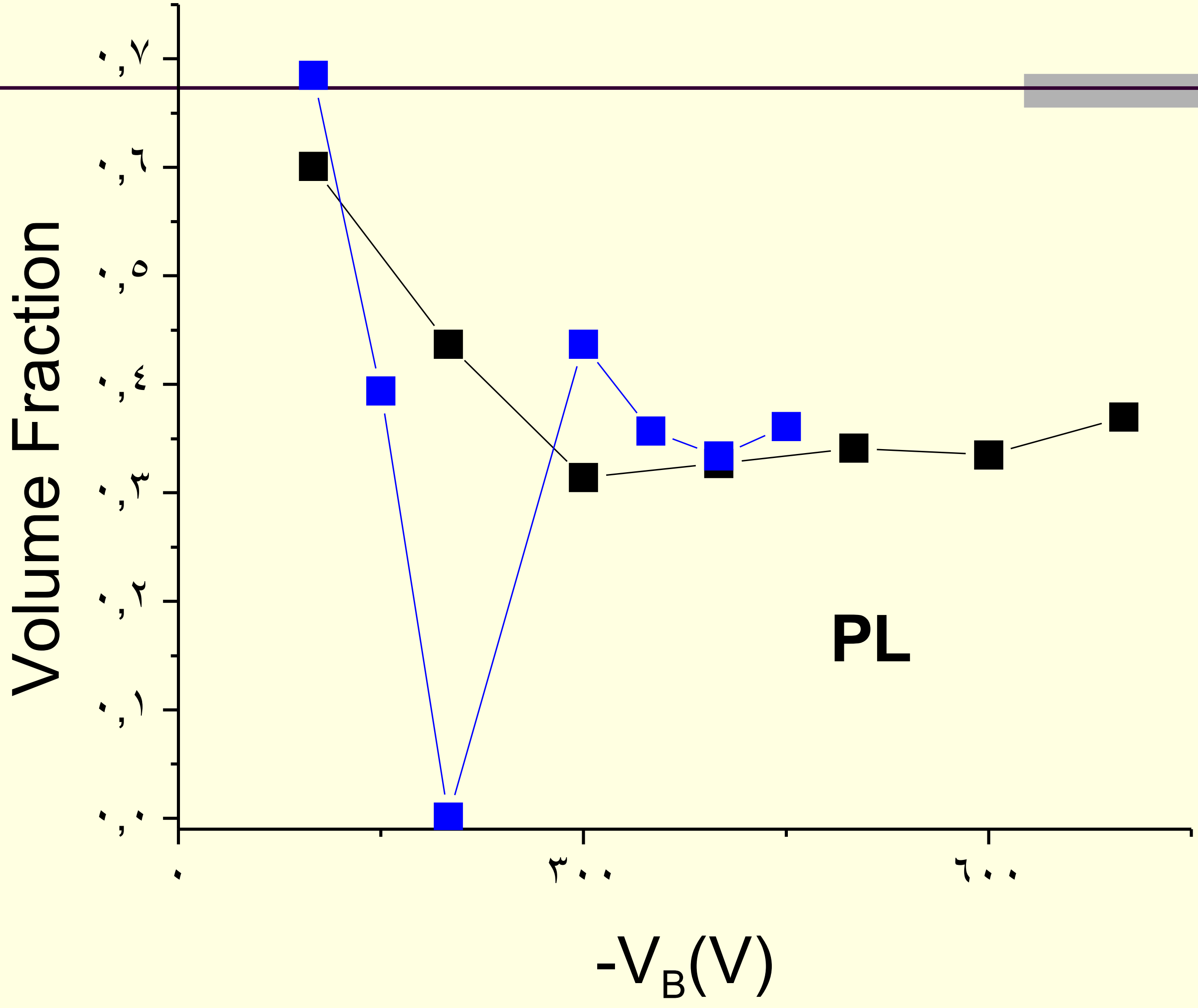
- O Laboratório de Filmes Finos está operando e ampliando as suas atividades em Física dos Materiais .



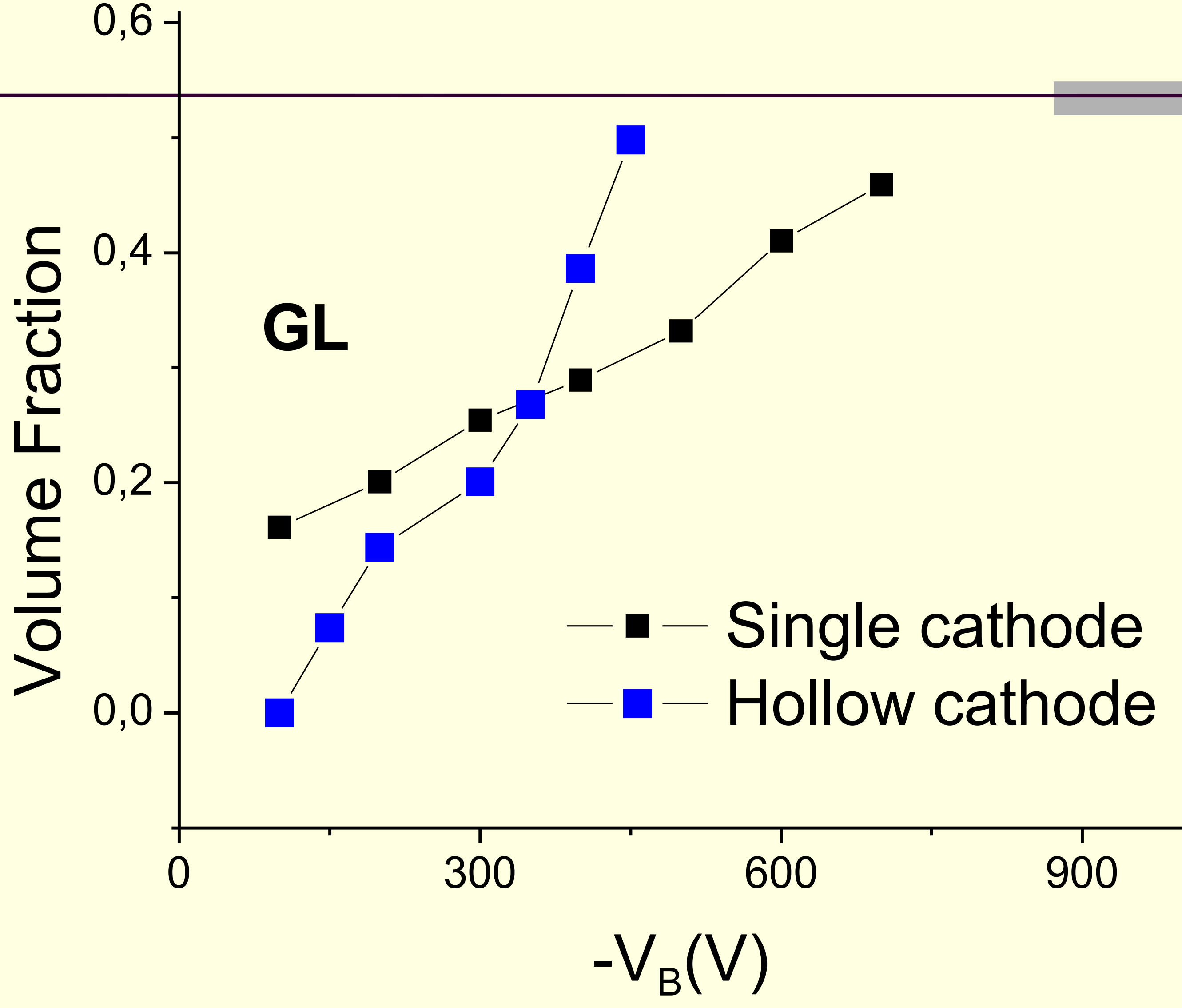
c=1.0
c=0.734
c=0.348
single cathode
hollow cathode
٦,٠
٥,٠
٤,٠
٣,٠
٢,٠
٠,٠
٠,٣
٠,٦
٠,٩
١,٢
١,٥
١,٨
٢,١
ε_1
ε_2



1,0
0,8
0,6
0,4
0,2
0,0
0
300
600
Volume Fraction
$-V_B(V)$
single cathode
hollow cathode
DL



Volume Fraction
٠,٧
٠,٦
٠,٥
٠,٤
٠,٣
٠,٢
٠,١
٠,٠
٠
٣٠٠
٦٠٠
-V_B(V)
PL


GL
Volume Fraction
0,0
0,2
0,4
0,6
0
300
600
900
-V_B(V)
Single cathode
Hollow cathode