Jednodimenzionální křemík

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M. Otevřel a P. Horváth

Polysilyleny (česky) – polysilylenes (anglicky)

Téze

1. Proč křemík s různou dimenzionalitou ?

2. Chemie křemíku s různou dimenzionalitou

3. Vlastnosti vedoucí k aplikacím

4. Proč plazma ?

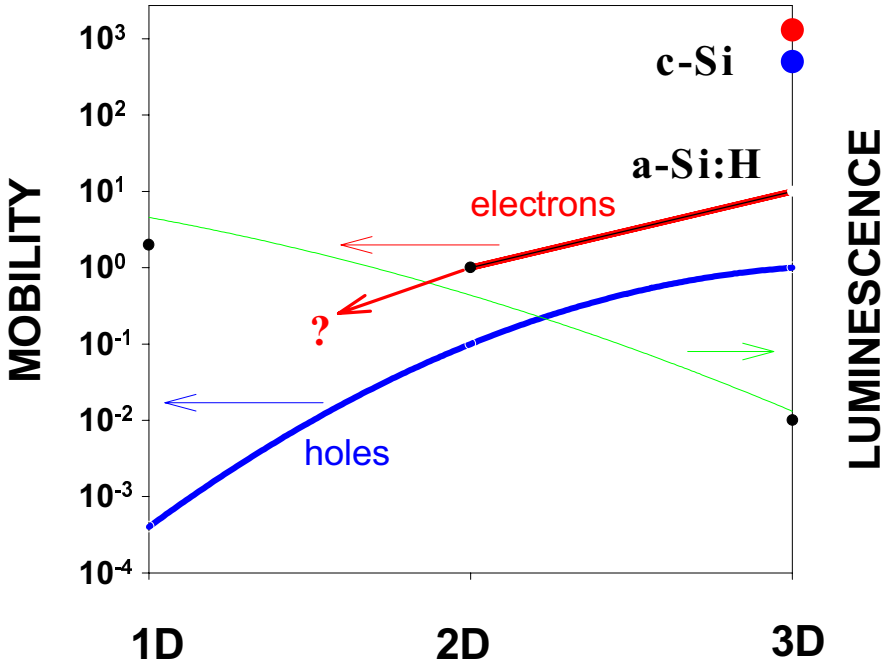
5. Degradace, metastabilita – rezisty?

1. Proč ?

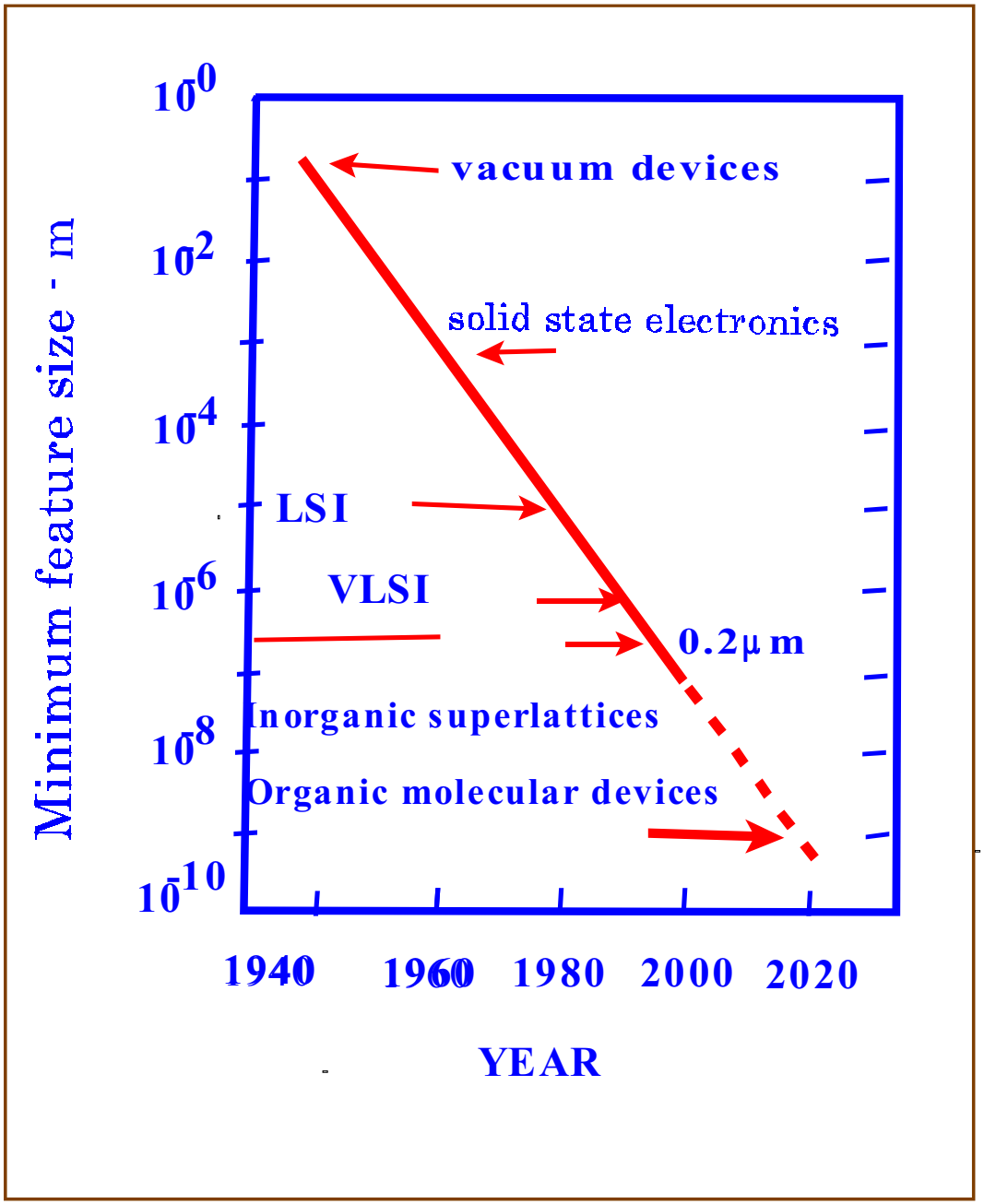
WHY

1D SILICONS?

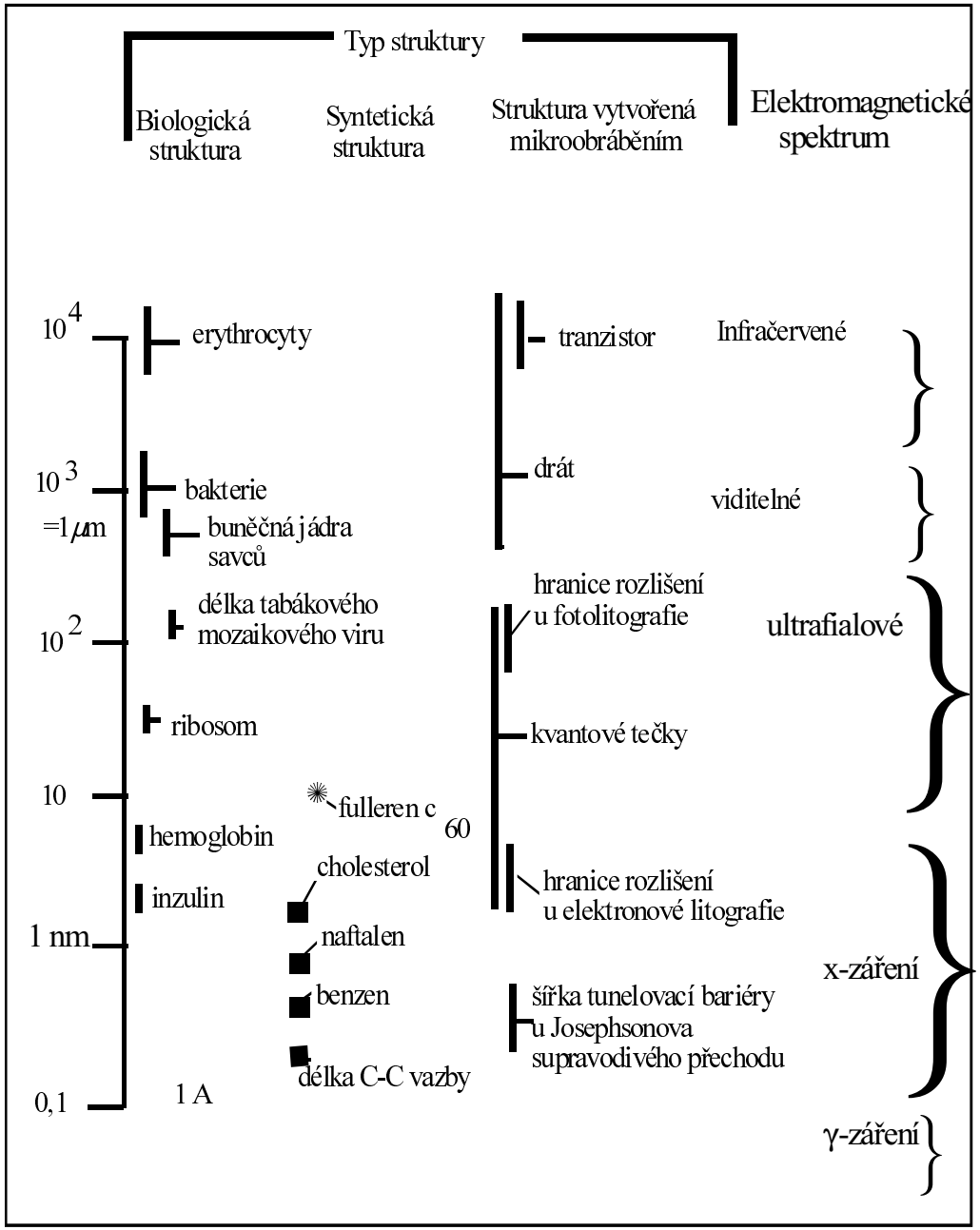
Silicons - mobility and luminescence



VÝVOJ VELIKOSTI SOUČÁSTEK

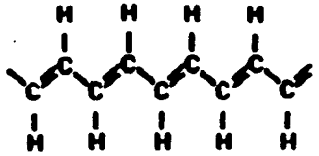


NANOSTRUKTURY

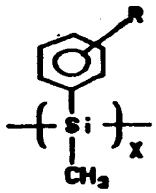


POLYMERIC PHOTOCONDUCTORS

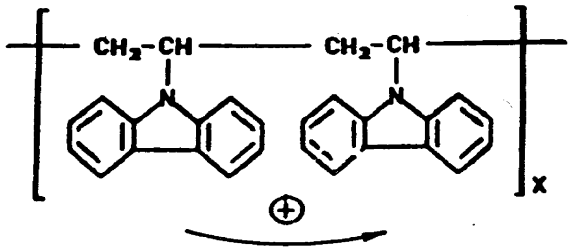
π-CONJUGATED BACKBONE
E.G. POLY(ACETYLENE)



σ-CONJUGATED BACKBONE
E.G. POLYSILANES



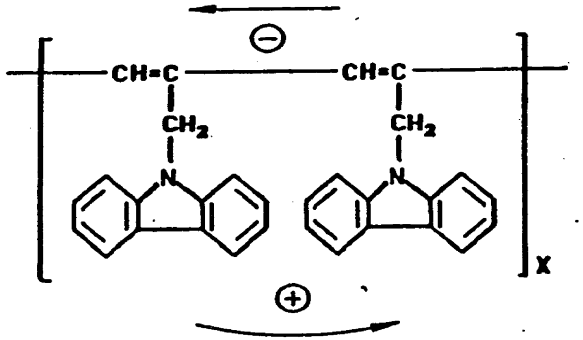
SATURATED BACKBONE WITH SIDE CHAINS CONTAINING π-CONJUGATED CHROMOPHORES
E.G. POLY(N-VINYLCARBAZOLE)



HOPPING TRANSPORT

CONJUGATED BACKBONE WITH SIDE CHAINS CONTAINING π-CONJUGATED CHROMOPHORES
E.G. POLY(N-(2-PROPINYL)CARBAZOLE)

QUASI-DELOCALIZED TRANSPORT
(COLLISIONS WITH LATTICE VIBRATIONS)



HOPPING TRANSPORT

2. Chemie 1D-3D křemíku

Silicons with different dimensionality

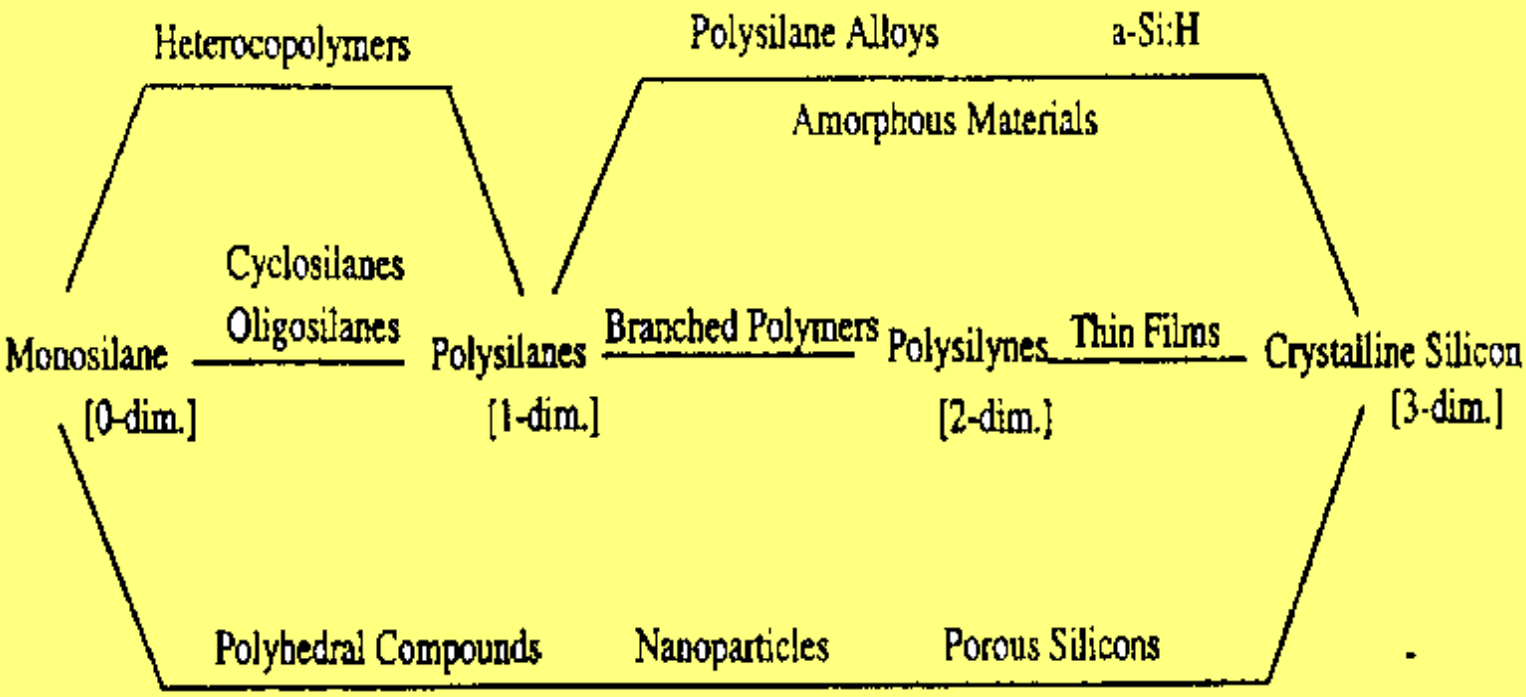
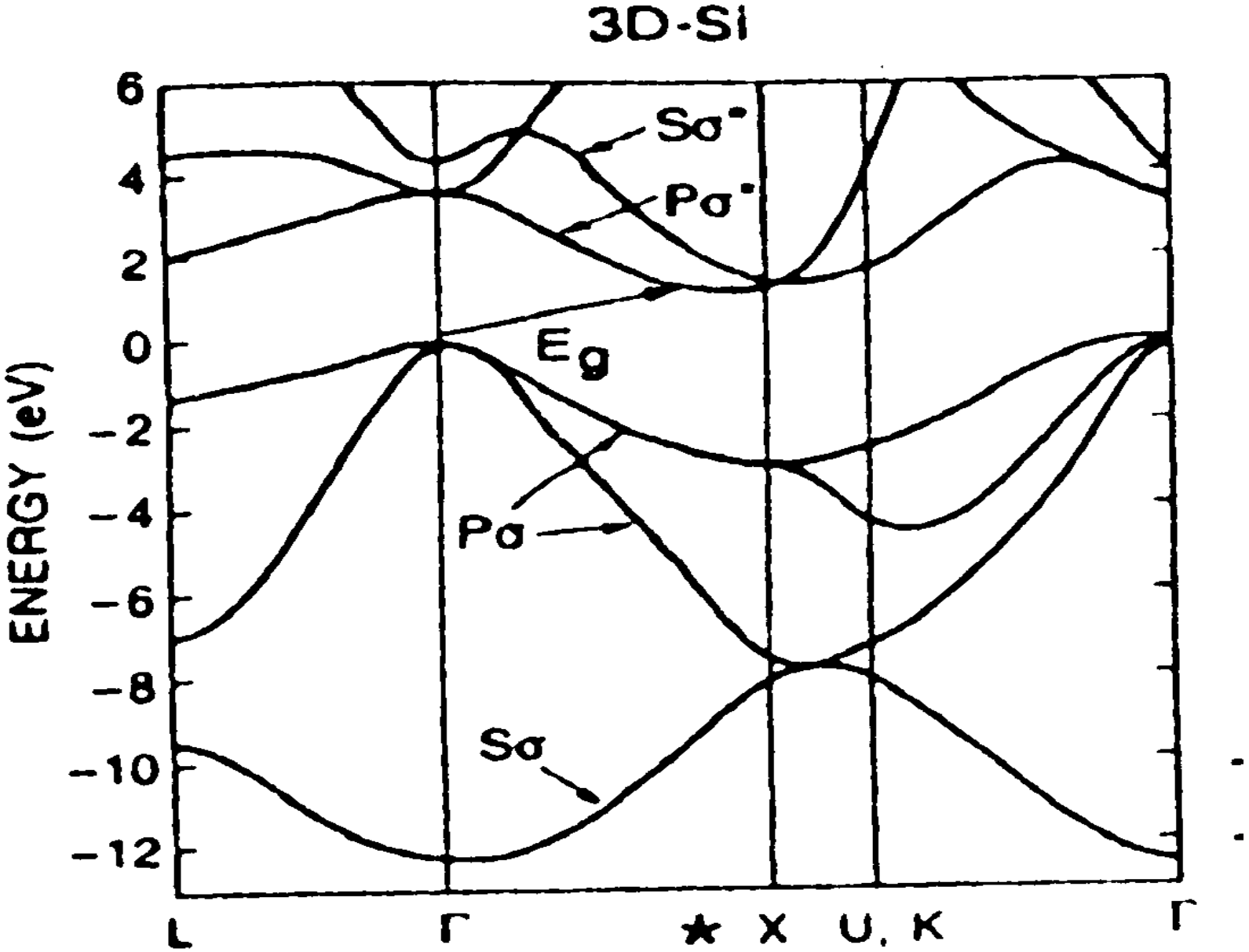


Fig. 3. An overview of silicon-based materials.

1D **2D** **3D**

N. Matsumoto: Jpn. J. Appl. Phys. 37 (1998)5425

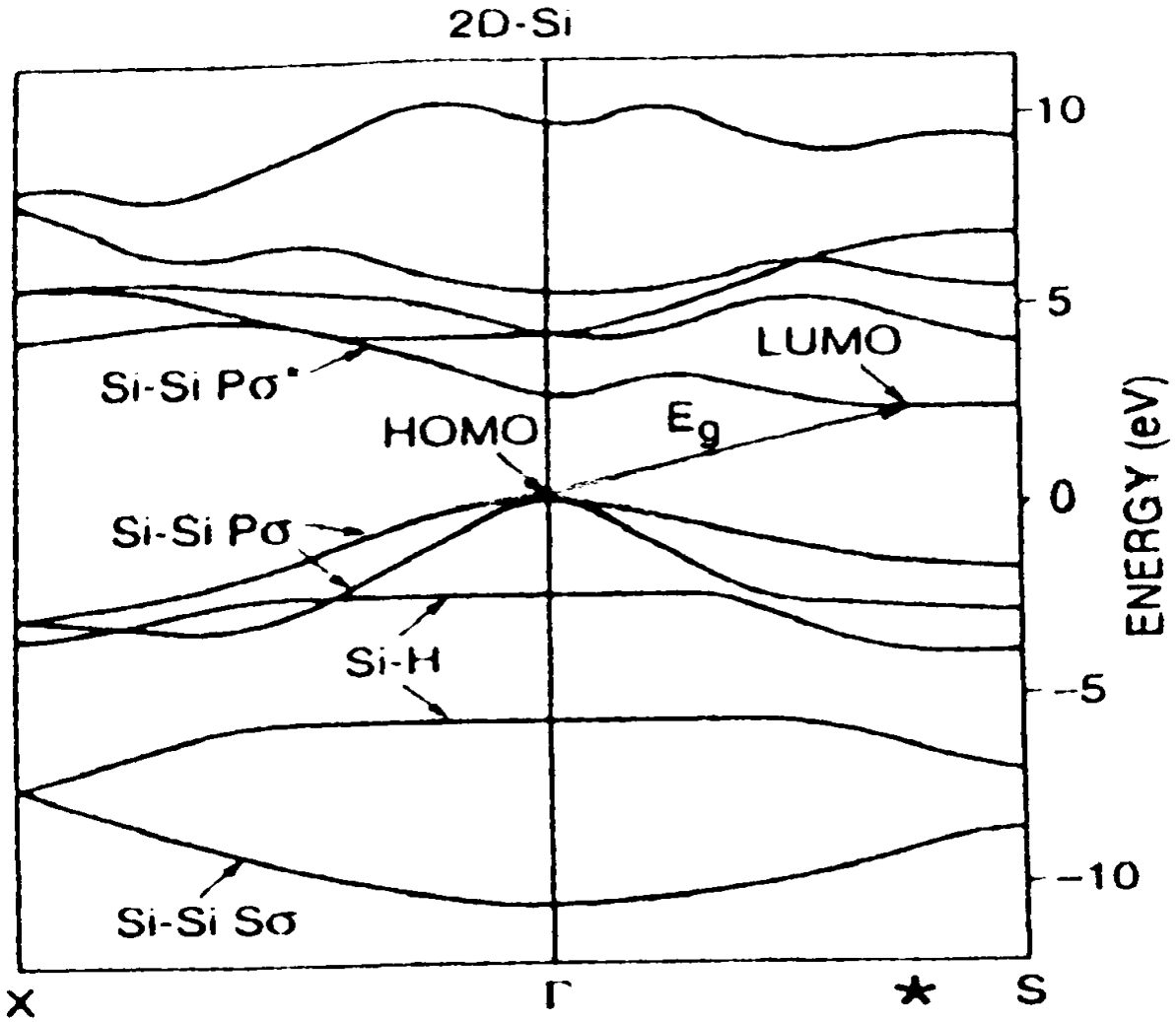
3D electron structure



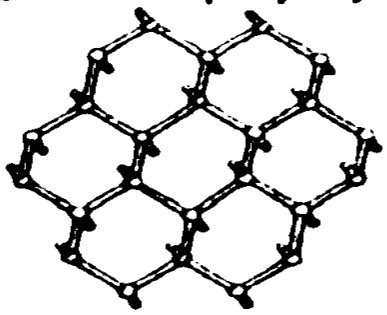
SILICON
DIAMOND STRUCTURE

L.Brus : Luminescence of Silicon Materials: Chahins, Sheets, Nanowires, Microcrystals, and Porous Silicon, J.Phys.Chem. 98,(1994)3575

2D electron structure

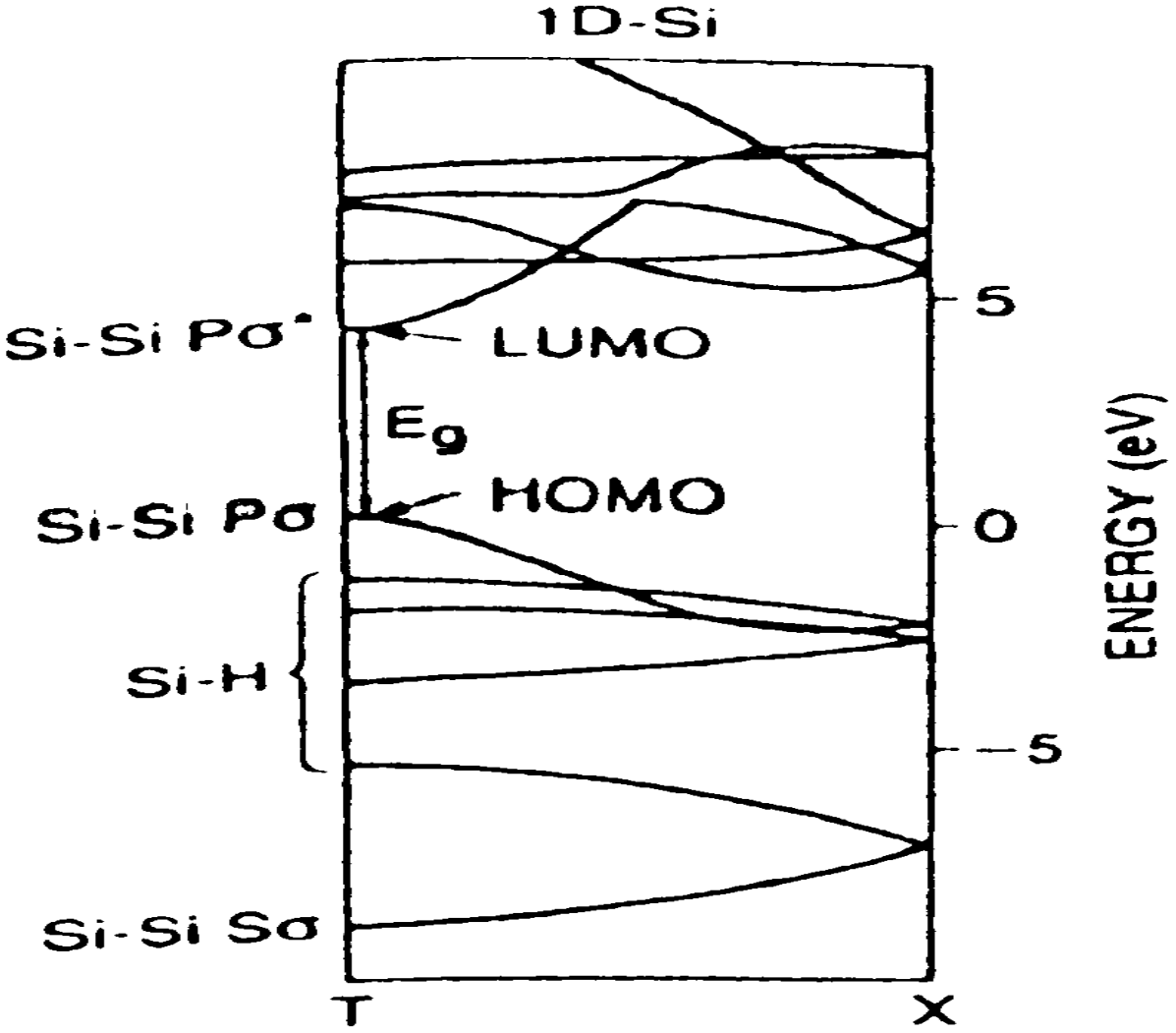


Puckered sheet polysilyne $(SiH)_n$

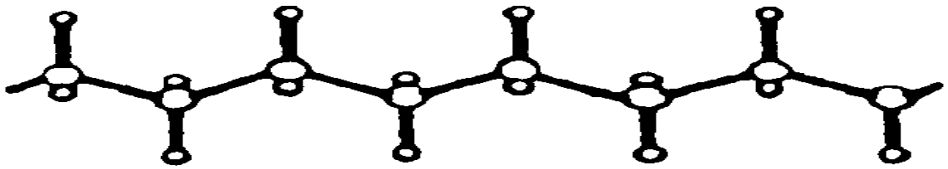


L.Brus : Luminescence of Silicon Materials: Chahins, Sheets, Nanowires, Microcrystals, and Porous Silicon, J.Phys.Chem. 98,(1994)3575

1D electron structure



Trans-polysilane $(SiH_2)_n$ chain



L.Brus : Luminescence of Silicon Materials: Chahins, Sheets, Nanowires, Microcrystals, and Porous Silicon, J.Phys.Chem. 98,(1994)3575

VIP

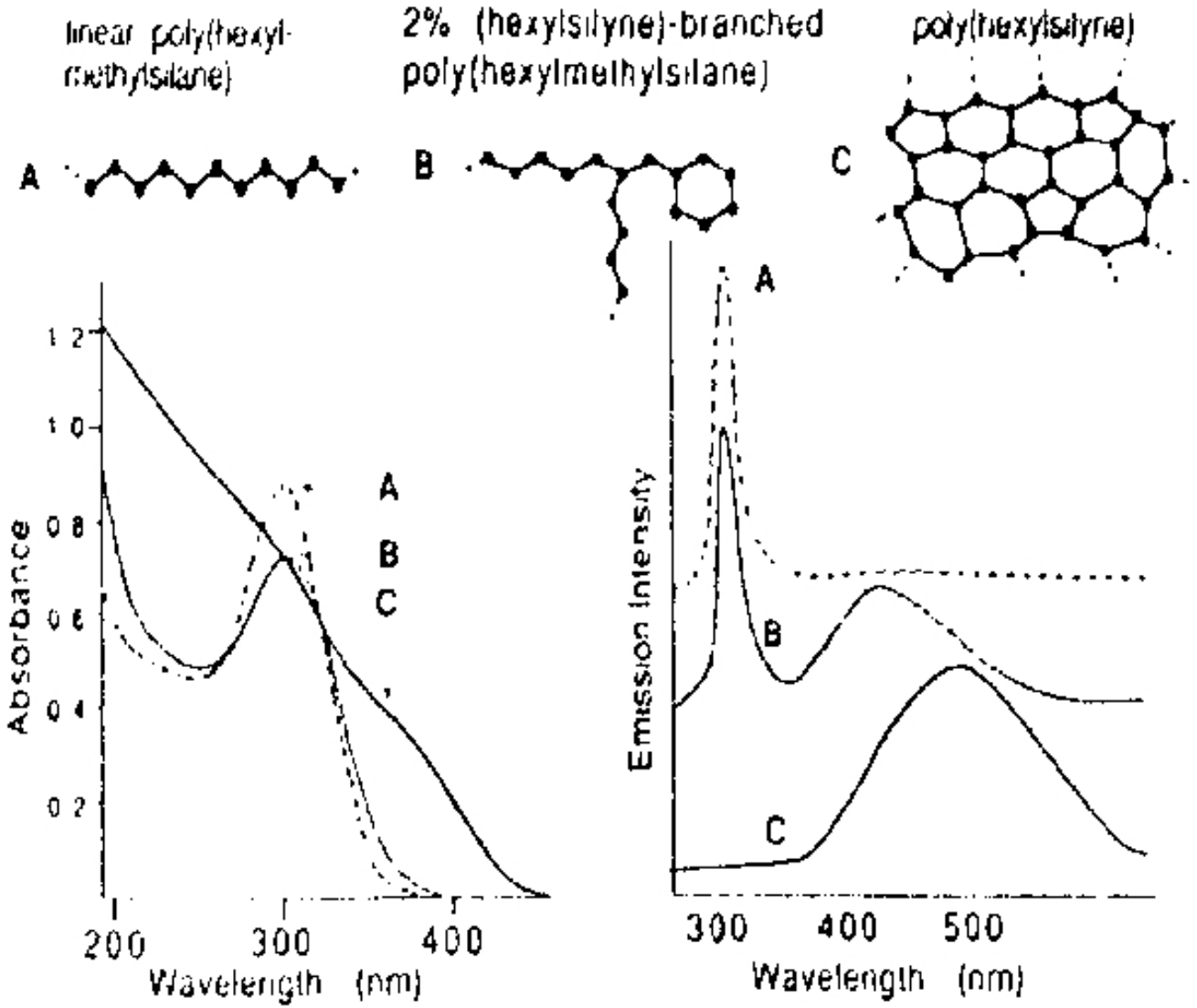


Figure 4. Optical absorption and emission spectra of 1D-Si and 2D-Si samples from ref 16a.

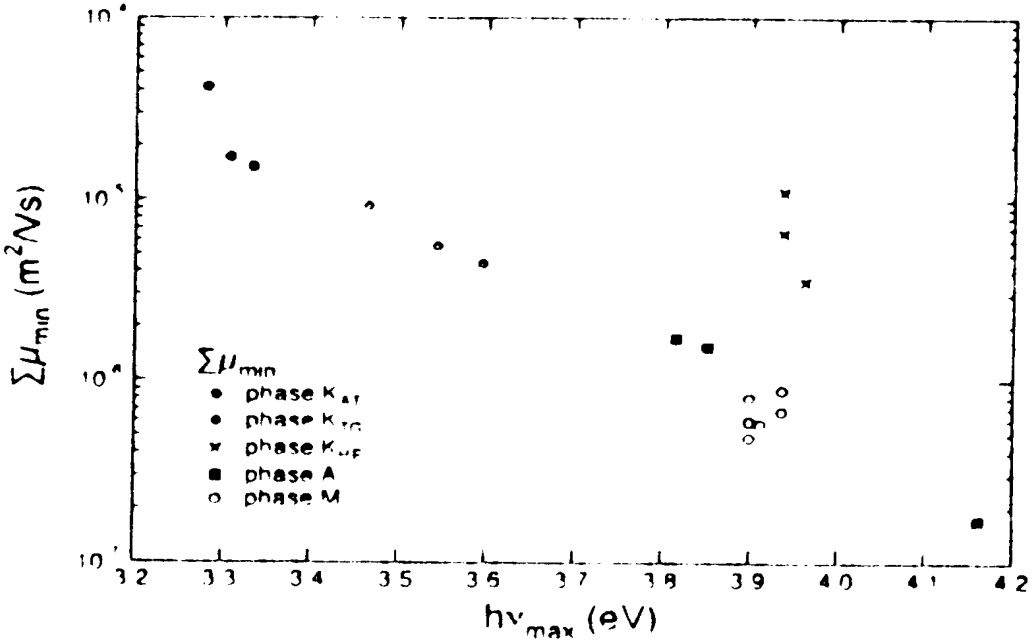
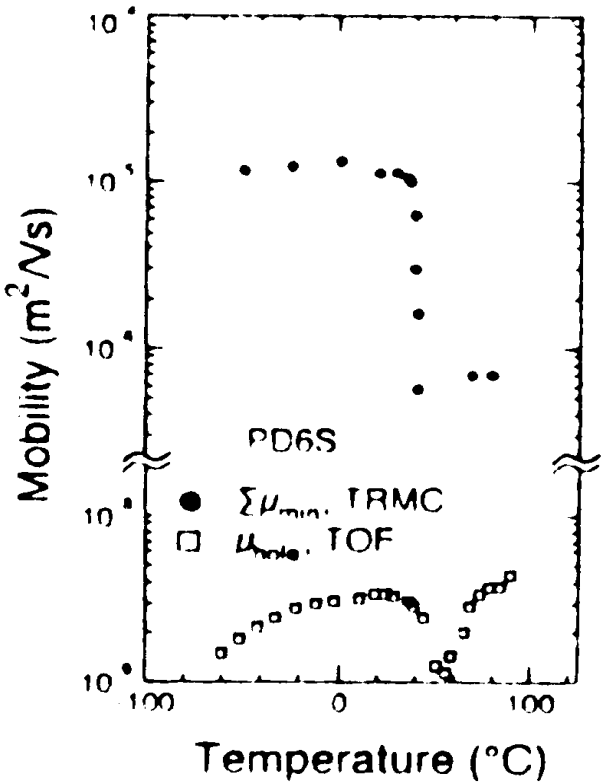


Figure 12. Charge carrier mobilities, $\Sigma\mu_{min}$, vs the UV-absorption maximum.



Garrelt P. vandder Laan, et al, Charge Carrier Mobilities in Sutbstiuted Polysilylenes: Influence of Backbone Conformation,

J.Phys. Chem. 100 (1996),5470

3. Vlastnosti a aplikace

Carbon

Silicon

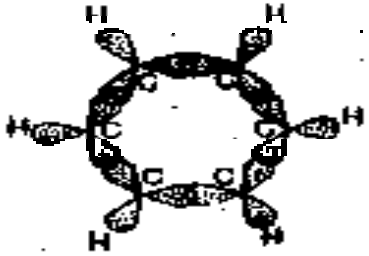
Ground state

$1s^2\,2s^2\,2p^2$

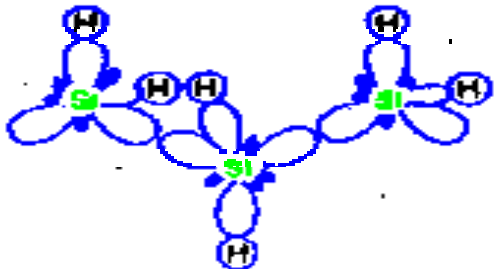
$1s^2\,2s^2\,2p^6\,\underline{3s^2\,3p^2}$

sp^3 hybrid orbitals
located on the silicon atom

Benzene

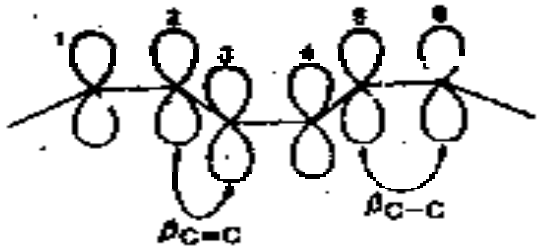


all-trans

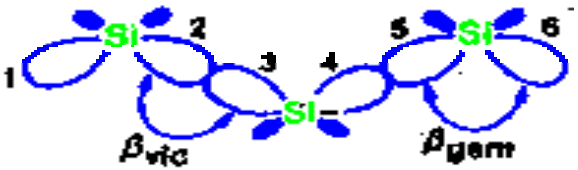


Linear chain

Polyene
π-conjugated chain of
interacting C 2p orbitals



Poly(silylene)
σ-conjugated chain of
interacting Si $3sp^3$ orbitals



Similar Germanium
$1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,3d^{10}\,4s^2\,4p^2$

TUNED

LUMINESCENCE

1D SILICONS prospect: UV (polarized) electroluminescence

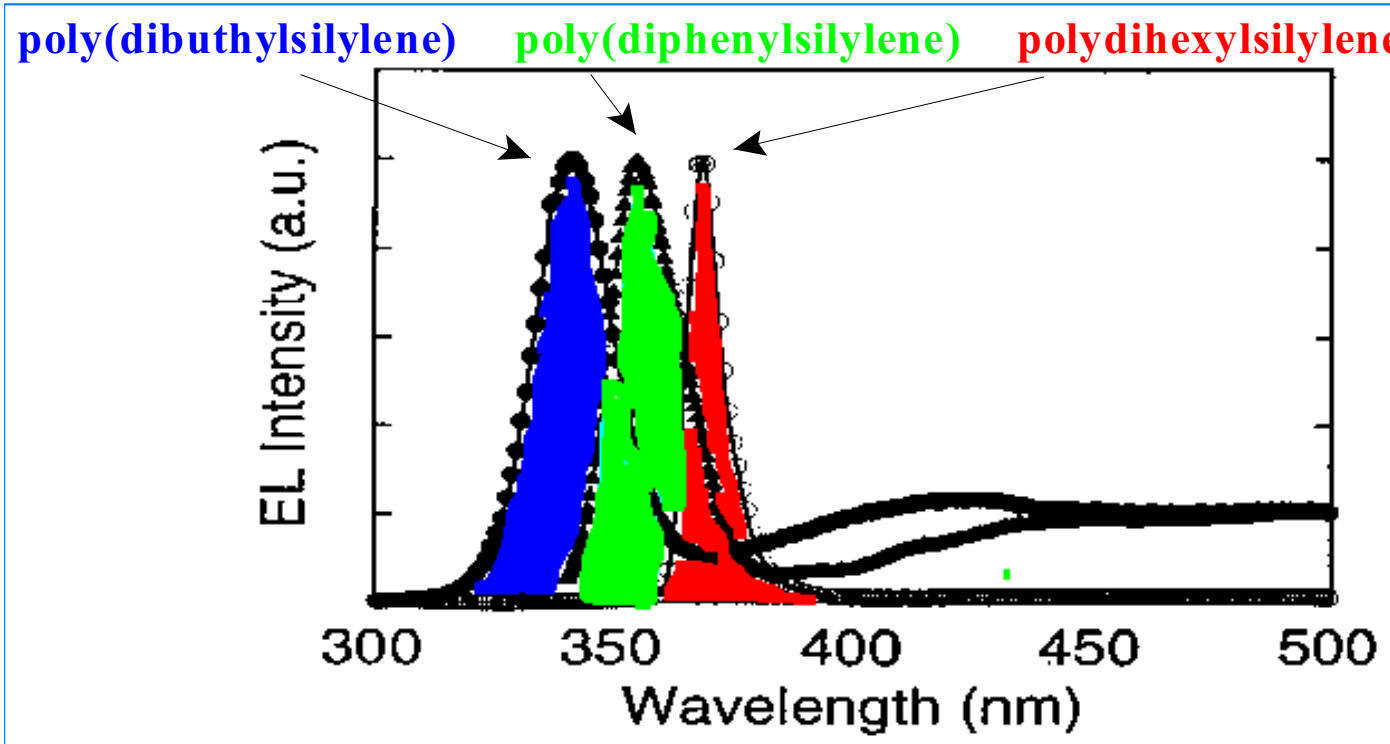


Fig. 7. The EL spectrum of PDBS (●), PDPS (▲) and PDHS (○). The spectrum was measured at 100 K for PDBS and PDHS and at 200 K for PDPS.

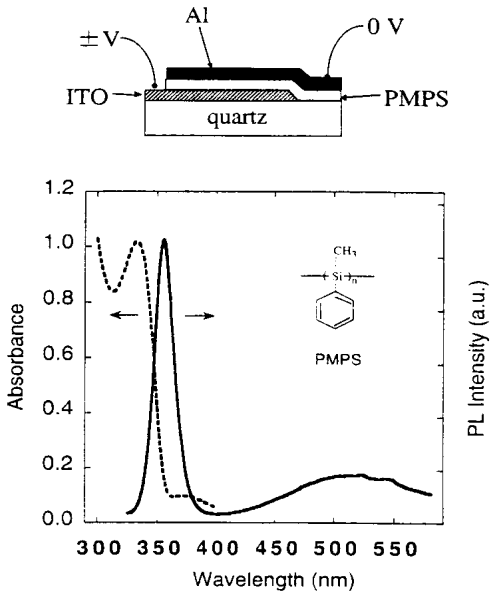
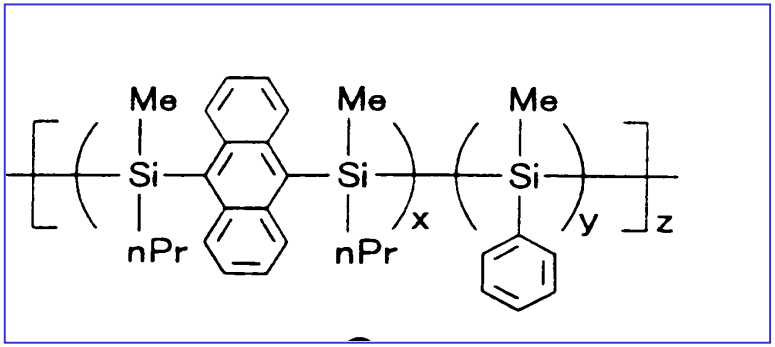
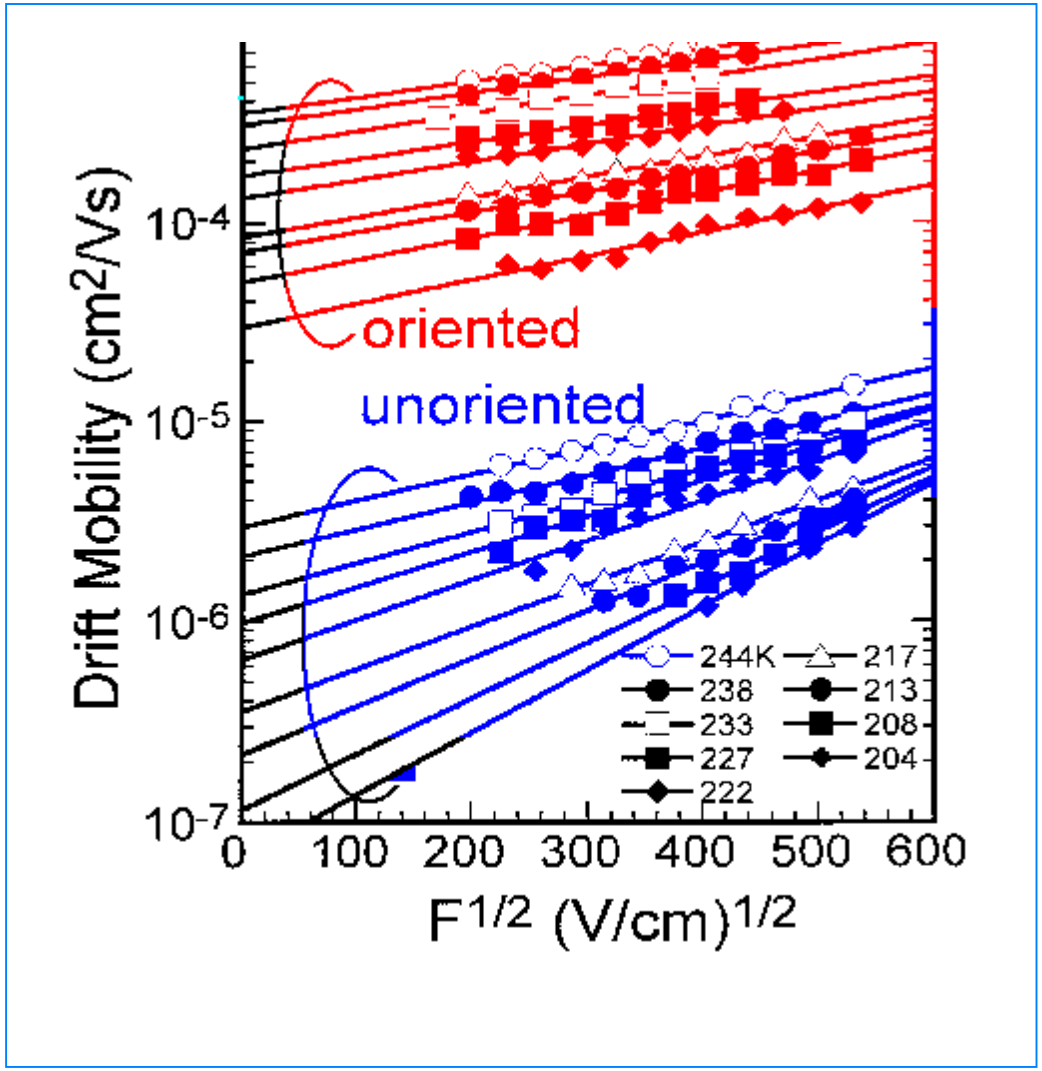


Fig. 1 A schematic diagram of the LED structure, together with absorption (broken line) and PL (solid line, excitation wavelength 300 nm) spectra of PMPS (thickness 120 nm).

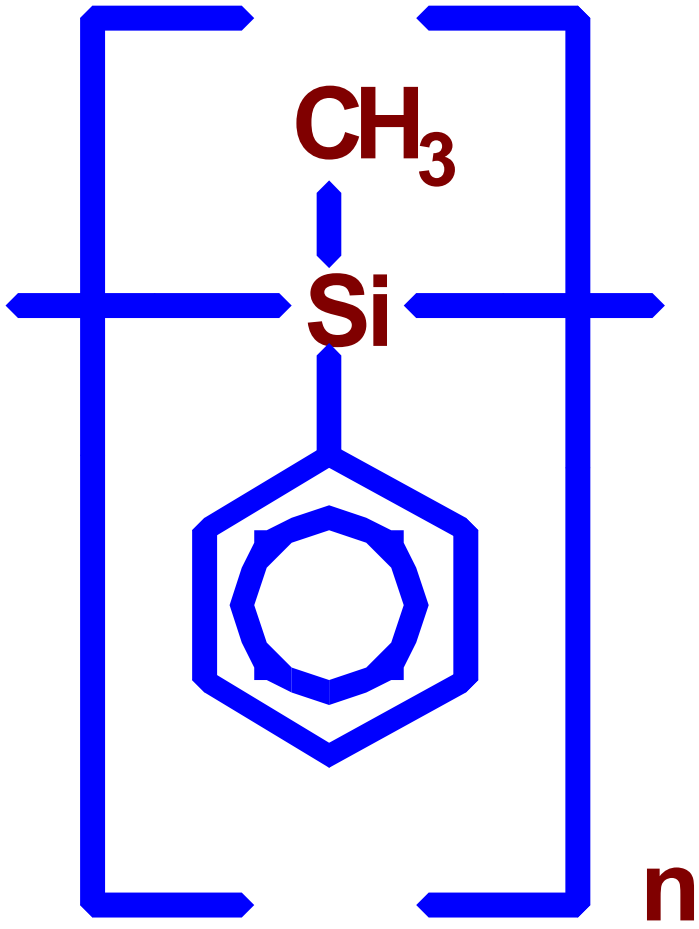


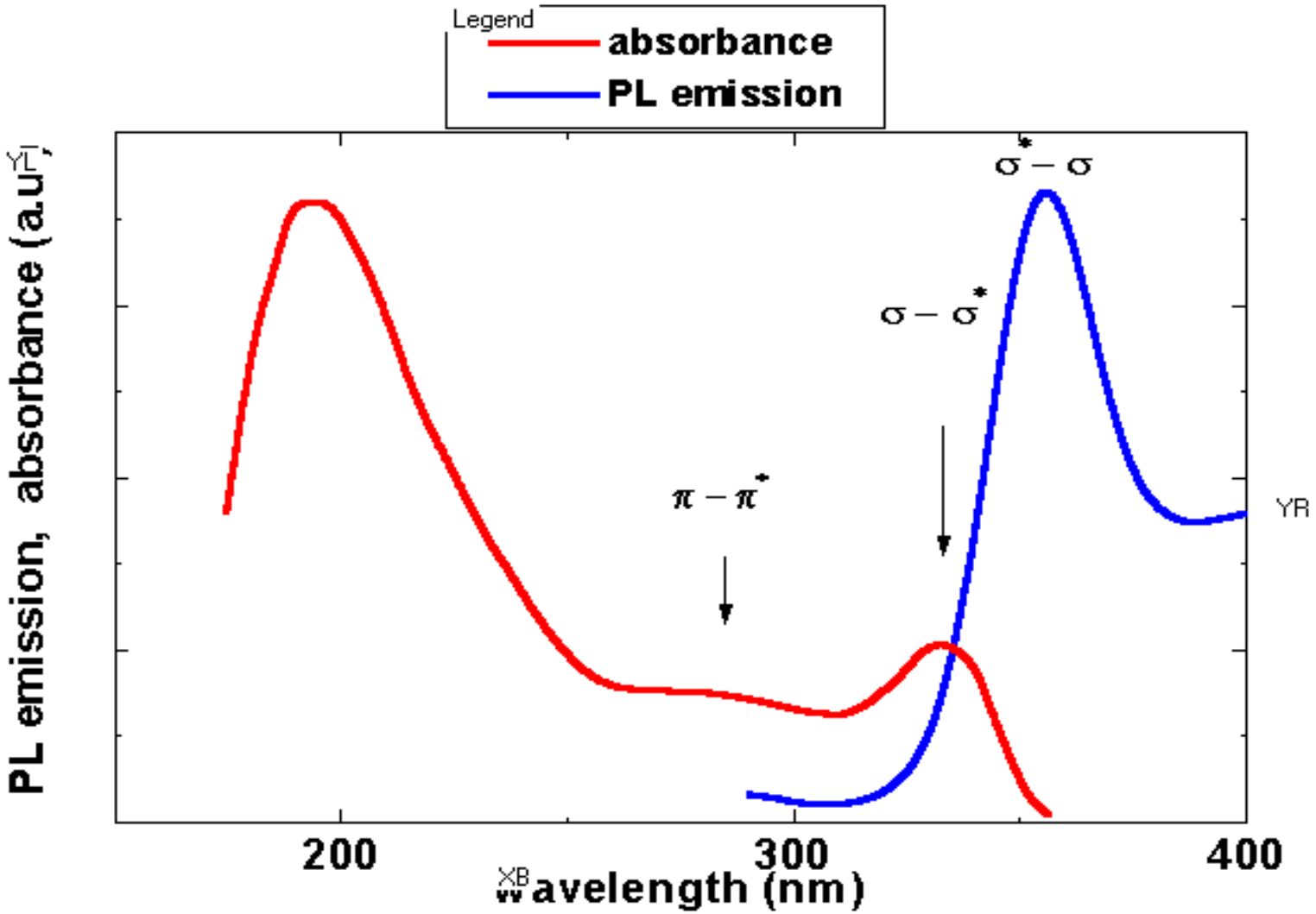
ORDERING

1D silicon-mobility
poly(di- npentylsilylane)



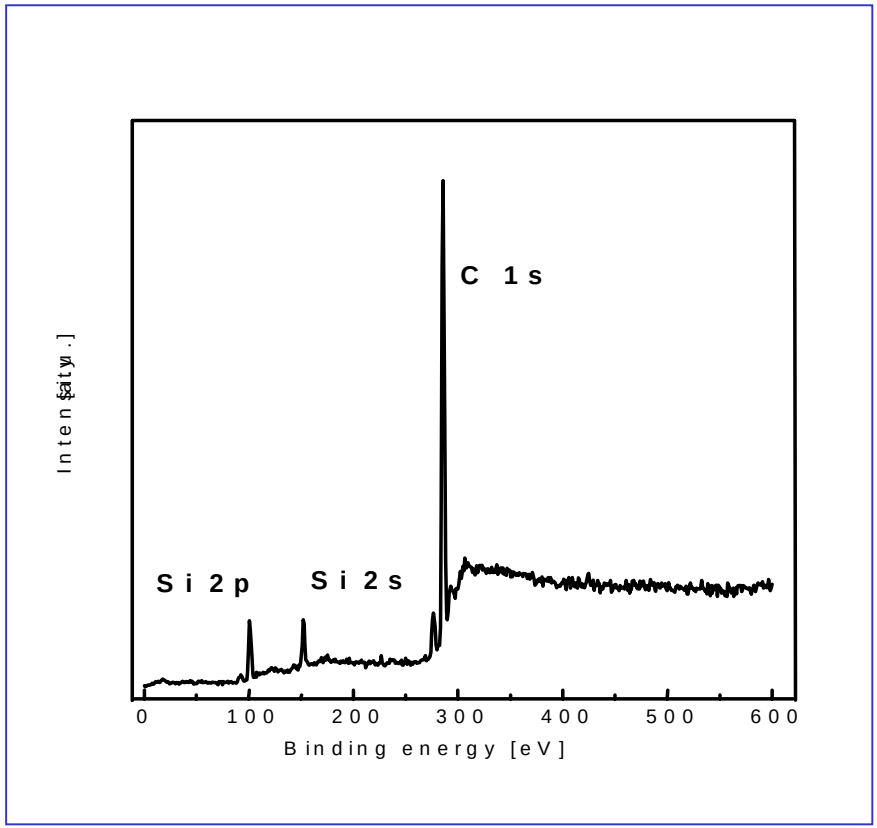
Y. Nakayama, K.Hirooka,K. Oka and R. West, 1999


CH3
Si
n



S. Nespurek, F. Schauer, and A. Kadashchuk : Visible Photoluminescence in Polysilanes, Chemical Monthly 132(2001),159-168,

Fotoelektronové spektroskopie



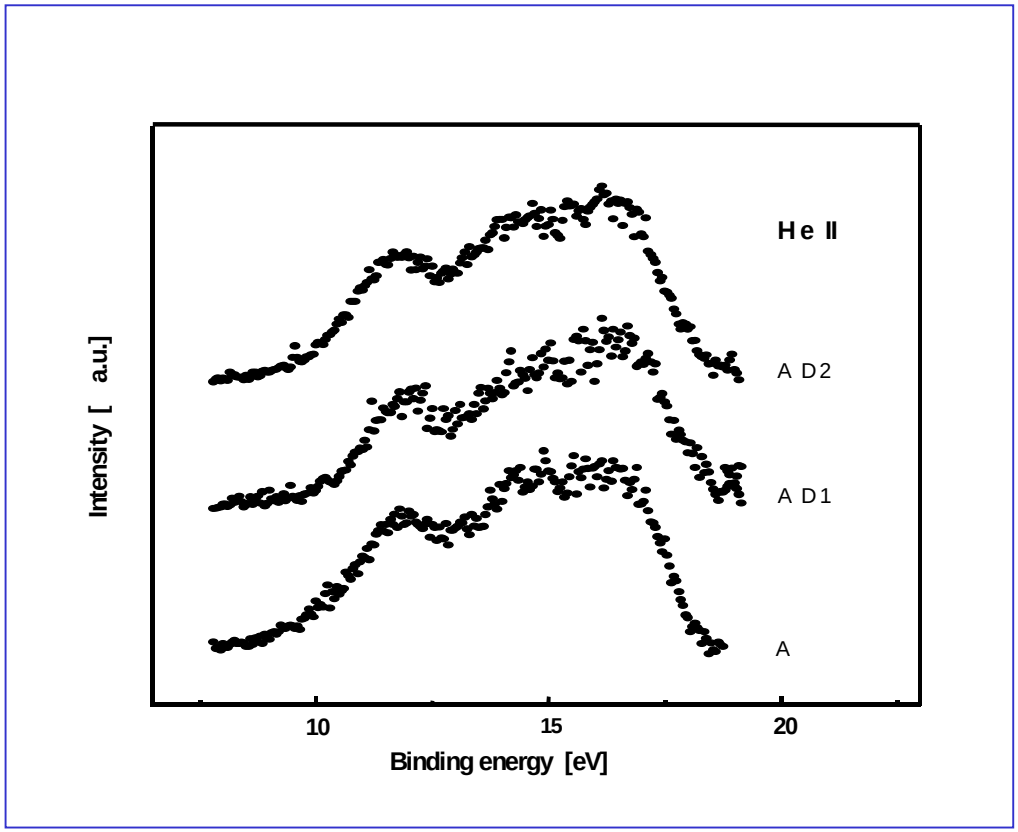


Fig. 2: A survey XPS spectrum from the pristine PMPSi; mind the absence of oxygen related lines [4]

Fig.3: UV induced valence band spectra of the pristine PMPSi surface (A) and after (D1) and (D2) degradation steps using Xe I resonant irradiation [4]

[4] J. Zemek, P. Jiricek, N. Dokoupil, F. Schauer, S. Nespurek: *Electron spectroscopy of poly [methyl-phenylsilylene]* films, to be published 2002.

4. Proč plasma?

UV laser ablation

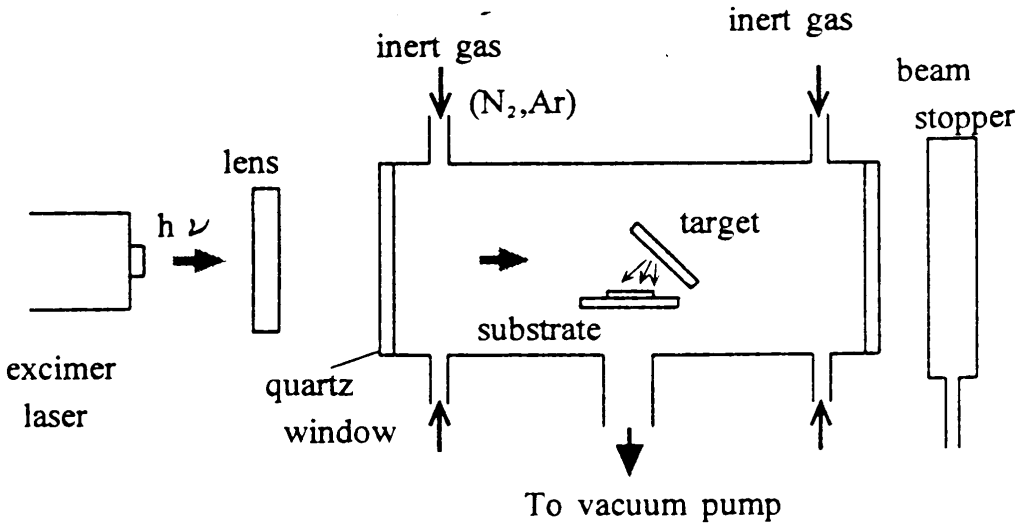


Fig. 1. Schematic diagram of the laser ablation reactor.

M.Suzuki, Y.Nakata, H.Nagai, K. Goto, O. Nishimura, T. Okutani,
Mater. Sci.Engineer. A146(1998)36

laser CVD

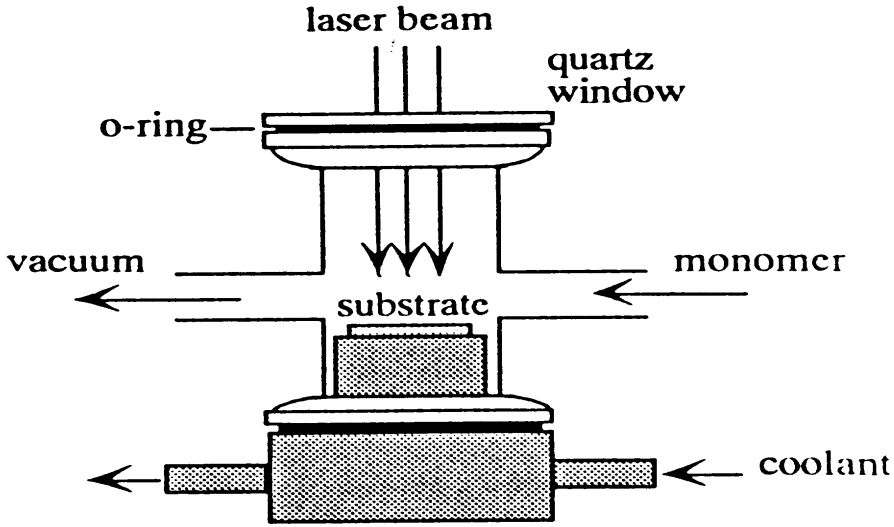


Fig. 2. Apparatus of laser CVD.

A . Watanabe, T.Kawato, M. Matsuda, M. Fujitsuka, O. Ito, Thin Sol Films, 312(1998)123

RFdischarge

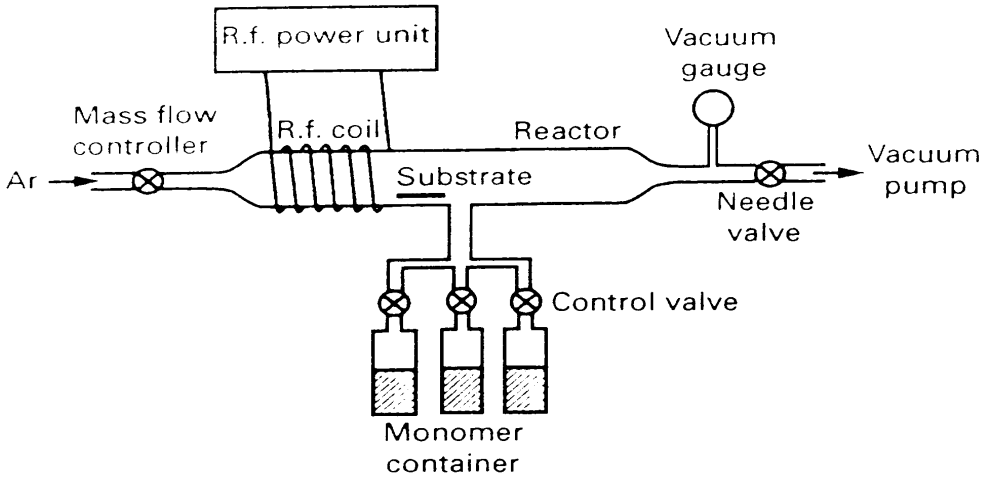
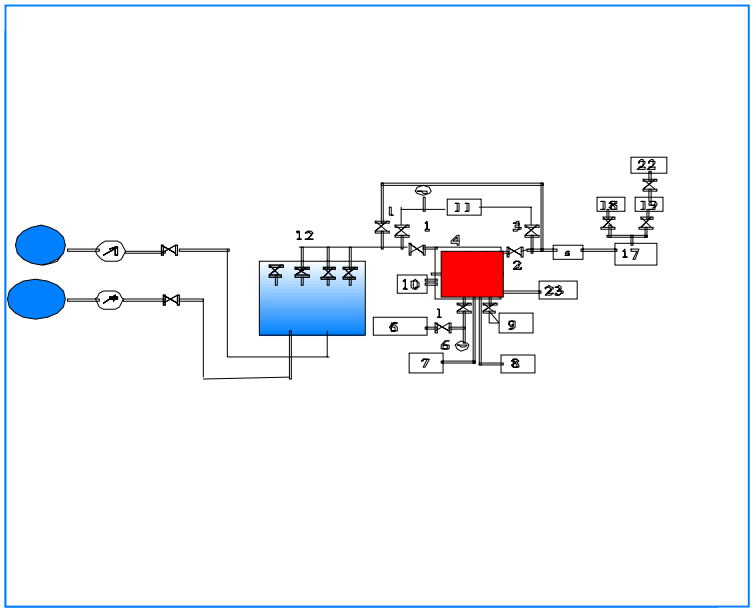


Figure 1 Schematic diagram of the reactor system.

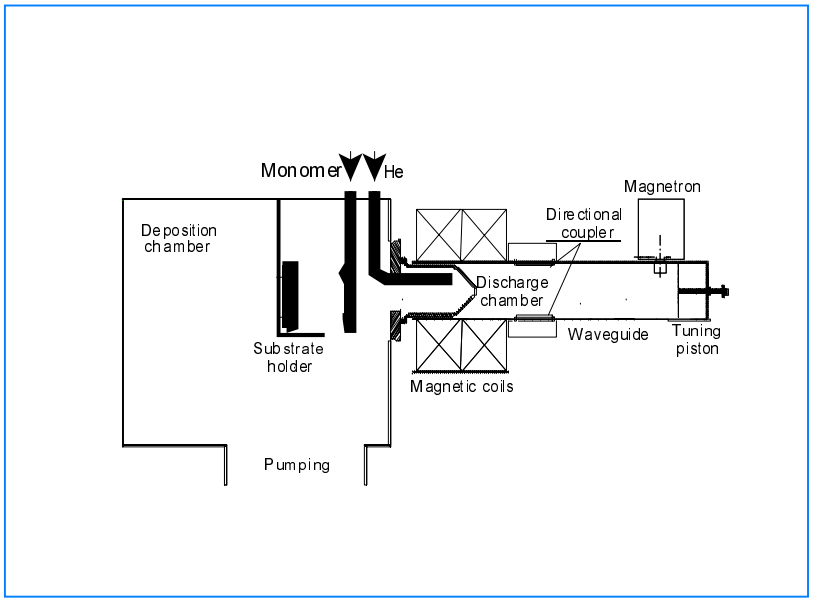
H. Nagai, Y. Nakata, M. Suzuki, T. Okutani, J. Mater. Sci.33(1998)1897

PLASMA TECHNIQUES USED

Radio Frequency Plasma Enhanced CVD

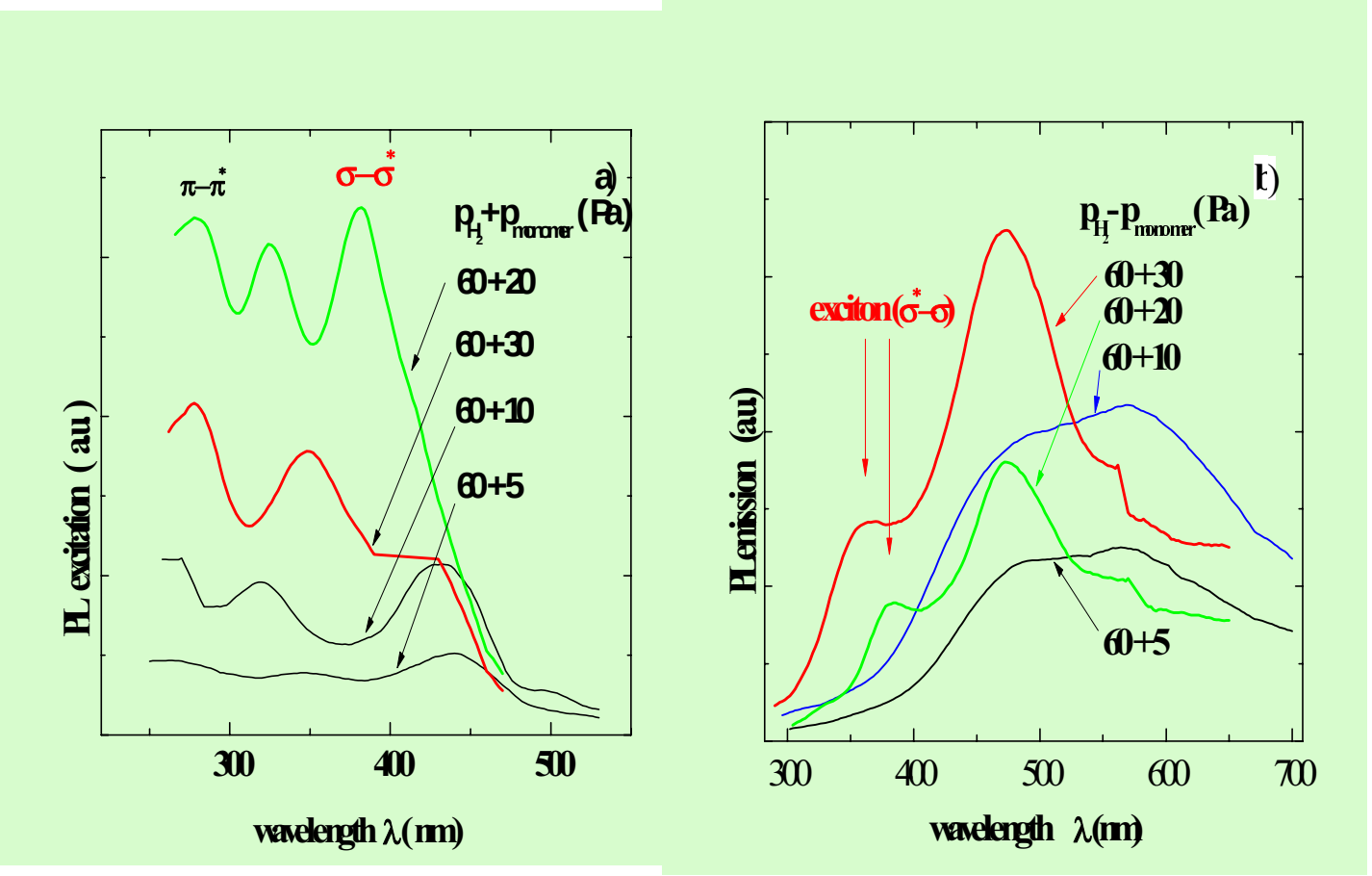


Microwave Frequency Plasma Enhanced CVD

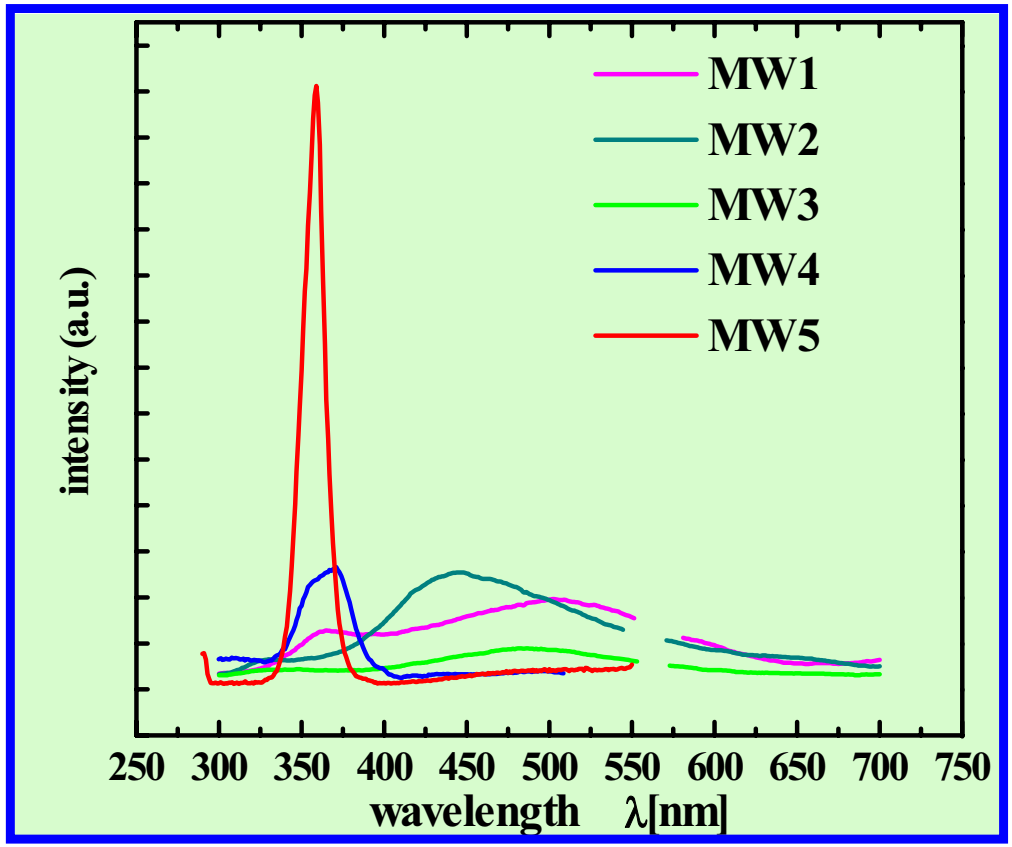


This work is supported by European Commission programme COST 518

Plasma polysilylenes - luminescence vs conditions



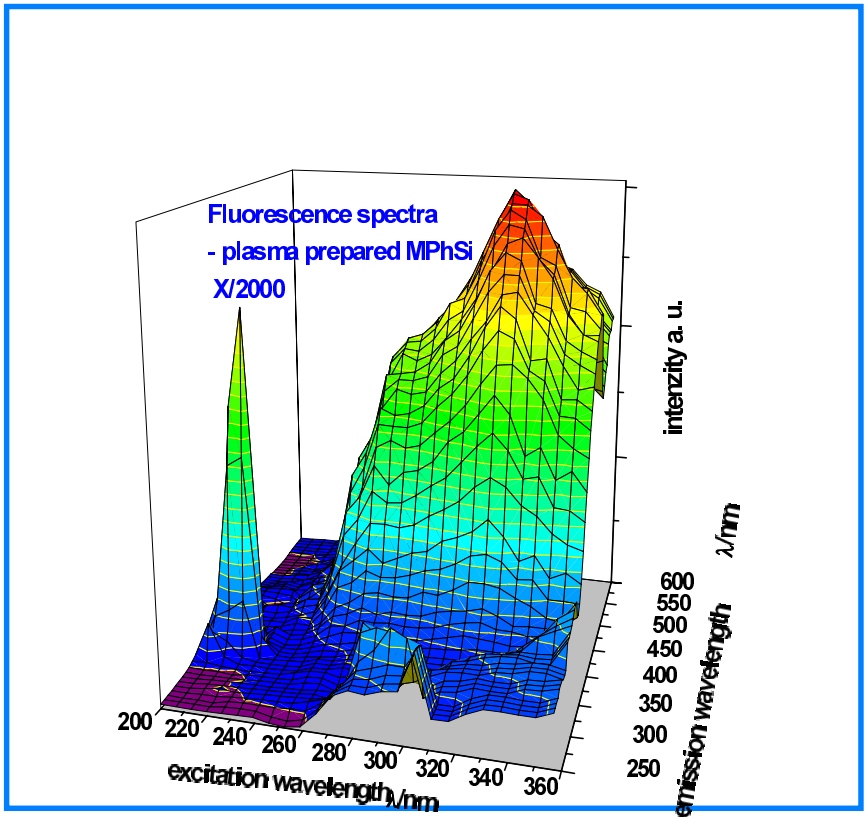
Microwave plasma - luminescence

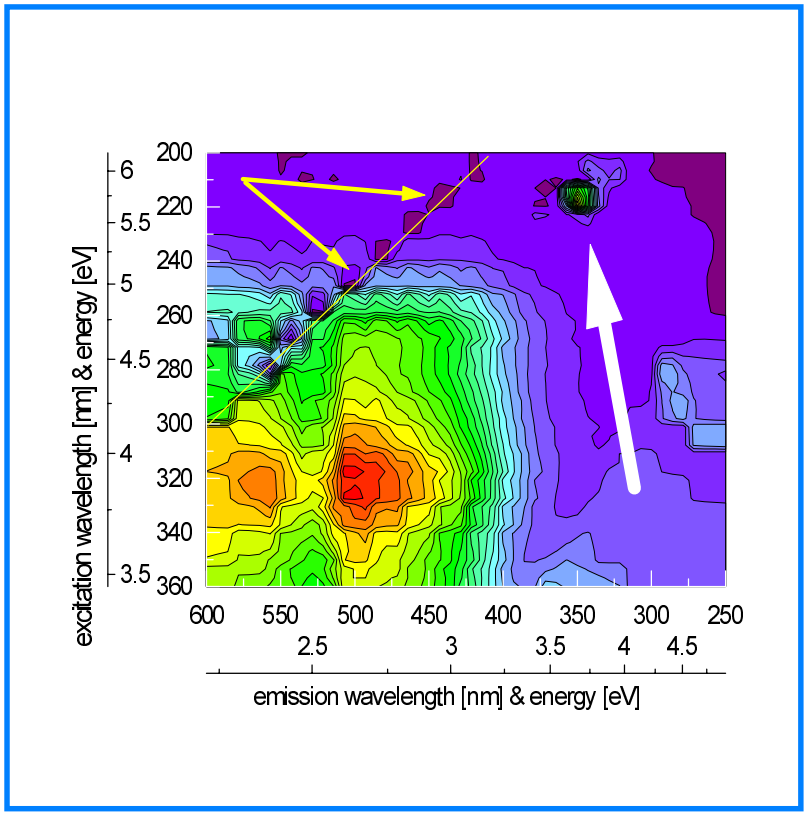


sample	flow rate of H2 (sccm)/ /pressure of H2 (Pa)	deposition pressure (Pa)	partial pressure of monomer (Pa)	substrate temperature (K)
MW1	15/14	19	5	320 - 350
MW2	15/18	30	12	"
MW3	15/18	20	2	"
MW4	40/0.080	0.085	0.005	390 - 410
MW5	40/0.100	0.130	0.030	360 - 390

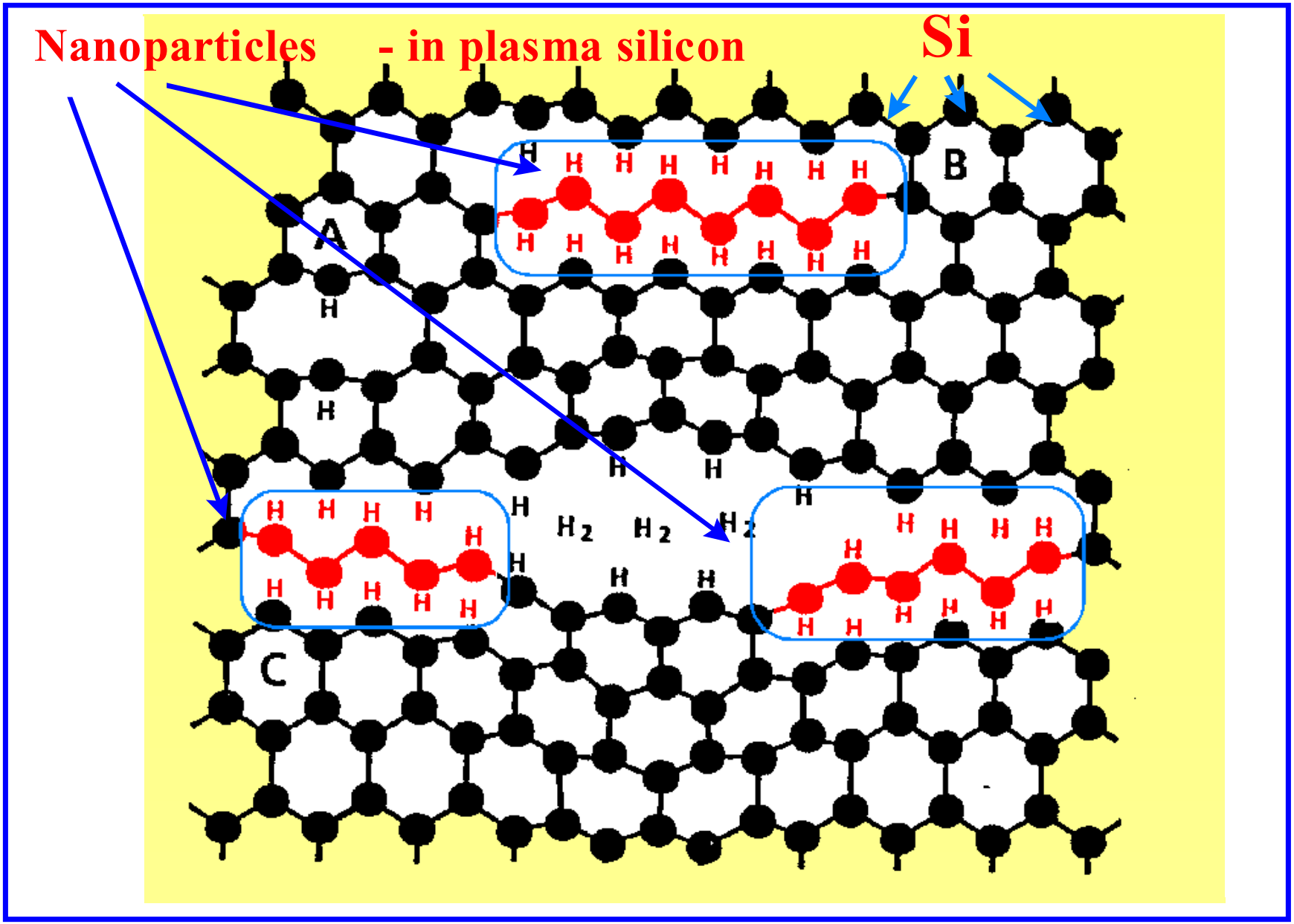
Radiofrequency plasma - luminescence

This work is supported by European Commission programme COST 518





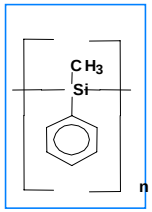
P.Horvath, F.Schauer, I.Kuritka, O.Salyk, M.Weiter, N.Dokoupil, S.Nespurek and V. Fidler: Luminescence in organic silicons prepared from organic precursors in plasma discharges, Chemical Monthly 132(2001),177-184 ,

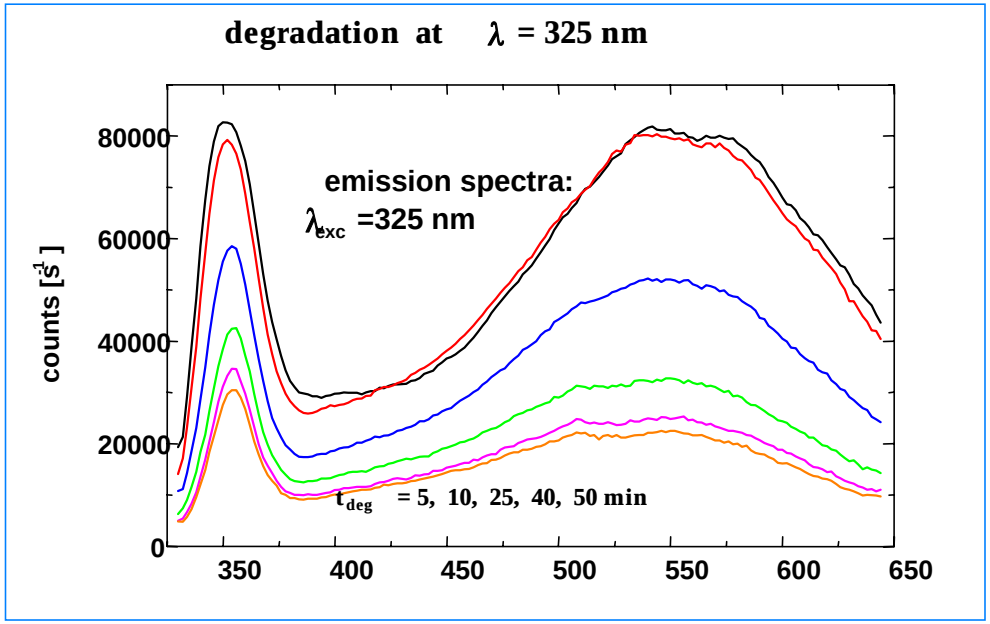


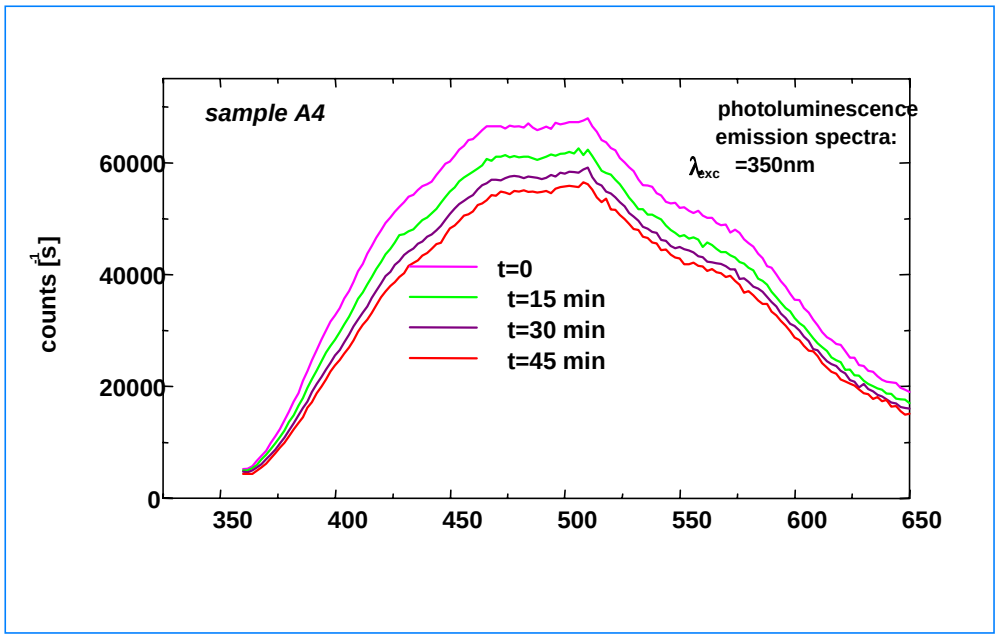
F. Schauer, I. Kuritka, N. Dokoupil and P. Horvath: Nanostructural effects in plasmatically prepared polysilylanes , to be published in Physica E, 2002

5. Degradace, metastabilita vs fotorezisty

Degradation of luminescence in PMPSi







Degradation of luminescence in PMPSi

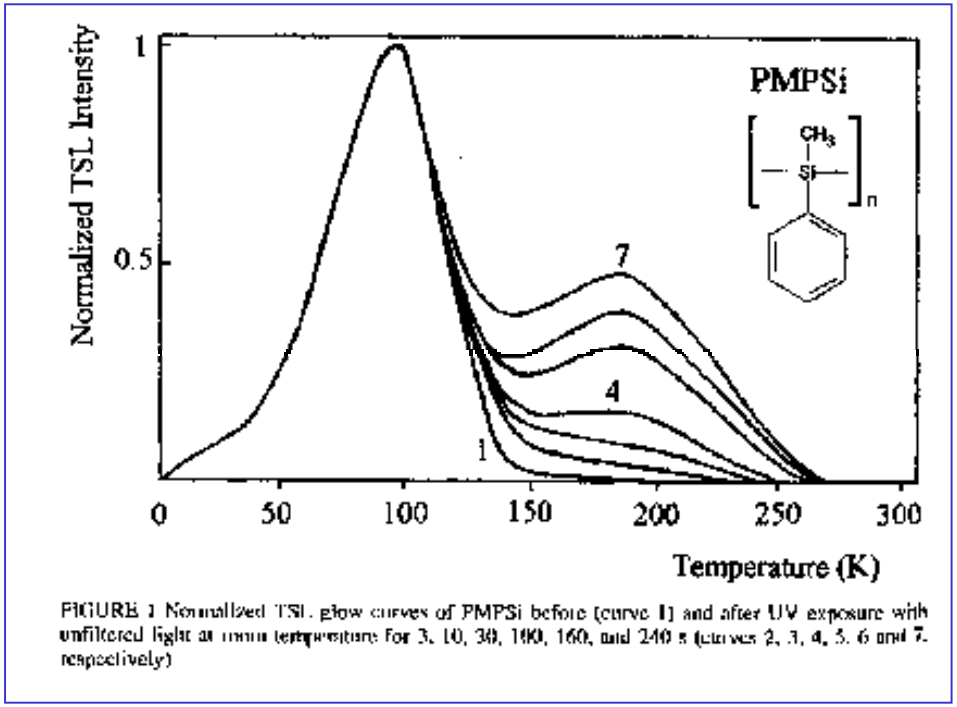
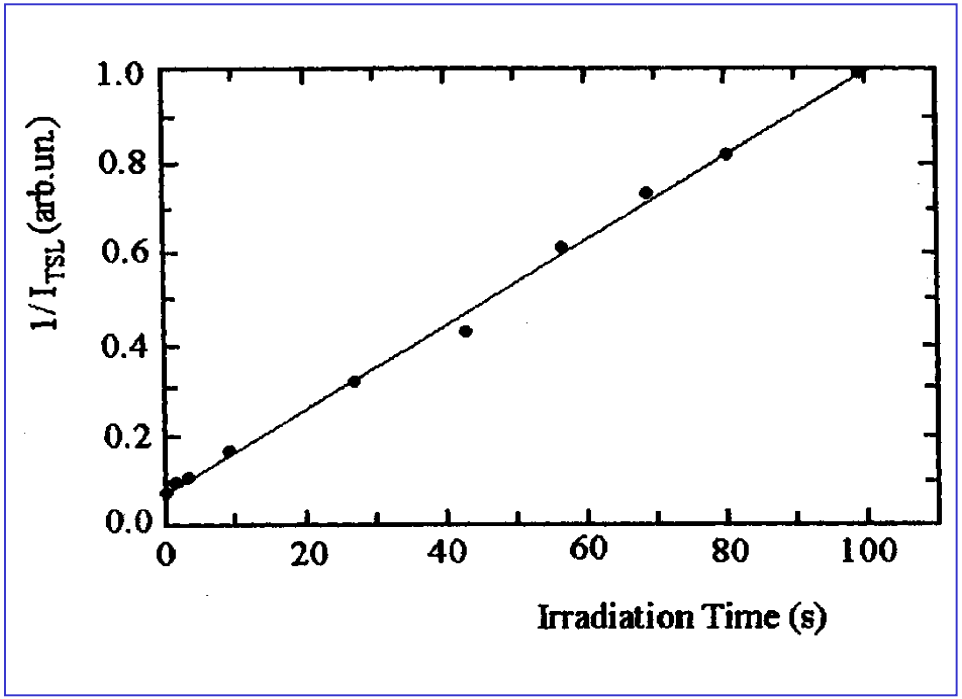
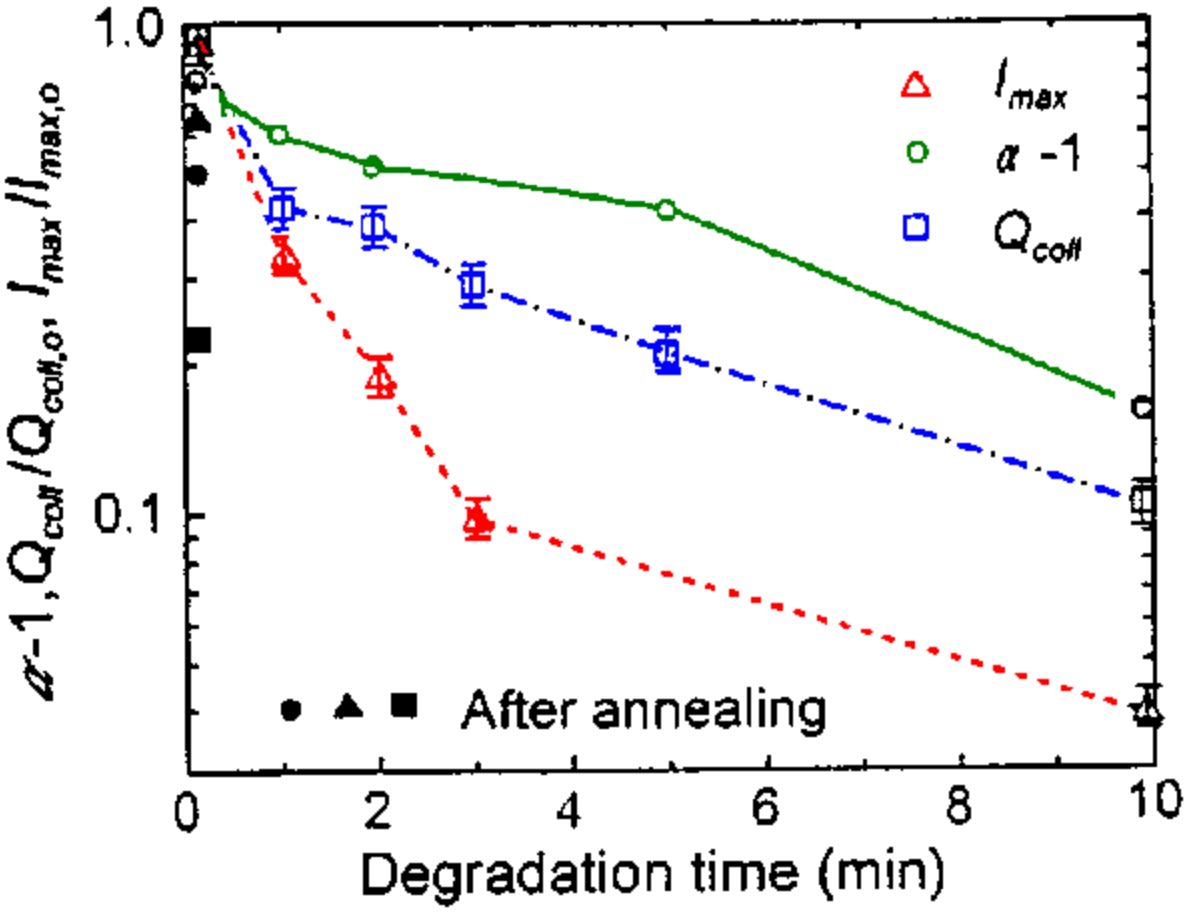


FIGURE 1 Normalized TSL glow curves of PMPSi before (curve 1) and after UV exposure with unfiltered light at room temperature for 3, 10, 30, 100, 160, and 240 s (curves 2, 3, 4, 5, 6 and 7, respectively)



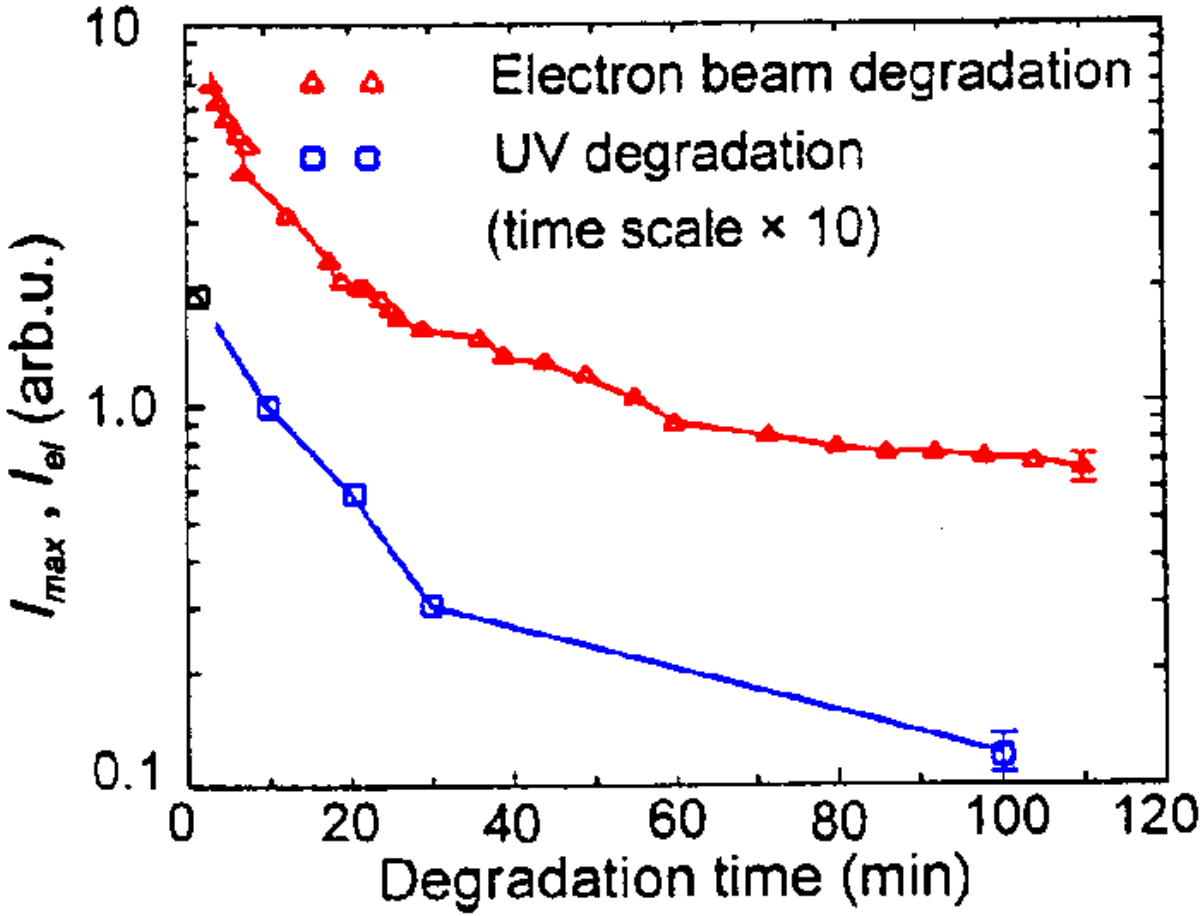
A. Kadashchuk, S. Nespurek, N.Ostapenko, Yu. Skryshevskii and V. Zaika: Mol. Cryst.Liq. Cryst. 355(2001),413

Degradation of transport in PMPSi



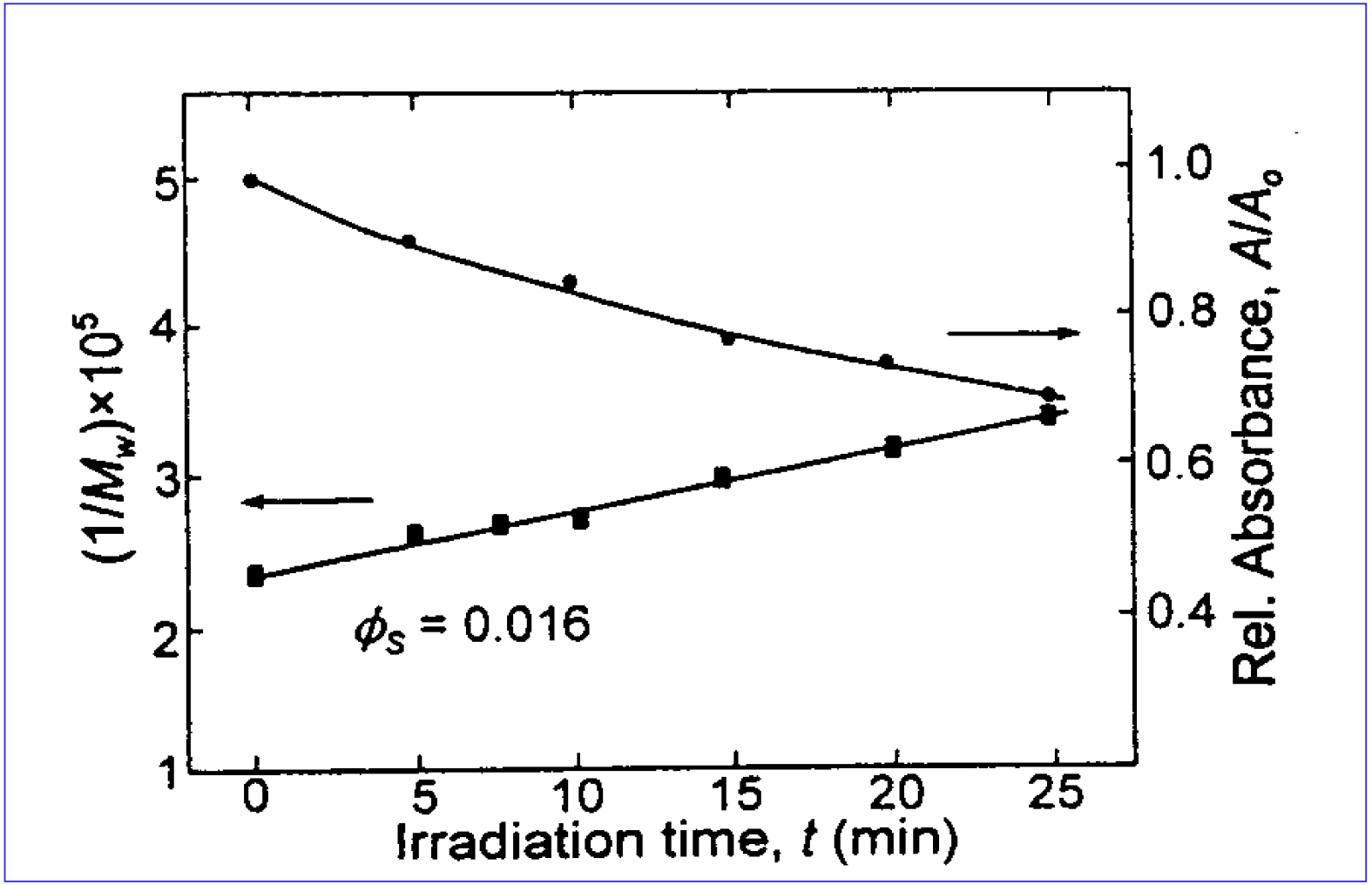
R. Handlíř, F. Schauer, S.Nešpůrek, I. Kuřitka, M. Weiter, and P.Schauer: Meta- stability in poly(methylsilylene) induced by UV radiation and electron beam, J. Non-Crystall. Solids (Hol.)227-230 (1998),669,

Degradation of kathodoluminescence in PMPSi



R. Handlíř, F. Schauer, S.Nešpůrek, I. Kuřitka, M. Weiter, and P.Schauer: Meta- stability in poly(methylsilylene) induced by UV radiation and electron beam, J. Non-Crystall. Solids (Hol.)227-230 (1998),669,

Molecular weight degradation in PMPSi



Degradation of PMPSi

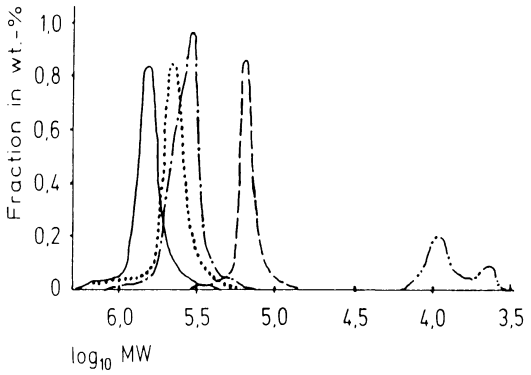


Fig. 5. Change in molecular weight distribution of PCHMS in cyclohexane solutions ($\approx 10^{-4}$ mol · L^{-1}) upon UV irradiation in air. (———): Original polymer; (· · ·): after irradiation for 4 s; (– · –): 8 s; (– – –): 15 s; (– · · –): 30 s

Deben Chen and Huiping Hu, Studies on the behaviour of photodegradation of poly(cyclohexylmethylsilane), Macromol. Chem. Phys. 195 (1994), 2981

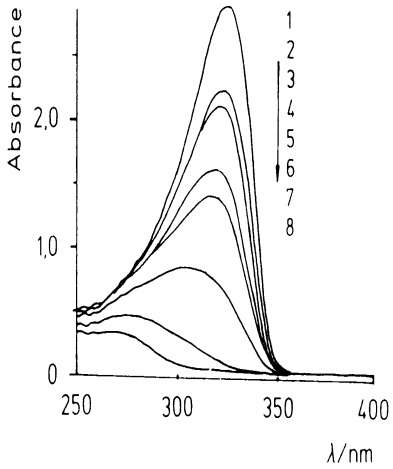
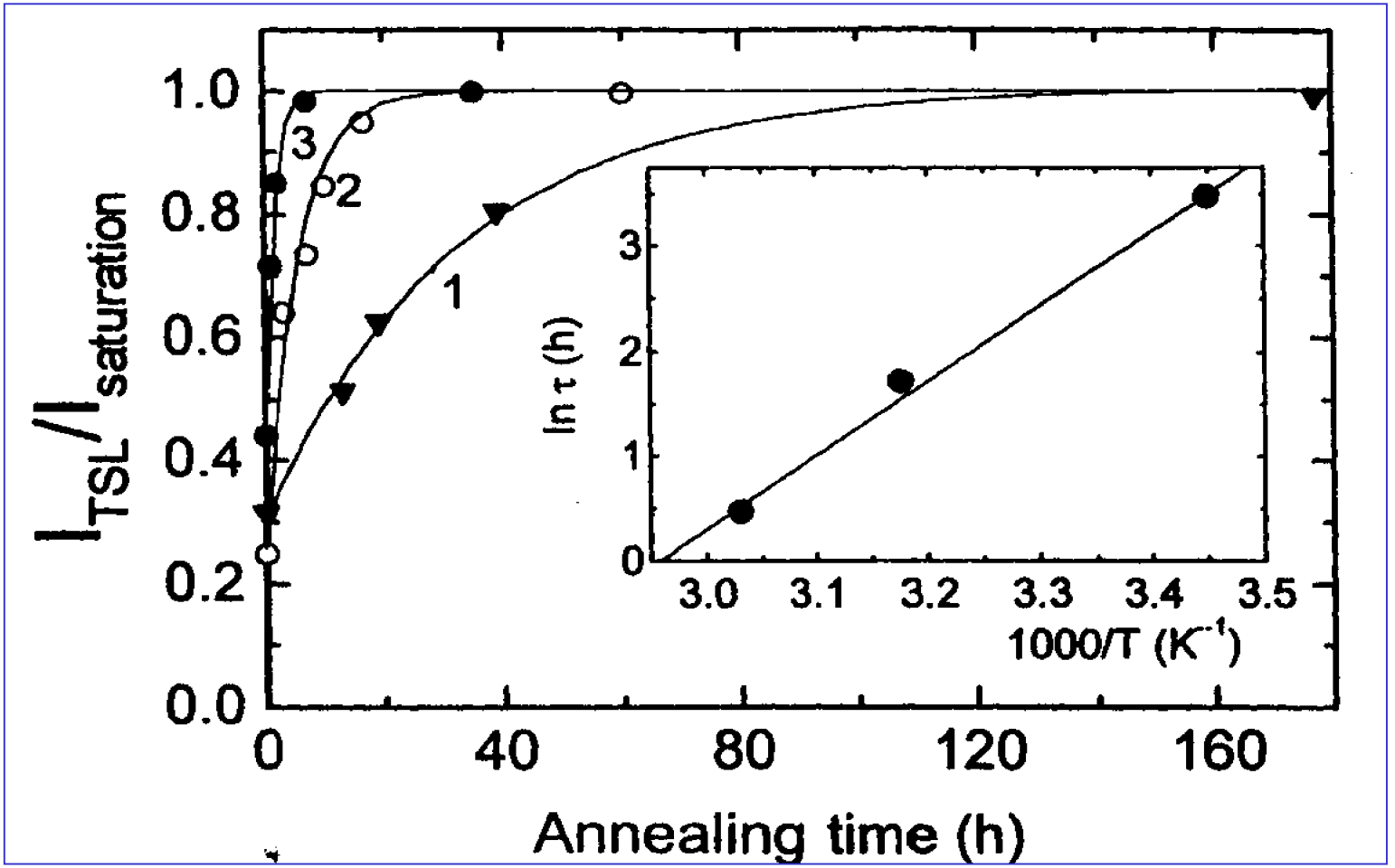
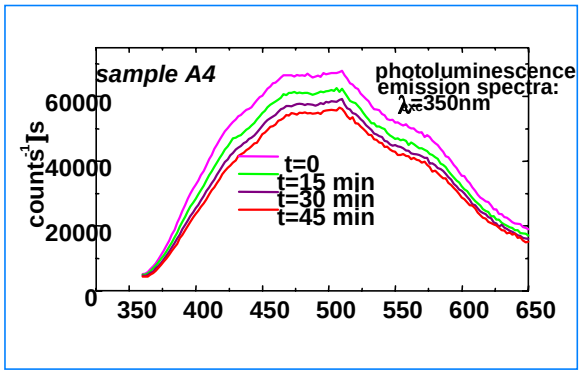


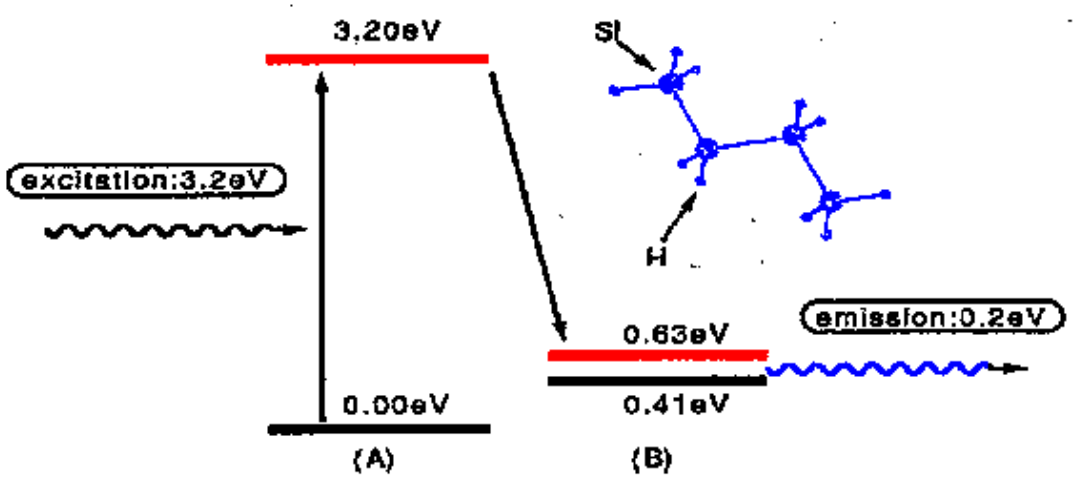
Fig. 3. Ultraviolet spectra of PCHMS in cyclohexane solutions ($\approx 10^{-4}$ mol · L^{-1}) before and after UV irradiation in air. (1) 0 s; (2) 2 s; (3) 6 s; (4) 10 s; (5) 12 s; (6) 15 s; (7) 30 s; (8) 1 min

Metastability in luminescence - PMPSi

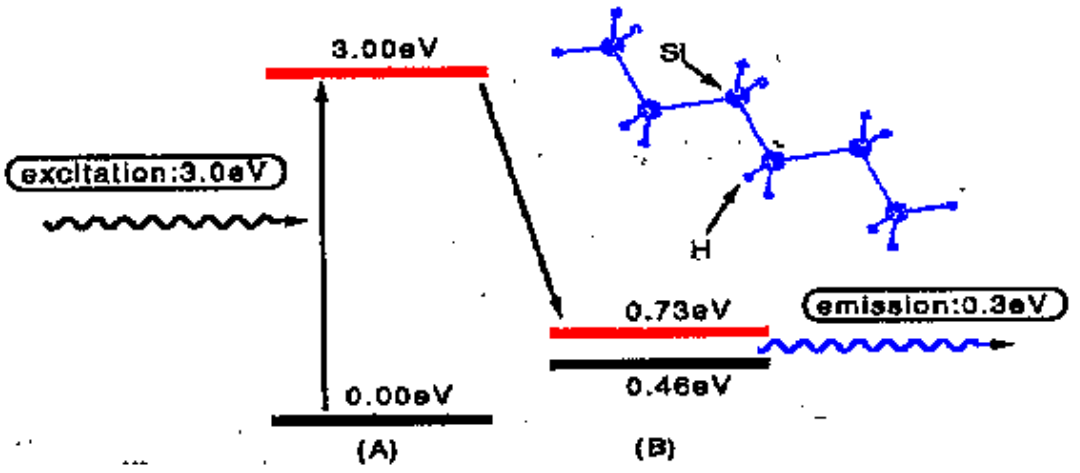


Nanostructural model



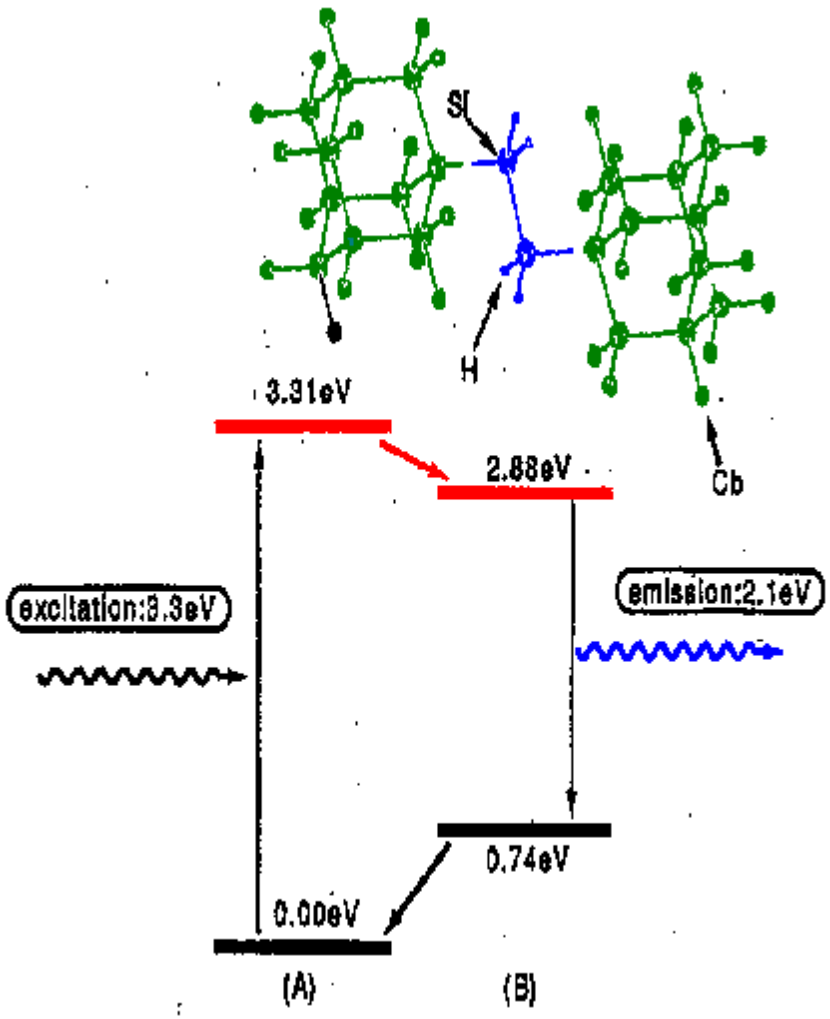


(a) Si_4H_{10} (trans planar type)

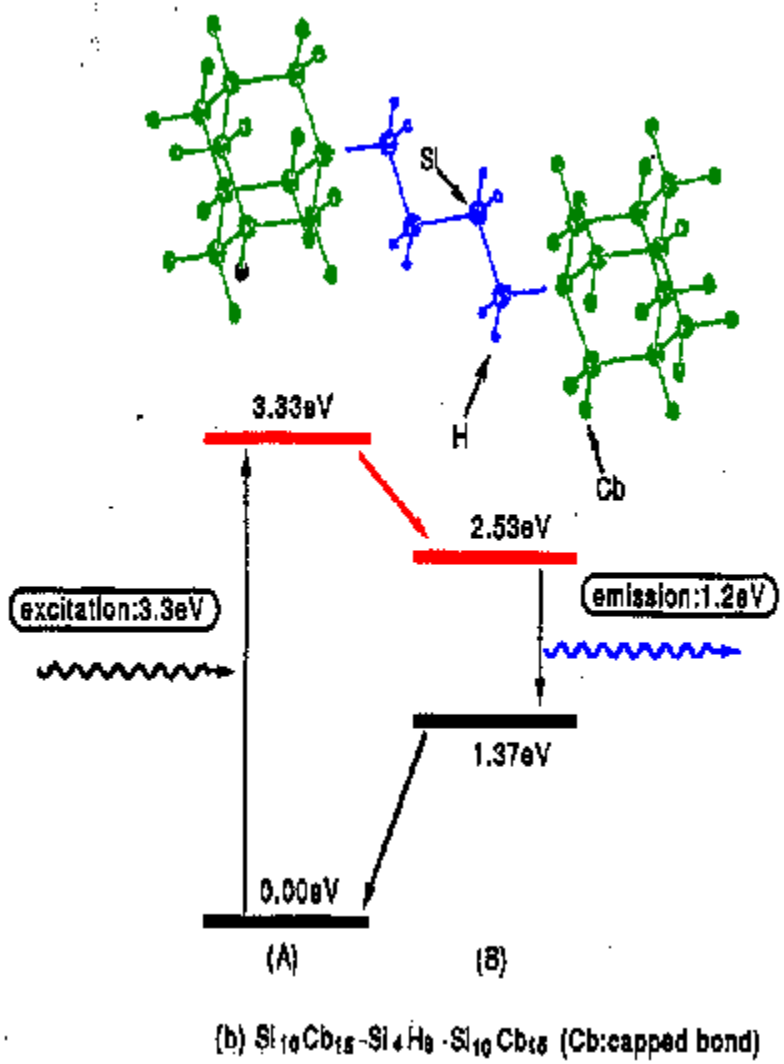


(b) Si_6H_{14} (trans planar type)

Nanostructural model



(a) $Si_{10}Cb_{15}$-Si_2H_4-$Si_{10}Cb_{15}$ (Cb:capped bond)



(b) $Si_{10}Cb_{15}$-Si_4H_8-$Si_{10}Cb_{15}$ (Cb:capped bond)

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