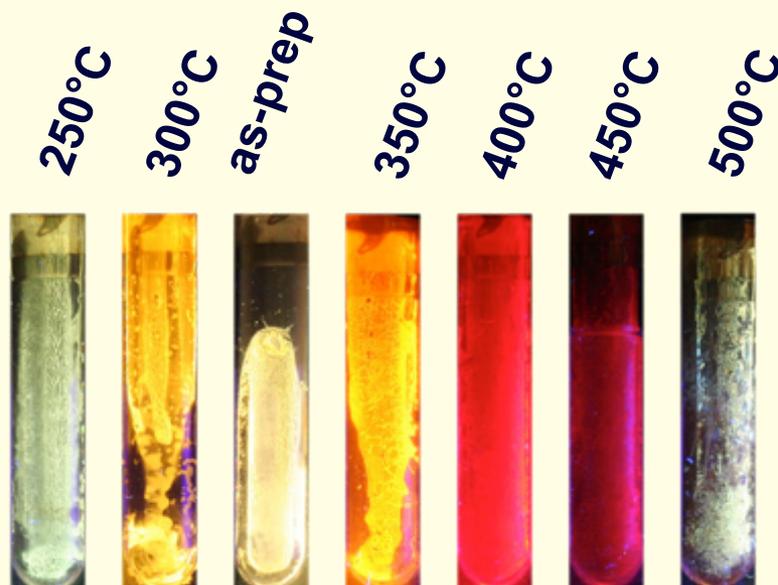


可溶性有機ケイ素高分子の新展開：酸素や水に極めて安定な 紫外・可視発光材料化と熱分解法による結晶シリコンへの物質変換



奈良先端科学技術大学院大学
物質創成科学研究科 藤木道也

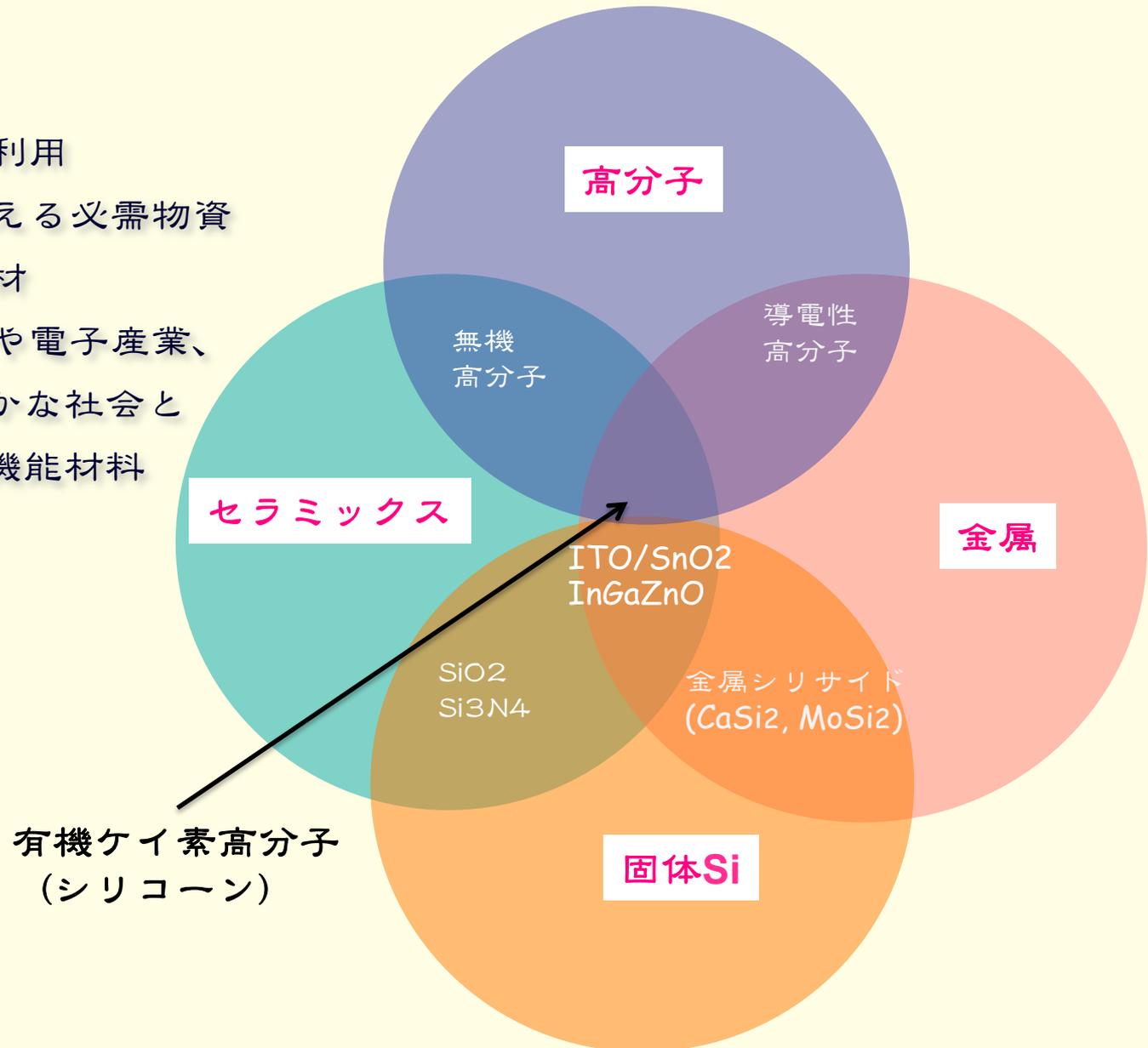
謝辞：川本義樹・加藤雅彦・藤本雄士・斉藤知来・細島進一・川部琢磨・郭起燮
(財)日本板硝子材料工学助成会 (2009年度)

Background: Importance of Polymers in Science and Industry

高分子とは？

四大基幹素材の一つ

- 幅広い分野と領域で利用
- 人類の現代生活を支える必需物資
- 産業の基幹となる資材
- 化学・繊維から医療や電子産業、航空宇宙分野まで豊かな社会と先端技術を実現する機能材料



Background: Importance of Silicon in Science and Industry

4族半導体

Si

3族-5族化合物半導体

2族-6族化合物半導体

Si以外の元素（特に第3周期以降）では

- 高い電子・正孔移動度
- 毒性
- 資源に乏しく、高価
- 安全管理に多大なコスト
- 発火性

シリコンが用いられる主な理由

1. 資源的に豊富（地殻中に27%）
2. 環境下において無害(低毒性/無毒)
3. 単結晶基板加工・薄膜化が容易
4. pn制御が容易
5. 高純度化が容易
6. 良好な透明・絶縁膜 (SiO_2)
7. 室温で適当なバンドギャップ(1.1eV)

短所

1. バルクSi結晶は非発光性（間接遷移）
2. 電子 ($\sim 600 \text{ cm}^2/\text{Vs}$)・正孔 ($\sim 100 \text{ cm}^2/\text{Vs}$)
移動度が比較的低い
3. 電子、光電変換デバイスに用途が限定
4. 電界発光デバイス/レーザー??

ref) 1.55 μm 光通信帯域で誘導Ramanレーザー
(Intel, *Nature* 2005)

緑色・赤色発光ポーラスSi

(L.T. Canham, *APL* 1990, *JAP* 1997,

Nature 1991) 引用回数 5000, 1000, 600回

Importance of Silicon both Science and Industry

アモルファスシリコン (α -Si) (結晶Siと比較して)

高分子: SiH_4 , Si_2H_6 (ガス状モノマー) の3次元架橋重合体

特徴

1. 自由な形状加工が可能
2. 大面積化が可能
3. 単純工程のため、低コスト化
4. 製造温度が比較的低温(300-350°C)

α -Si : insoluble Si-Si bonded polymers
A mixture of 1D, 2D, networks
with H-termini

短所

1. SiH_4 , Si_2H_6 など自然発火性ガスの使用
2. 非発光性欠陥準位(free radical)の形成
3. 電子・正孔移動度($\sim 10 \text{ cm}^2/\text{Vs}$)がかなり低い

多結晶Si (poly-Si)

現状：アモルファスシリコン (α -Si) のSi-Si吸収帯にエキシマーレーザー照射
Si-H結合の解裂/脱水素反応 (化学的はフラッシュ熱分解法)

安全な新しい工業化プロセスを視野に入れて

- 危険な SiH_4 , Si_2H_6 ガスの代替ソース
- 頻繁に保守を必要とする高価でエキシマーレーザの不使用
- 大気下で安定で、溶媒可溶性な固体Siソースは可能か？

1954: Pearsonら(AT&T Bell研究所)

c-Siを用いた太陽電池の発明

→1958: バンガード1号(米国海軍:人工衛星)に搭載

1975: Spear, LeComberら(Dundee大学)

不可能とされていた水素終端 α -Si:Hのpn制御に成功

1976: Carson, Wronski (RCA)

α -Si:Hを用いた太陽電池を試作

1979: Spear, LeComberら(Dundee大学)

α -Si:HをTFT試作に成功

1970: IBM Esaki-Tsu ら

半導体超格子の基本概念の提唱と実証

1970s-90s: III-V族 GaAs/InGaAs 研究が活発化
SiO₂石英系ファイバー用LD光源 (1975-1980)

1988: 古川 (九工大)
Siにおける量子サイズ効果 : E_g の増大 *nc-Si:H*

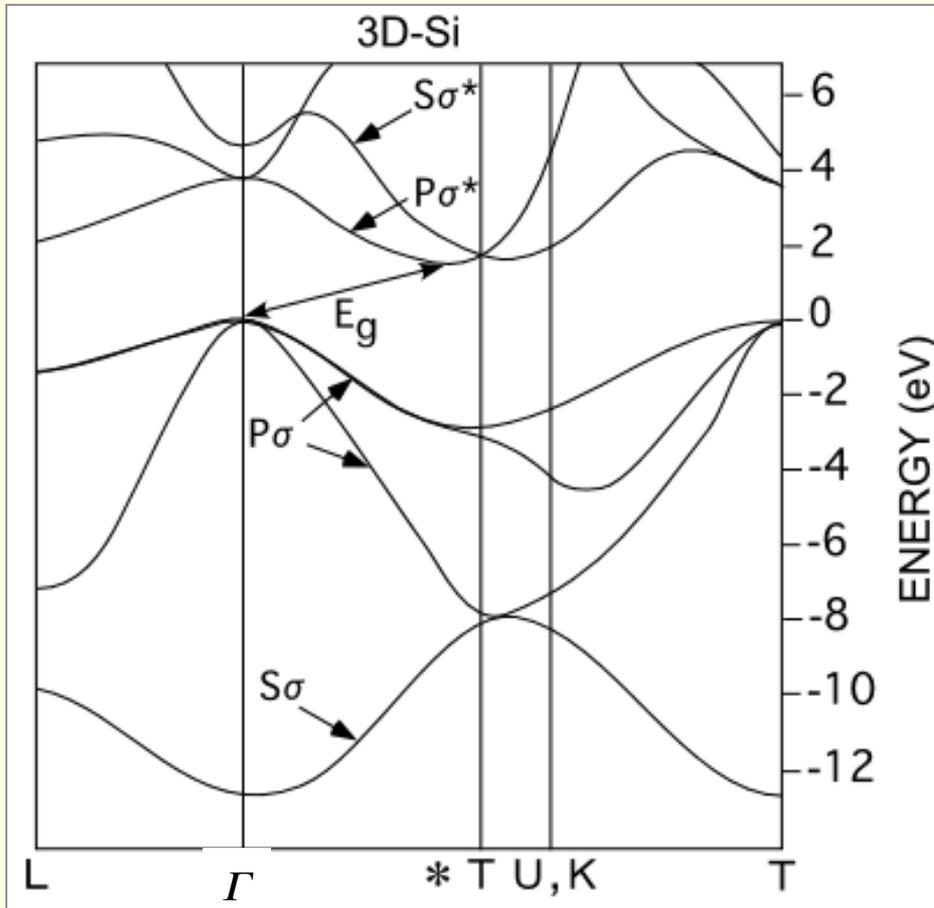
1990: 高木ら(キャノン)
SiH₄のCVD法で作製した *nc-Si:H*が量子サイズ効果により室温で赤色発光

1990: Canham (Royal Signals and Raders)
ポーラスシリコン (*por-Si*)から量子細線効果により室温で強く赤色発光

1991: Lehmann, Gösele (Duke Univ)
*por-Si*が量子細線化により E_g が *c-Si*より 0.5eV以上ブルーシフト

1980-1990: 空气中で安定で、溶媒可溶性の鎖状シリコン高分子:
Organopolysilane
量子細線効果により室温で強く紫外発光

Silicon shines on

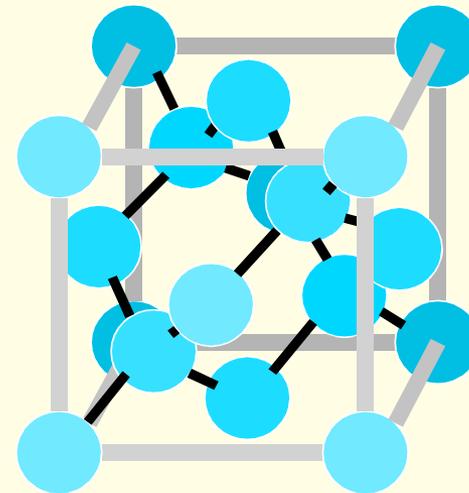


Band gap **3-D type**

Direct type **3.4 eV (365nm)** → 殆どのパイ共役高分子

Indirect type **1.1 eV (1127nm)**

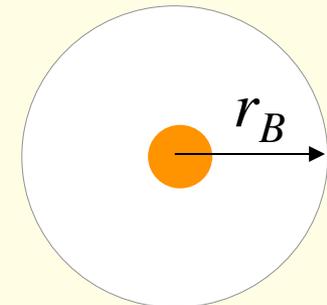
L. Brus, *J. Phys. Chem.*, 1994, 98, 3575



Heisenberg uncertainty

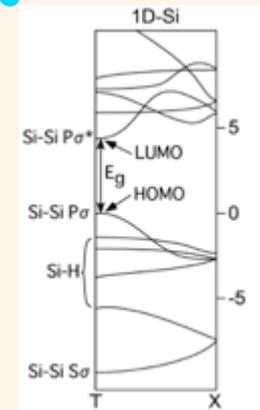
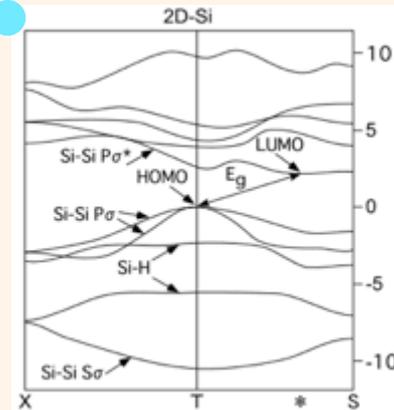
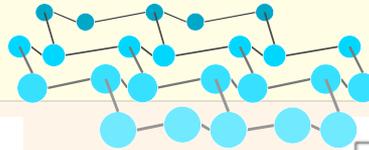
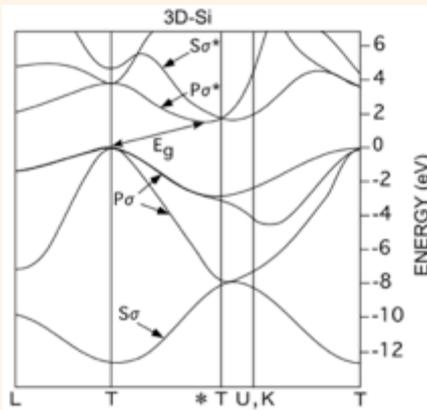
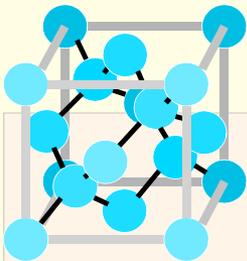
$$\Delta p \cdot \Delta x \geq (1/2)\hbar$$

$$\Delta E \cdot \Delta t \geq (1/2)\hbar$$



Bohr radius (4.9nm)
 $\propto \epsilon (\sim 11.7) \times 1/e_{\text{eff}}$

Crossovers between 0-D, 1-D, 2-D, and 3-D. How Silicon shines on



Band gap	3-D	2-D	1-D
Direct gap	3.4eV (365nm)	2.61eV (475nm)	3.89eV (319nm)
Indirect gap	1.1eV (1127nm)	2.48eV (500nm)	

L. Brus, *J. Phys. Chem.*, 1994, 98, 3575

Light-emission from

- loss of k -selection rule (Heisenberg principle)
- decrease in dimensionality (3D \rightarrow 2D, 1D, 0D)
- inversion dissymmetry by polar structure (O,F)
- inversion dissymmetry by TO phonon

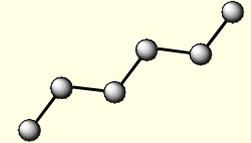
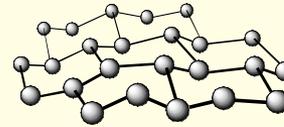
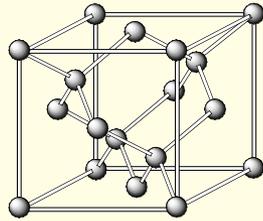
• **In Physics...**

• **In Chemistry...**

14族元素の骨格次元性とバンドギャップ (E_g)

Question: Is it possible to tailor optical band gap between 0.1 and 5.5 eV ?

Possible approaches: network Si, Si-Ge alloy, 2D-3D meso-structure, 0D (nano cluster)



(eV)

14 Group

骨格の階層性

3D	2D-3D	2D	1D-2D (発光性)	1D direct gap (発光性)	0D
indirect gap (非発光性)					

元素の階層性

C	5.5		-		ca. 8
Si	1.1	1.8-2.3	2.3		ca. 3-4
Ge	0.7	1.35	-		ca. 3-4
Sn	0.1 (direct gap)		-		ca. 3
Pb	(0)		-		-

In Physics

- a-Si:H_x by plasma CVD of SiH₄ and Si₂H₆

D. J. Wolford et al, *Appl. Phys. Lett.*, **1983**, 42, 369

- Porous Si by electrochemical etching

L. T. Canham, *Appl. Phys. Lett.*, **1990**, 57, 1046

- nc-Si by sputtering Si in H₂ gas

S. Furukawa, *Phys. Rev. B*, **1988**, 38, 5726

- nc-Si into SiO₂ by ion implantation

Brongersma et al, *Appl. Phys. Lett.*, **2000**, 76, 351

- nc-Si by plasma CVD of SiH₄

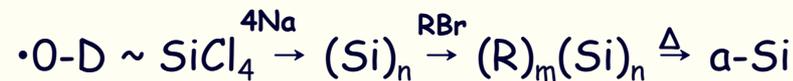
Y. Kanemitsu, *Phys. Rev. B*, **1994**, 49, 16845

H. Takagi et al, *Appl. Phys. Lett.*, **1990**, 56, 2379

- a-Si/SiO₂ superlattice

D. J. Lockwood et al. *Nature*, **1995**, 378, 258

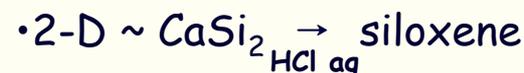
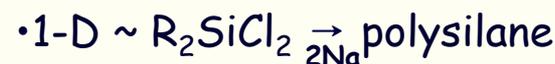
In Chemistry



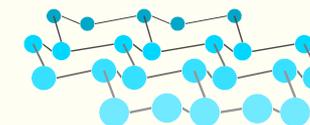
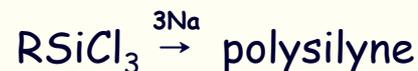
A. Watanabe, *J. Organomet. Chem.*, **2003**, 685, 122.



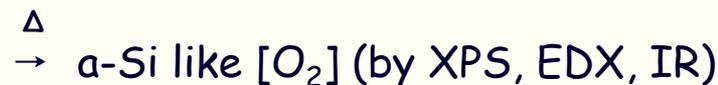
K. Furukawa et al, *Jpn. J. Appl. Phys.*, **1994**, 33, L413



M. Stützmänn et al, *Phys. Rev. B*, **1993**, 47, 4806.



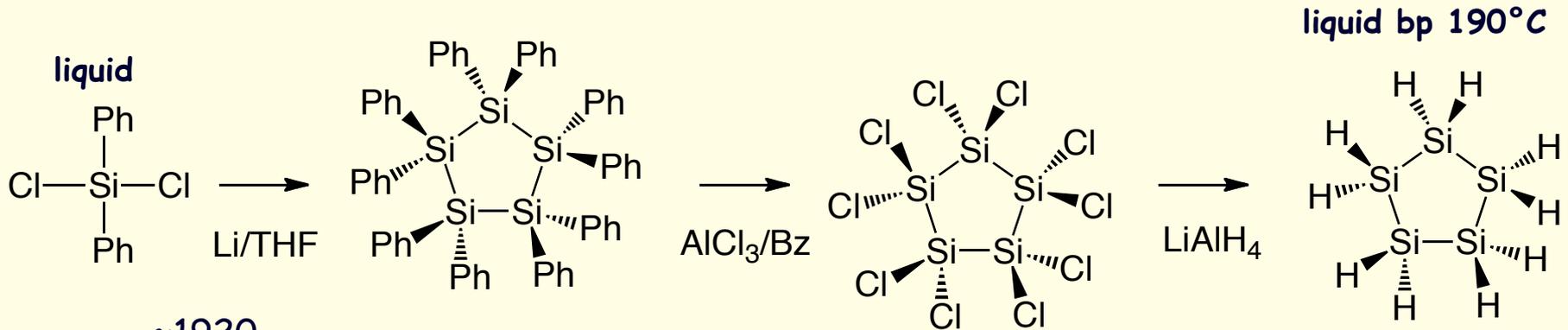
K. Furukawa et al, *Macromolecules*, **1990**, 23, 3423.



M. Fujiki et al, *Chem. Mater.*, **2009**, 21, 2459.

Solution Processable Poly-Si for TFT

T. Shimoda *et al.* (Seiko-Epson & JSR groups), *Nature*, 2006, 440, 783-786



~1920
Kipping 反应

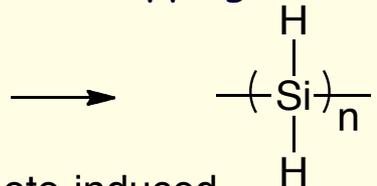


photo-induced ring opening reaction upon 405 nm irradiation

in CPS

in GloveBox

Si-H結合: C-H結合と違ってO₂やH₂Oに敏感: 変質・分解

pyrolysis
1. 300°C, 10min
2. a-Si 300-400°C
3. 540°C 2h

in GloveBox

1975 Hengge CPS

a-Si:H

308nm XeCl laser

poly-Si

spin coat $\mu \sim 108 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

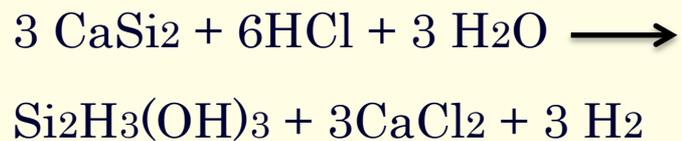
ink jet $\mu \sim 6.5 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$

cf.

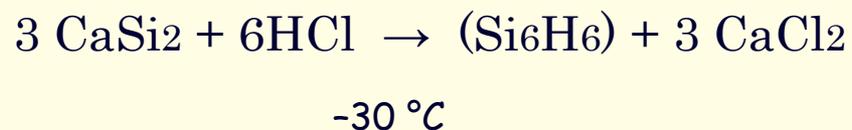
>> μ (高分子半導体)

> μ (分子性半導体)

H. Okamoto, Y. Sugiyama, H. Nakano (Toyota R&D). *Chem. Eur. J.*, **2011**, *17*, 9864-9887.



Shaken with surfactants (SDS) for 10 days



$(\text{Si}_6\text{H}_6)_n$ treated with n-decylamine

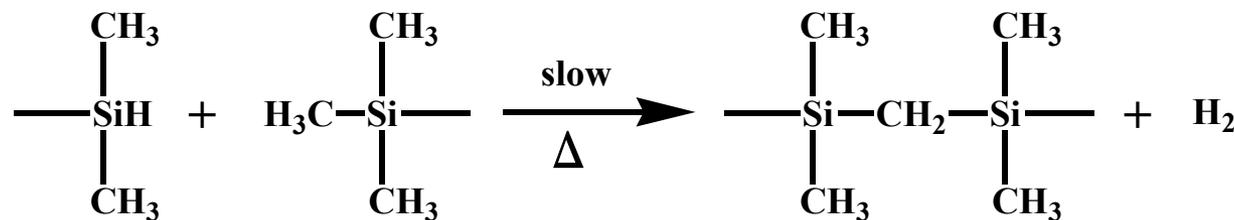
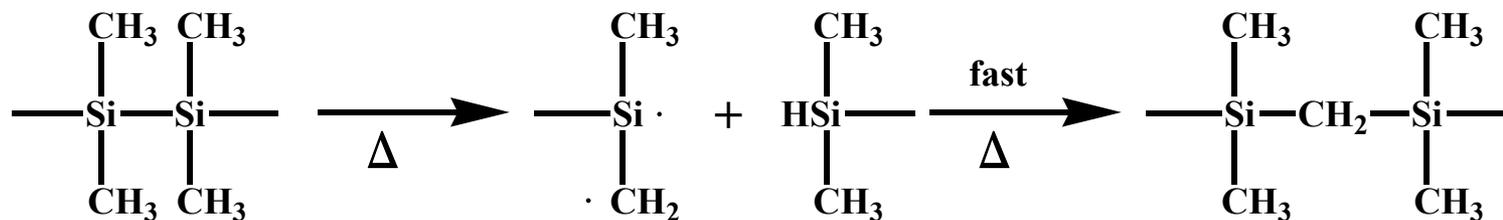
Reaction mechanism of polycarbosilane : Precursor for ceramics

矢島プロセス $R = \text{Me} \rightarrow \beta\text{-SiC}$

C. A. Burkhard, *J. Am. Chem. Soc.*, **1945**, 67, 2173-2174.

Yajima, S.; Hasegawa, Y.; Hayashi, J.; Okamura, K. *J. Mater. Sci.* **1978**, 13, 2569-2576.

Interrante, L. V. et al. *Chem. Mater.* **1999**, 11, 2038-2048.



$\beta\text{-SiC}$

H. Ichikawa, *Development of Organosilicon Polymers*, CMC, **1989**, 187-196.

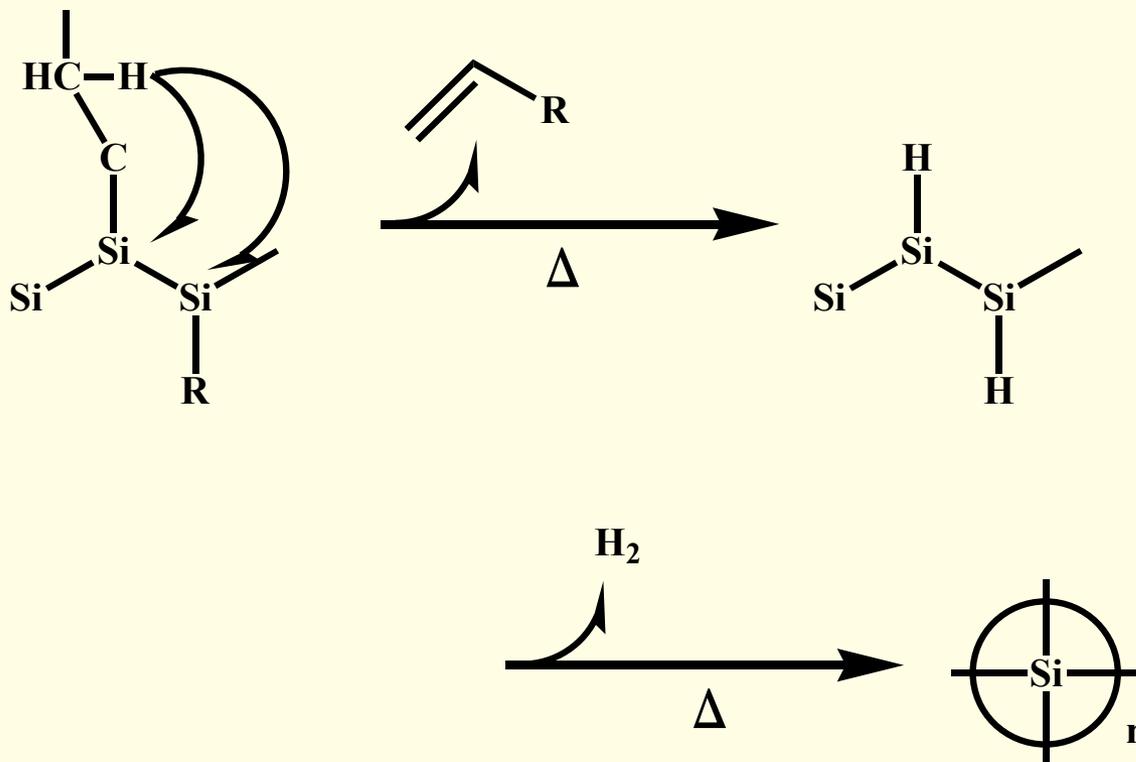
Hypothesis: A possible production of (Si)_n from soluble Si-containing polymer due to β-H elimination reaction by flash pyrolysis in vacuo

矢島プロセス R = Me → β-SiC

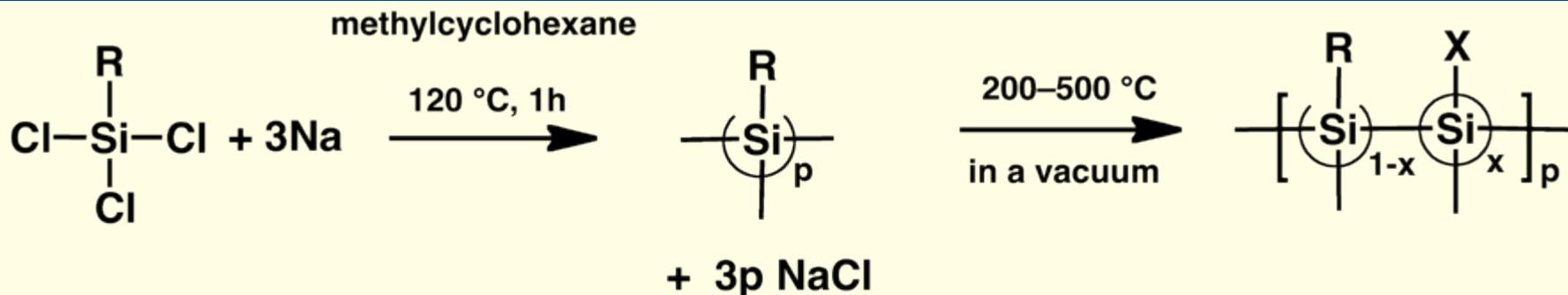
素朴な疑問そして作業仮説

R => Et → β-SiC (?)

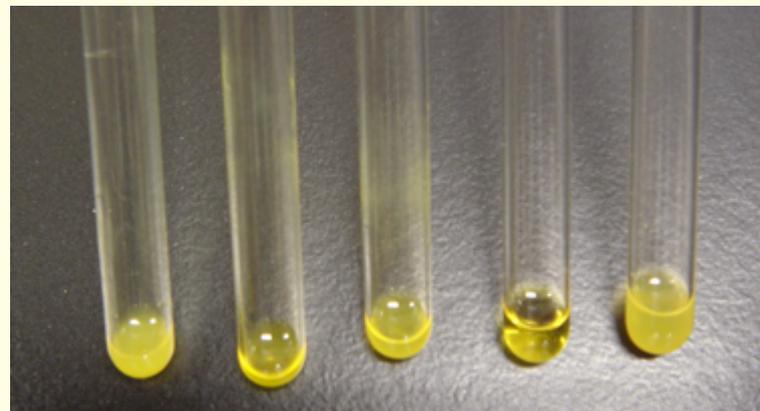
β-水素を有するRが自己還元剤



One-pot synthesis of soluble polysilyne : (RSi)_n

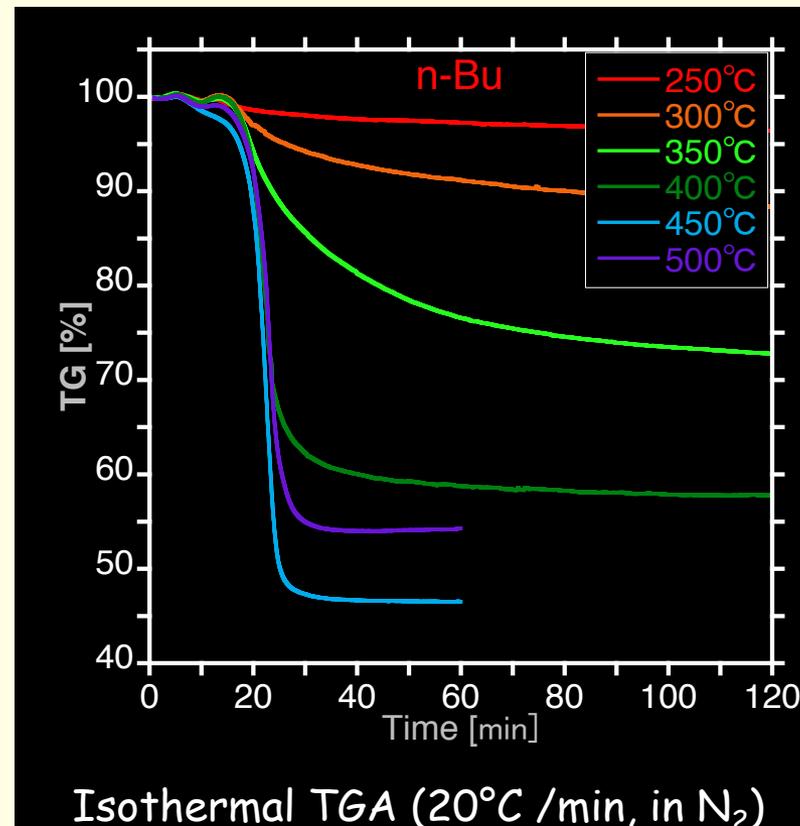
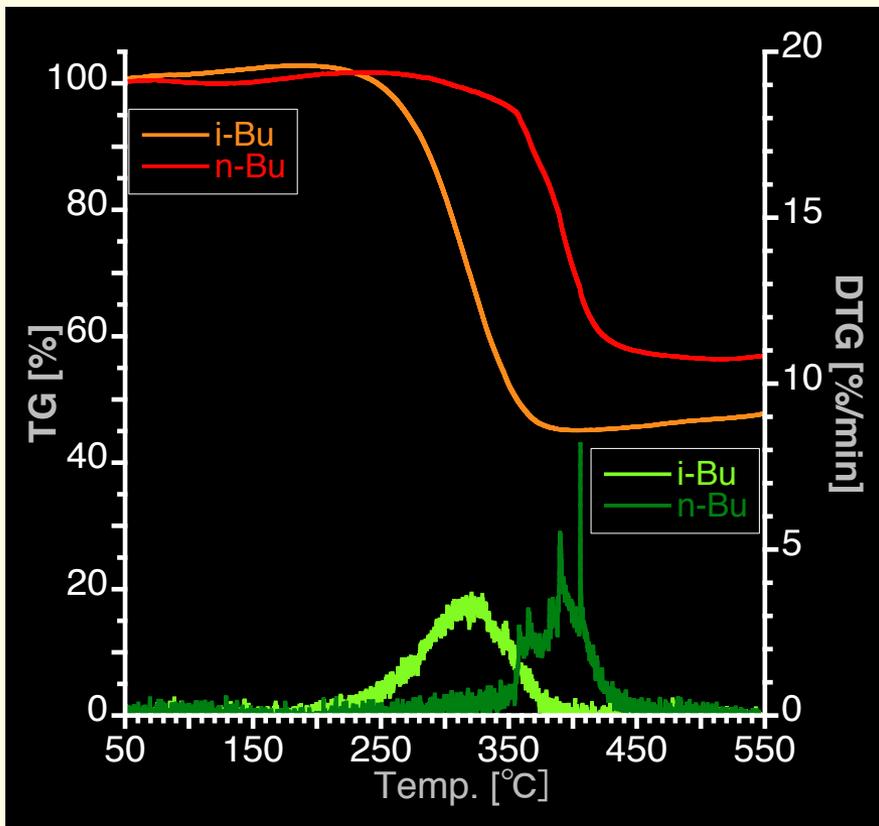


R = CH₃, C₂H₅, n-C₃H₇, n-C₄H₉, n-C₅H₁₁, n-C₆H₁₃,
n-C₈H₁₇, n-C₁₀H₂₁, n-C₁₂H₂₅, i-C₄H₉, CF₃(CH₂)₂



K. Furukawa et al, *Macromolecules*, **1990**, 23, 3423.

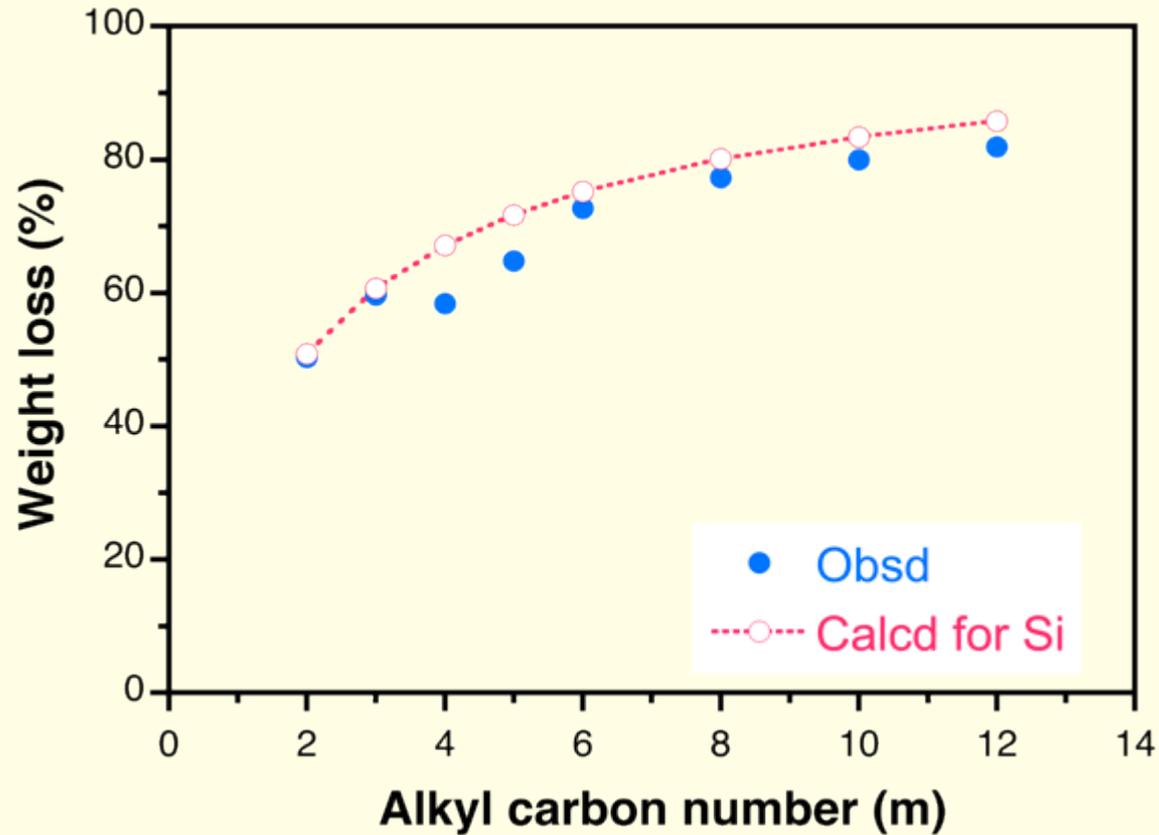
Pyrolytic properties of $(n\text{-BuSi})_n$ in N_2



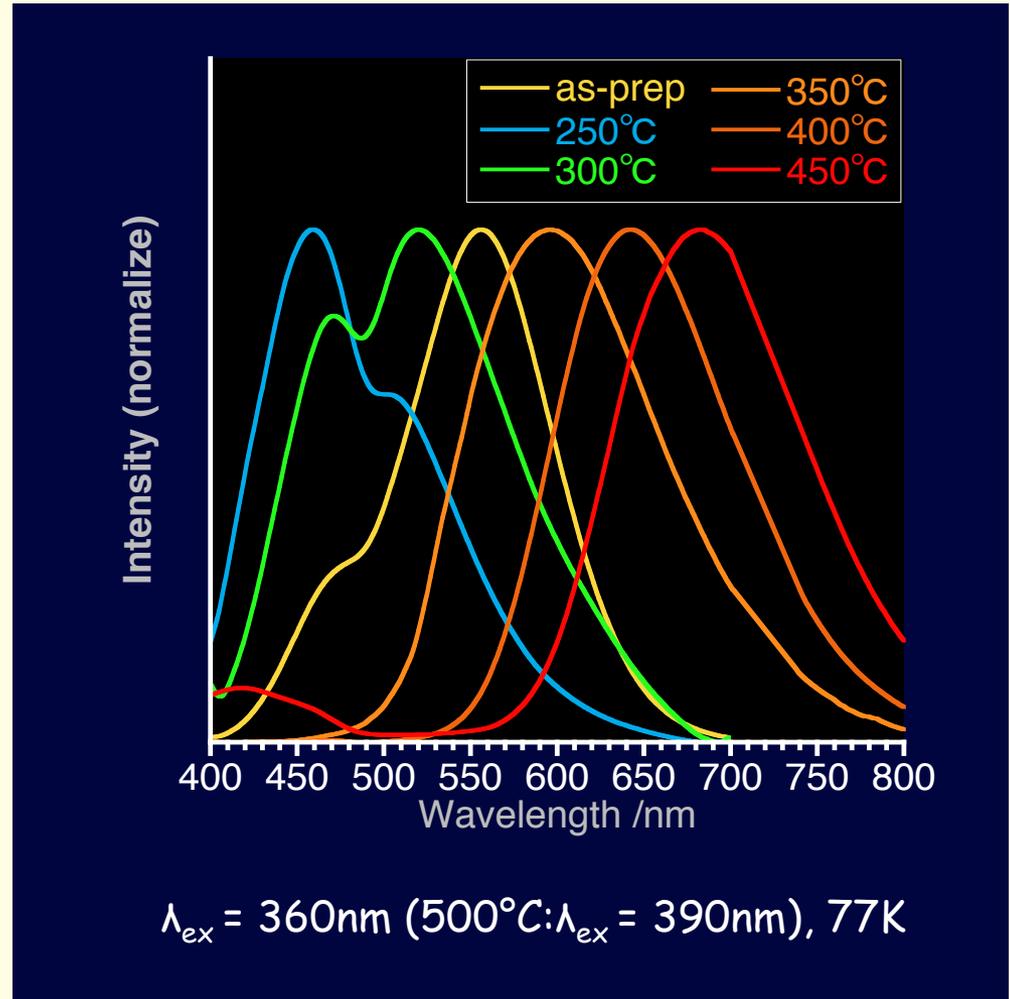
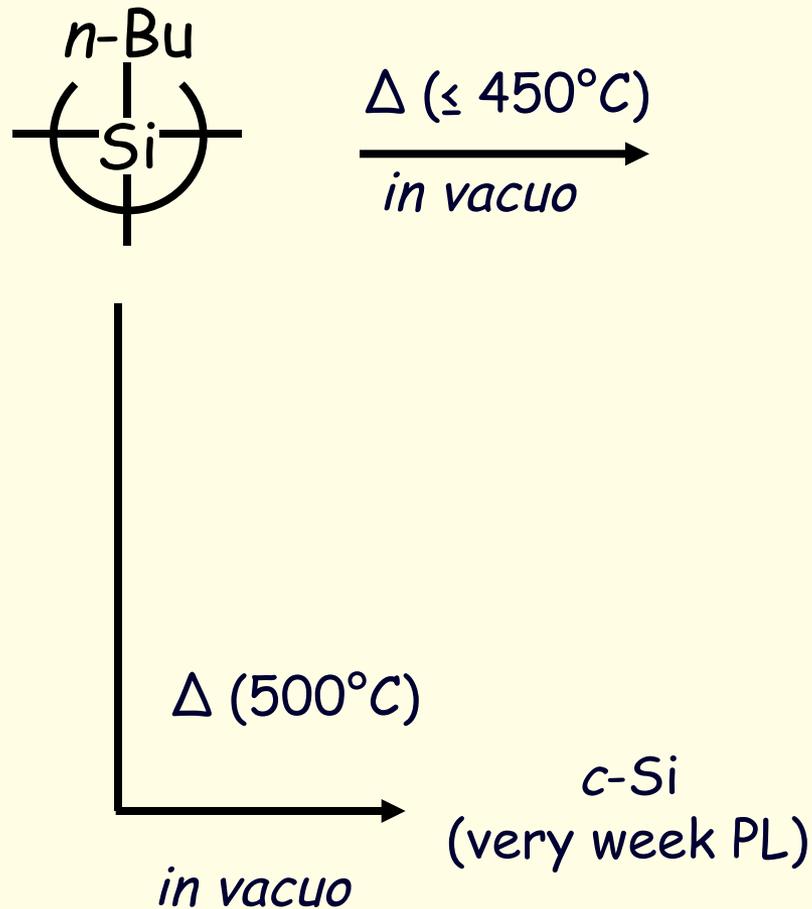
SNP	Weight loss (%)	
	obs	calc (R/RSi)
i-Bu	56.9	67.0
n-Bu	43.3	67.0



Pyrolytic properties of $(n-C_nH_{2n+1}Si)_n$ in N_2

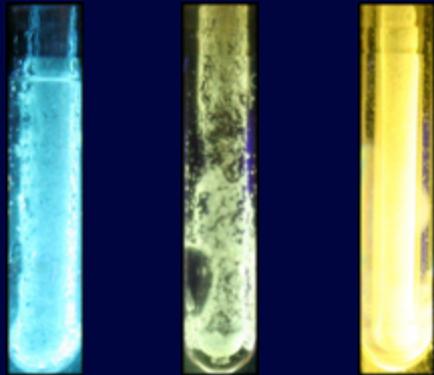
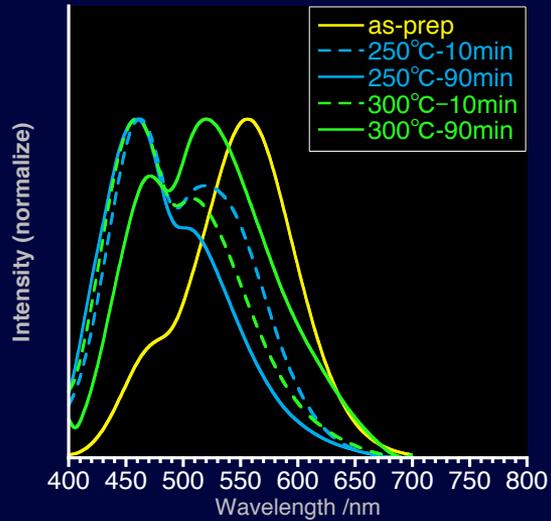


Broad change in PL spectra of pyrolytic n -Bu-polysilyne : $(n\text{-BuSi})_n$



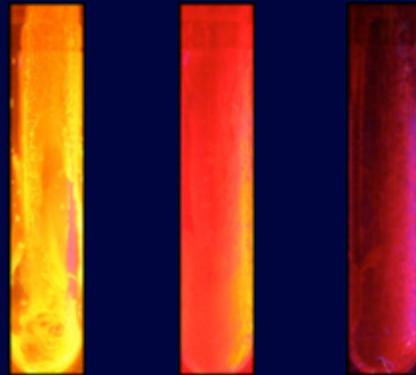
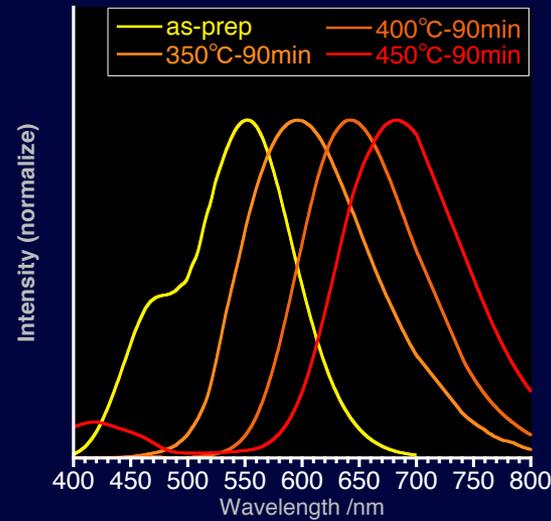
Photolumuminescence from pyrolyzed $(n\text{-BuSi})_n$ (77K, $0.5\text{mW}/\text{cm}^2$)

Ex= 360nm



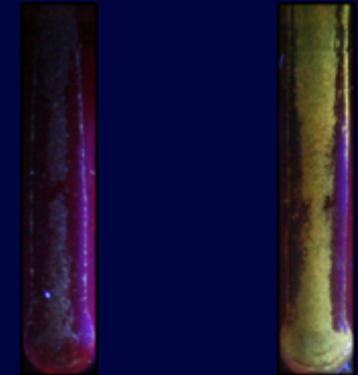
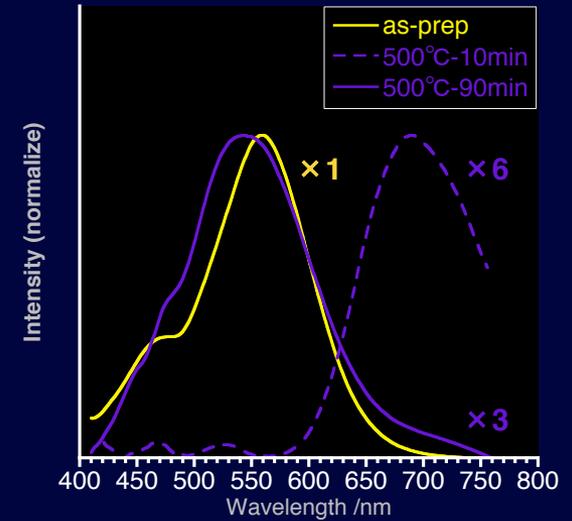
250°C 300°C as-prep

Ex= 360nm



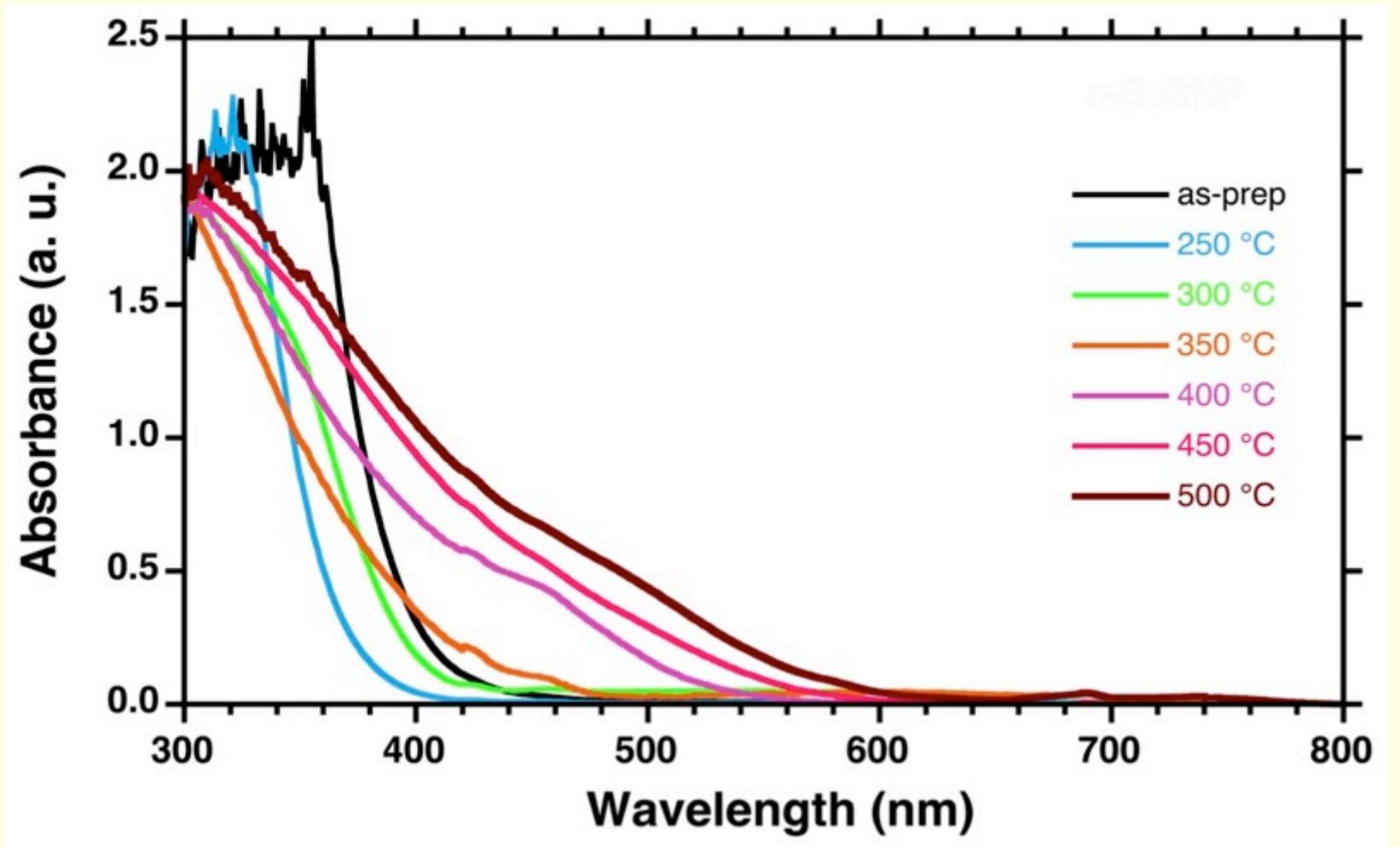
350°C 400°C 450°C

Ex= 390nm



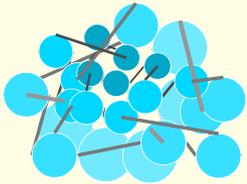
500°C (10min) 500°C

Absorption spectra of pyrolyzed (n -BuSi) $_n$ films (r.t.)



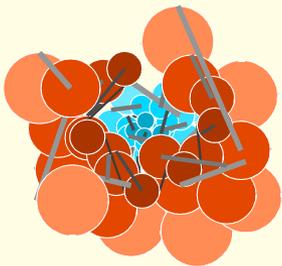
500 °C (10min) 500 °C

•Nanocrystal



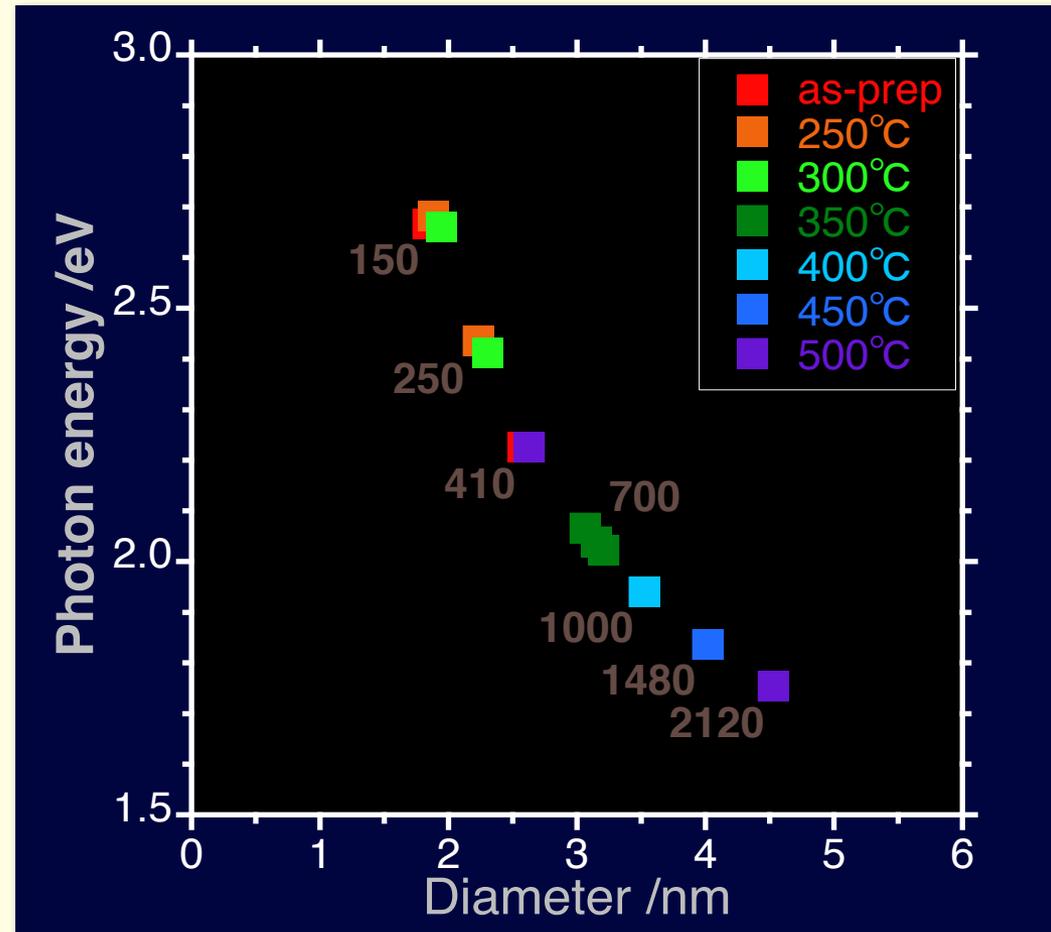
$$E_g \sim E_g^{\text{bulk}} + 29.6 \text{ (eVÅ)}/D$$

$$E_g^{\text{bulk}} = 1.1 \text{ eV}$$
$$D = \text{Si diameter}$$



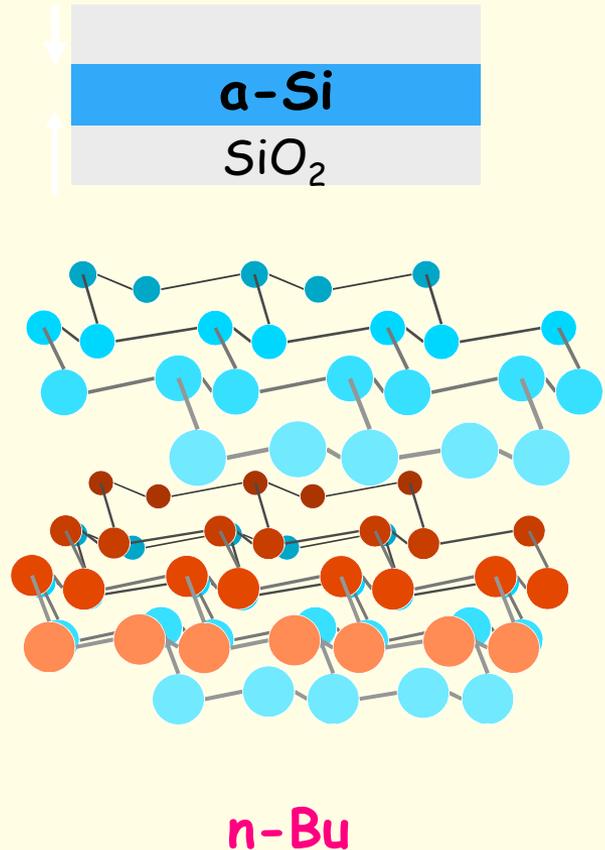
L. E. Ramos *et al.*
Phys. Stat. Sol. (b), **242** (2005) 3053

(n-BuSi)n



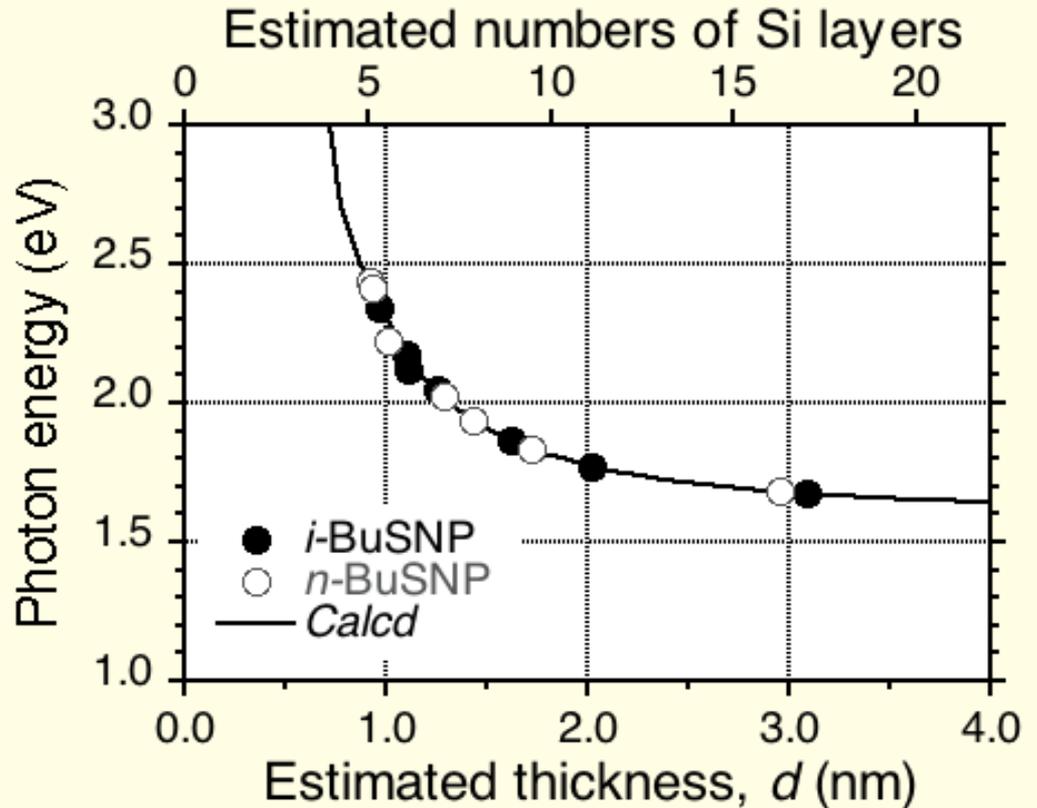
The origin of red-shift at 350-450°C

• Superlattice

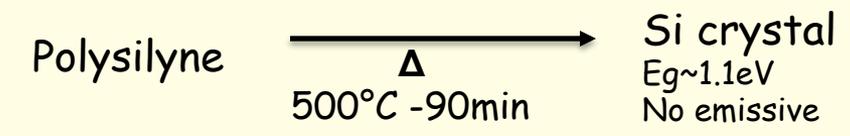
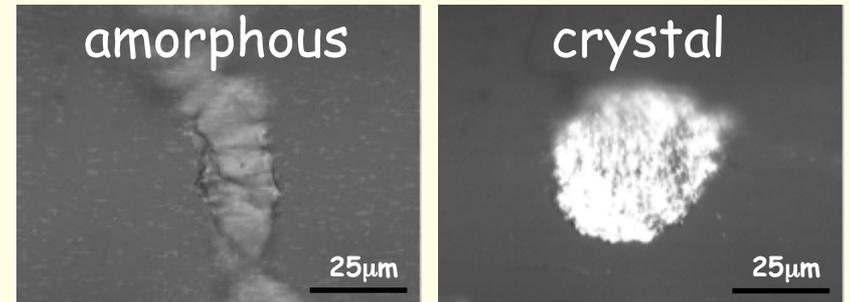
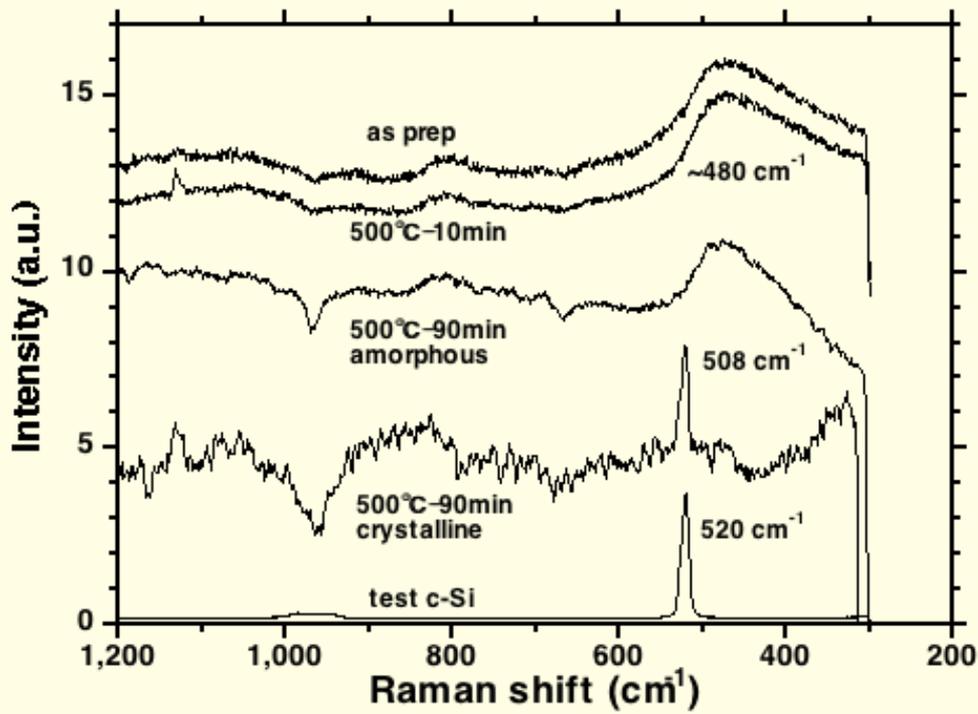


$$E_{\text{PL}} (\text{eV}) = 1.6 + 0.7/d_{\text{Si}}^2$$

d_{Si} = Si film thickness



The origin of marked decrease in deep red emission band at 500°C



PL intensity ($\sim 850\text{nm}$)
 markedly decreased

Exposed to air

Highly emissive Si-based particle

Dispersed in various solvents

Functional Groups	Region / cm^{-1}
Si-Si	~ 480 (a-Si)
Si-H	985-800

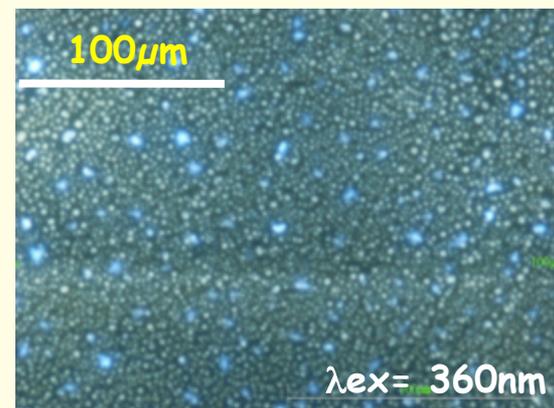
Intense blue emission particles dispersed in various solvents



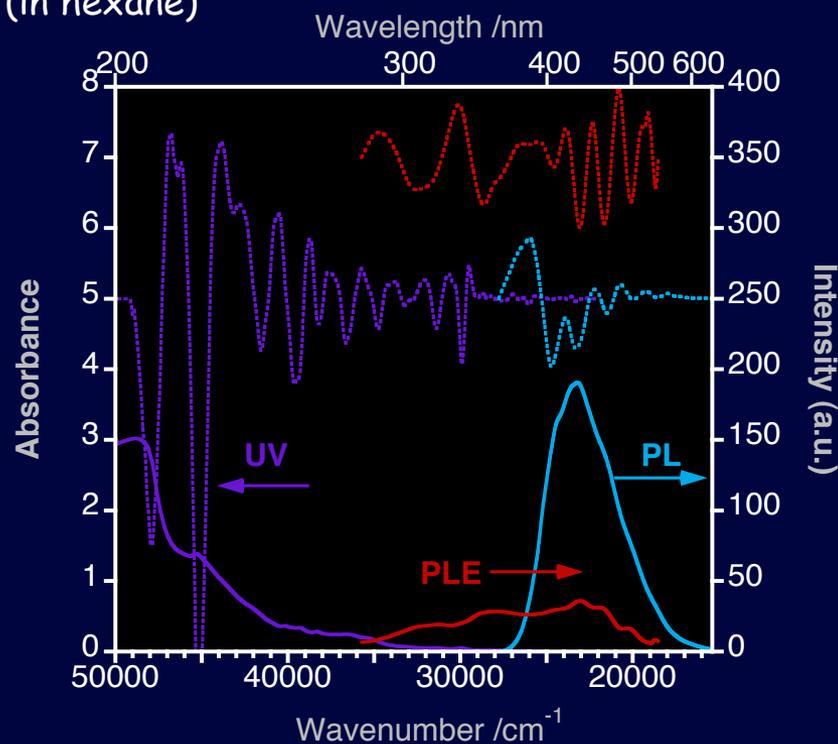
λ_{ex} 365nm,
1.0mW/cm², r.t.

Φ_F = 23% (DMF)
21% (THF)
14% (Hexane)
1% (Water)
 τ = 4.8 nsec, > 10nsec (THF)

cast on quartz



(in hexane)



Functional Groups

Region /cm⁻¹

Si-Si

~480 (this work)

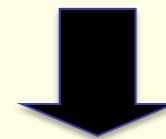
Si-O-Si

1090-1010 (ref)

cf Si-Si (c-Si)
(a-Si)

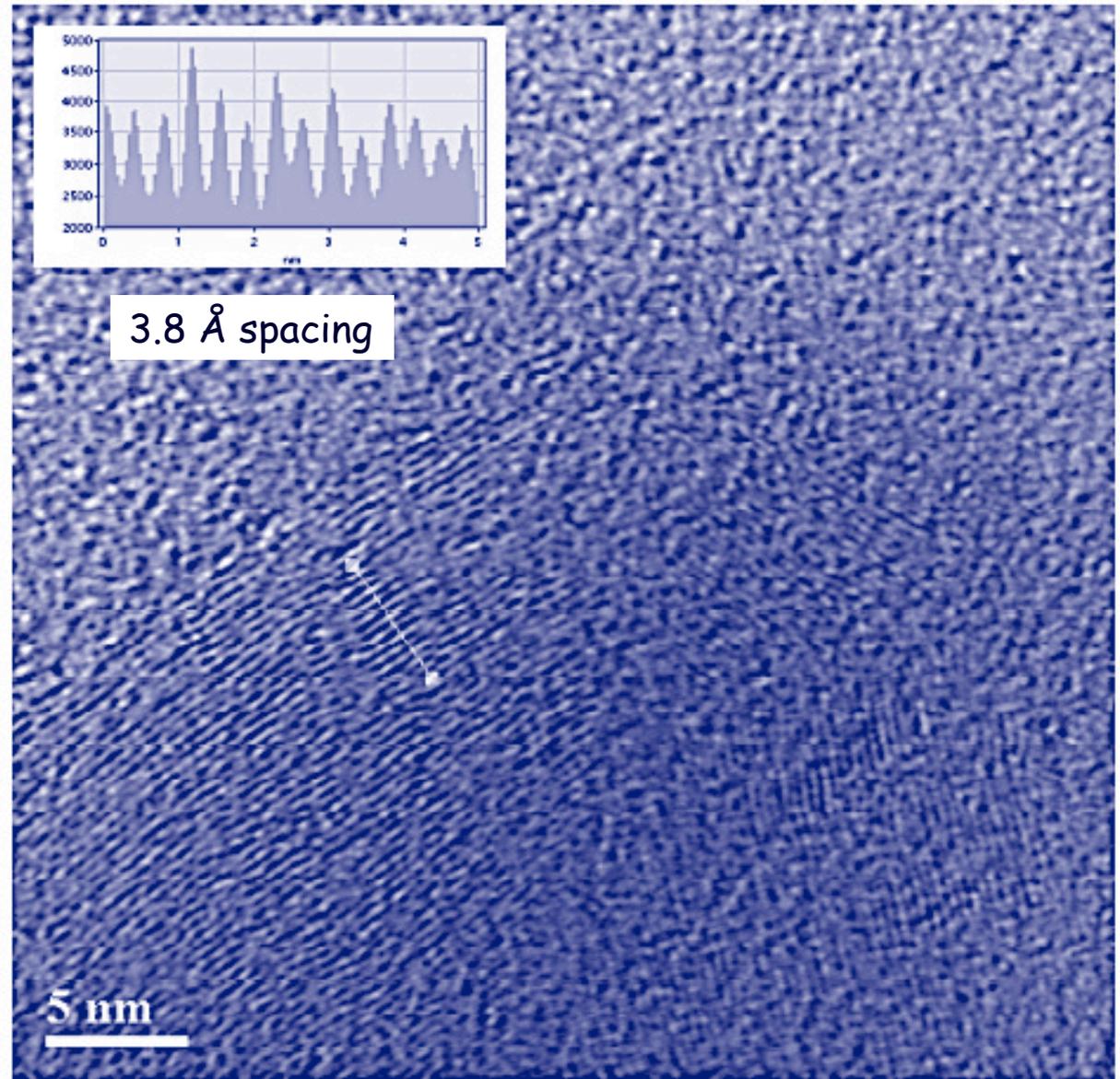
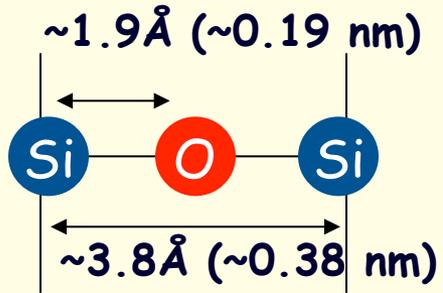
508cm⁻¹ (this work)
~ 460cm⁻¹ (this work)

1500±150cm⁻¹



electron-phonon
Si-Si and Si-O-Si coupling ?

TEM and EDX



alike nm-size Baumkuchen ?

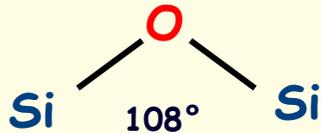
Nanometer-size Baumkuchen of pyrolyzed $(n\text{-BuSi})_n$ exposed to air

Highly elongated by 10-23% with highly opened angle ($\sim 180^\circ$) Si:O = 1 : 3 (EDX)



$$R(\text{SiOSi}): 3.24\text{-}3.64 \text{ \AA} \sim (1.62\text{-}1.82 \text{ \AA}) \times 2 \text{ \AA}$$

$$R(\text{SiOSi}) : 4 \text{ \AA} \sim 2 \times 2 \text{ \AA} \text{ by forcing polysiloxane}$$



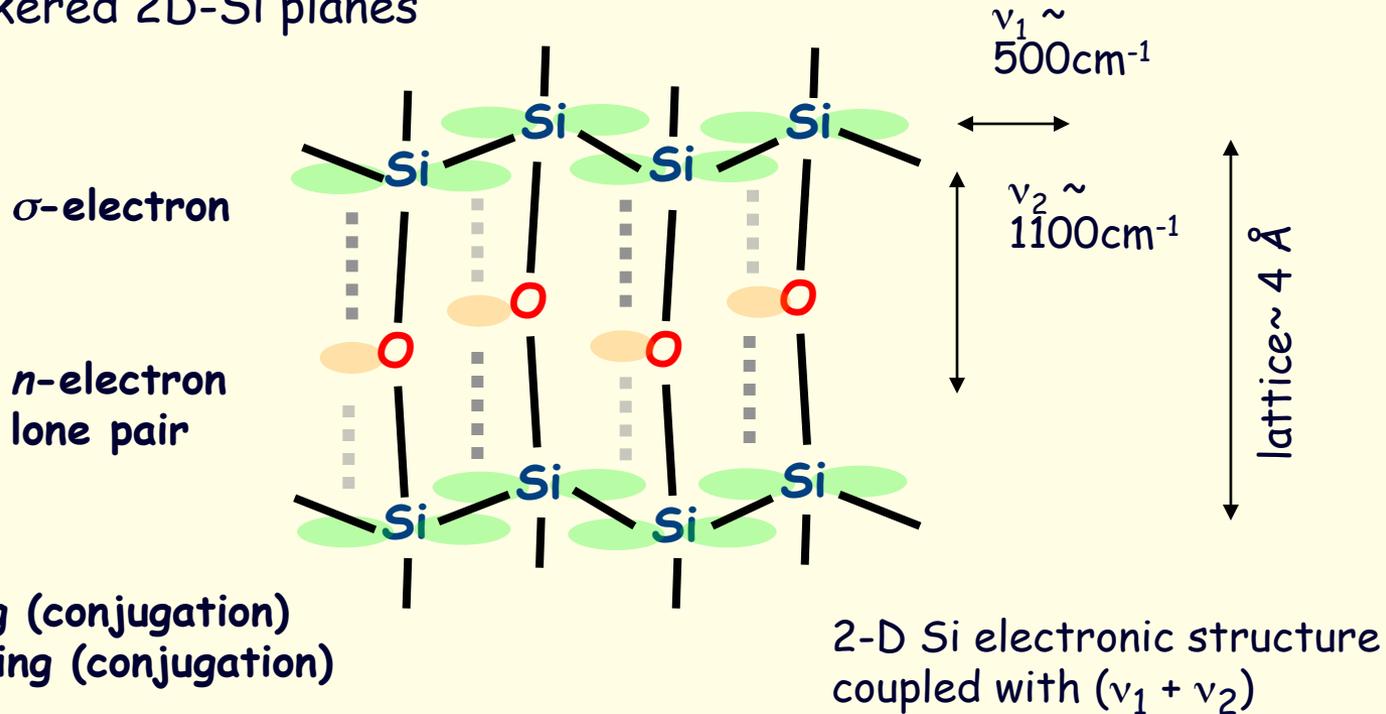
$$R(\text{SiOSi}): 2.6 \text{ \AA} = \sin(108^\circ/2) \times 1.6 \text{ \AA} \times 2$$

Ref)

1. J. S. Nicoll et al. *Phys. Chem. Min.*, **20**, 617-624 (1994)
2. E. M. Lupton et al., *NIC Symp.*, **32**, 57-64 (2006)

Schematic explanation by chemists Baumkuchen Silicon (pyrolized $(n\text{-BuSi})_n$ exposed to air)

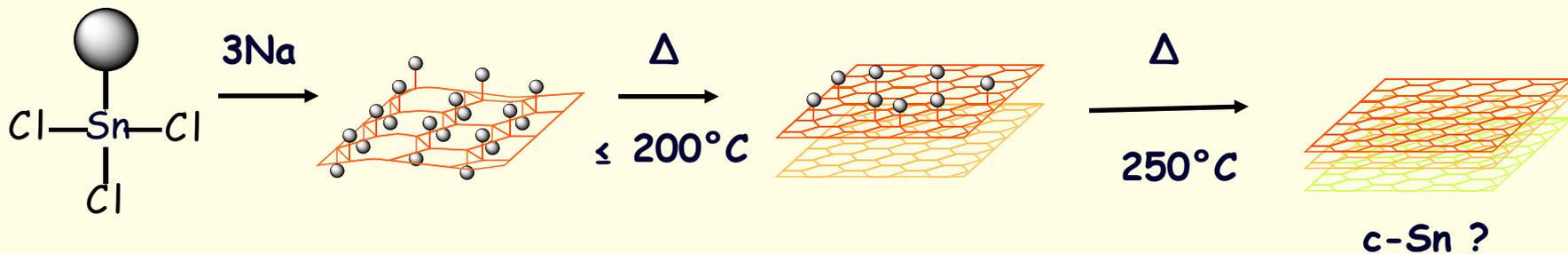
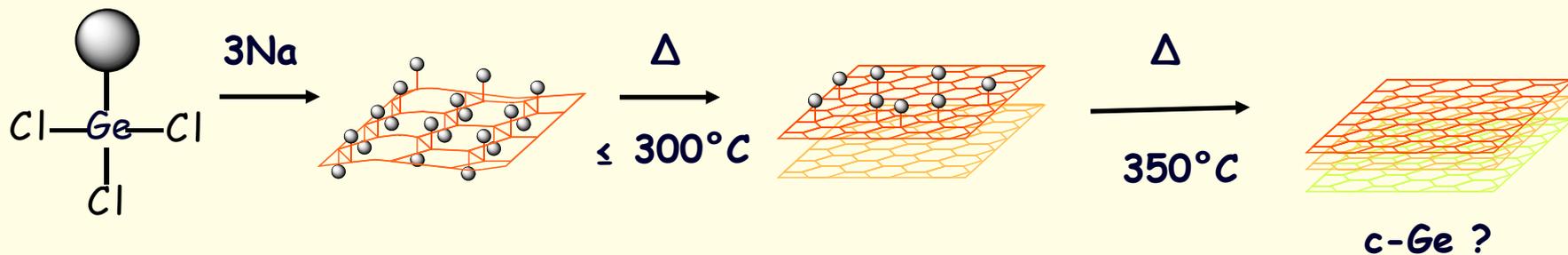
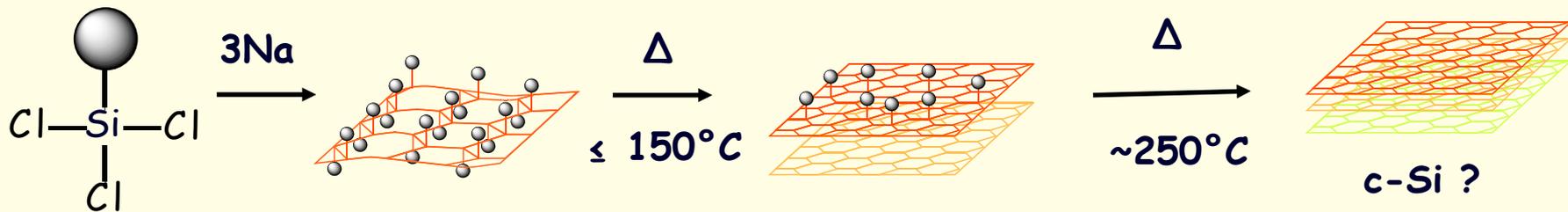
Puckered 2D-Si planes



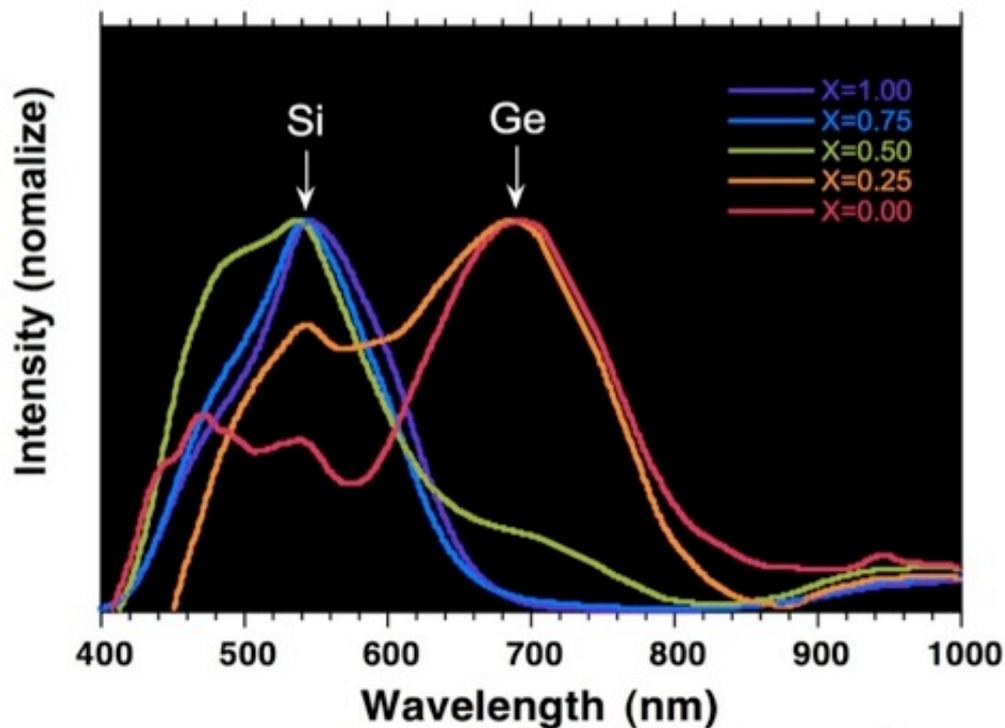
To design light-emission silicon materials

- loss of k -selection rule (decrease in size, introduction of disorder)
- dimensionality decrease (3D \rightarrow 2.5D, 2D)
- introduction of dissymmetry by polar oxygen
- introduction of dissymmetry by electron-phonon coupling (Si-Si / Si-O-Si)

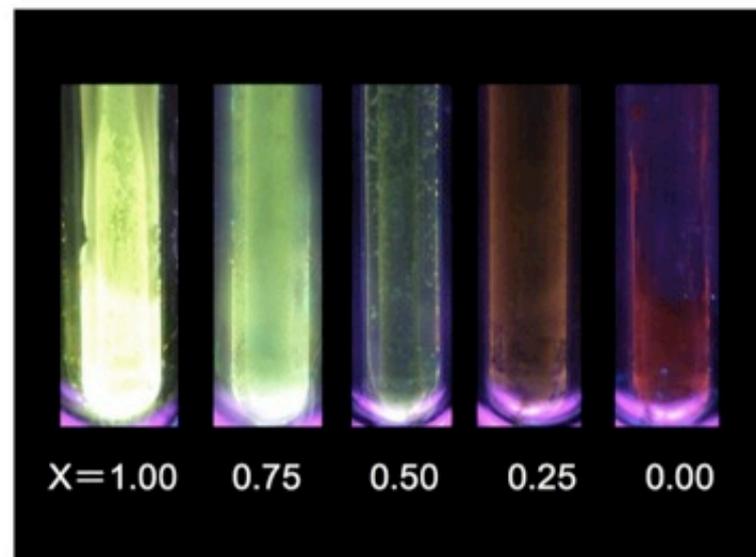
Band-gap engineering from organo (Si/Ge/Sn) polymers



PL spectra of [(n-BuSi)_x-*block*-(n-BuGe)_{1-x}]_n



PL spectra $\lambda_{\text{ex}}=360\text{nm}$, 77K



PL $\lambda_{\text{ex}}=365\text{nm}$, 77K

✗ 発光波長ピークのレッドシフト

○ Si由来の発光強度(540nm)が減少し、
Ge由来の発光強度(690nm)が増加

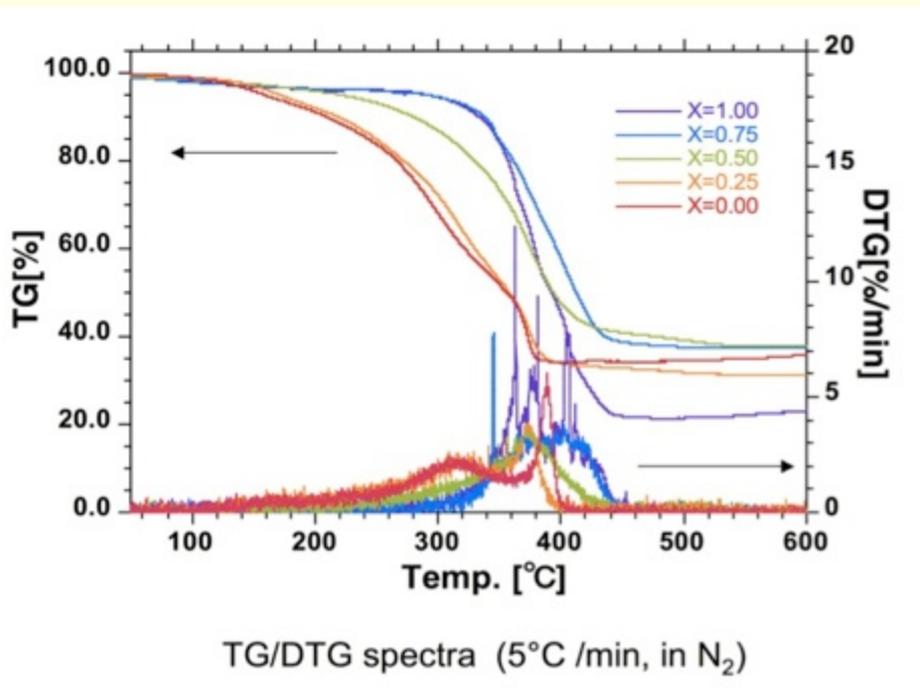


Si、Ge原子が骨格中で不均一に分布し、
同種の原子が互いに集まったドメイン構造
を形成

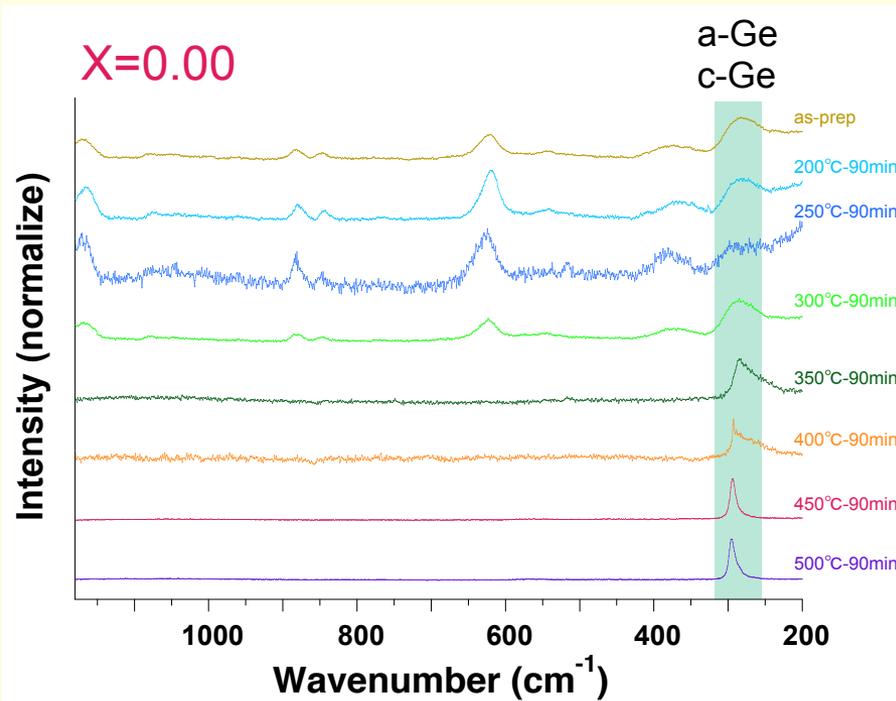
(HRTEM,EELSの結果と一致)

Thermogravimetric (TG), Differential TG (DTG), Raman analyses

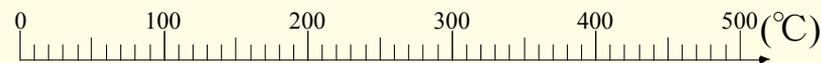
TG/DTG diagrams (5°C /min, in N₂)



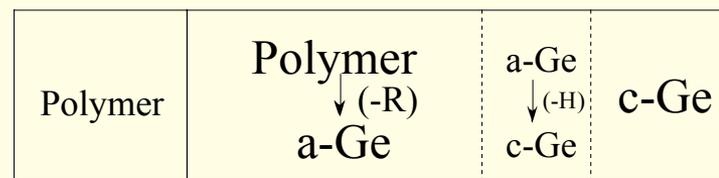
Raman spectra



X=0.00

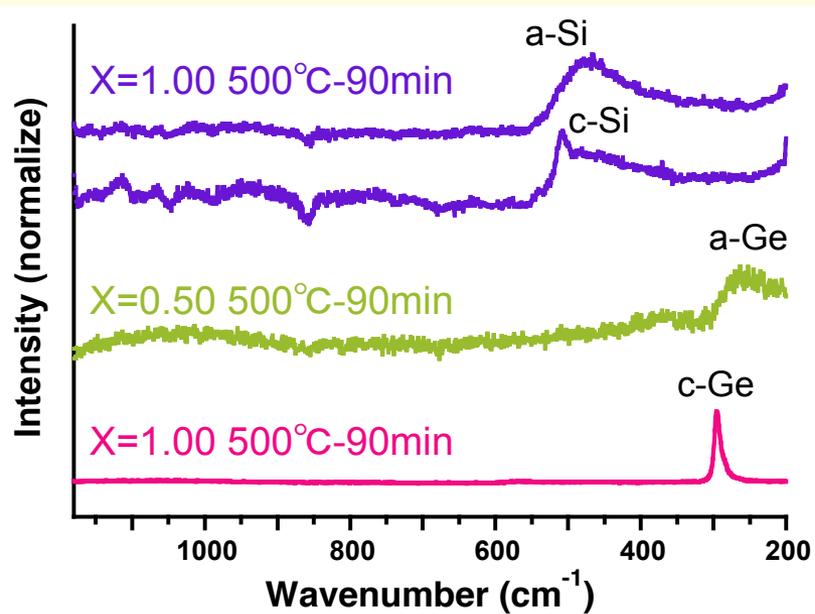


Polymer	熱分解開始-終了温度 (°C)
X=1.00	336-439
0.50	257-538
0.00	122-378

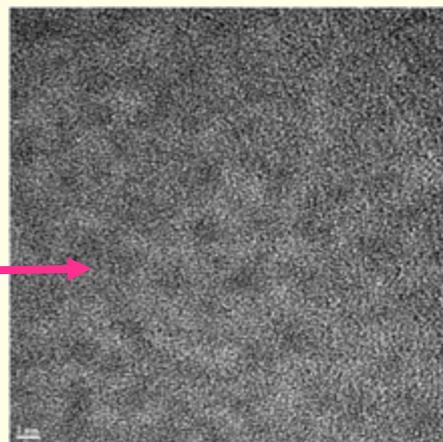


Raman, HR-TEM, EELS of pyrolytic $[(n\text{-BuSi})_x\text{-}i\text{block}\text{-(n-BuGe)}_{1-x}]_n$ film

Raman spectra

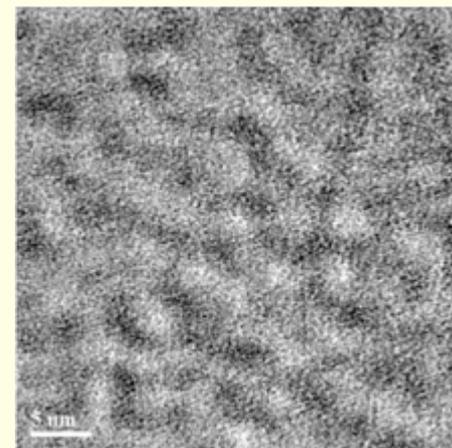


TEM
X=0.50, 500°C-90min

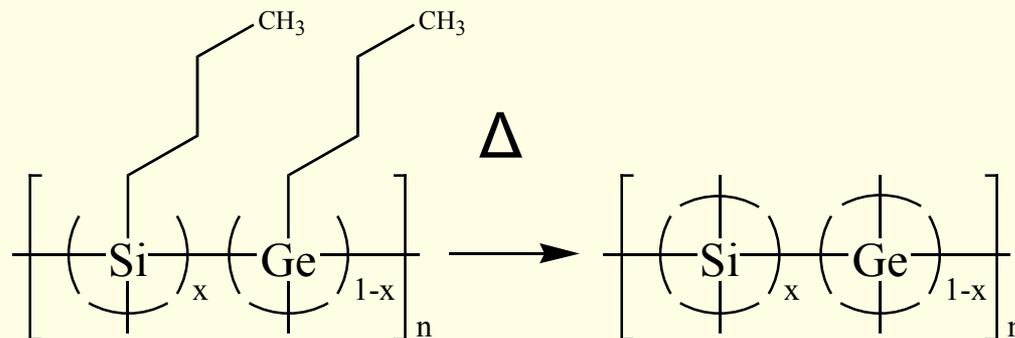


Amorphous

EELS
X=0.50, 500°C-90min



Ge map



アルキルポリシリルン

Δ (200–500° C)

n-Bu
i-Bu



熱分解物

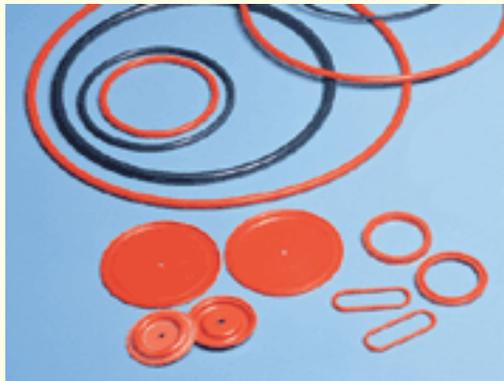


欠点

$\Phi < 1\%$ (at RT)
耐酸化性 → 低
耐水性 → 低い
熱分解物も同様

元素周期表

13	14	15	16	17	18
B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar



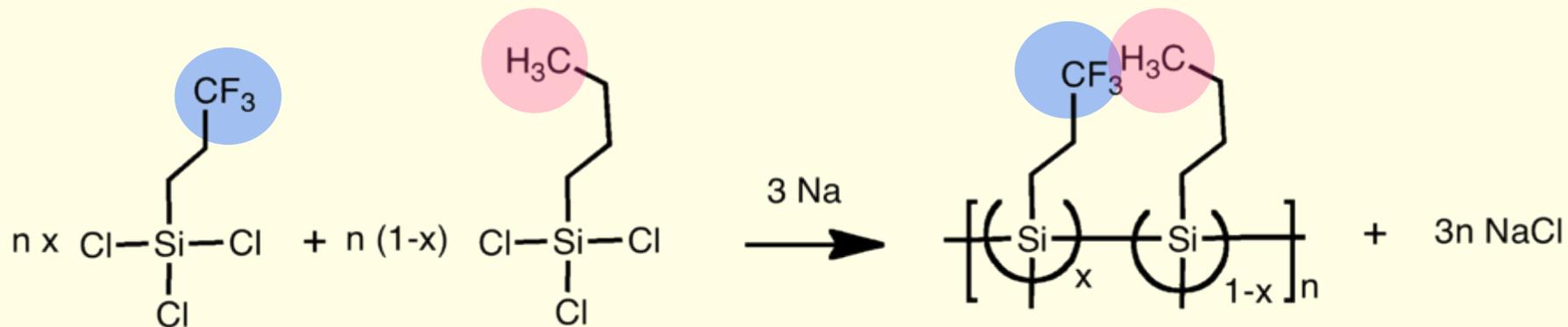
高耐久・高効率可視発光材料の設計指針

フッ化アルキル基の導入



- ・撥水性, 撥油性 → 安定性
- ・電子吸引性 → 耐酸化性
- ・2DSi電子構造の制御
- ・発光波長の制御
- ・アルキルポリシリンとの共重合

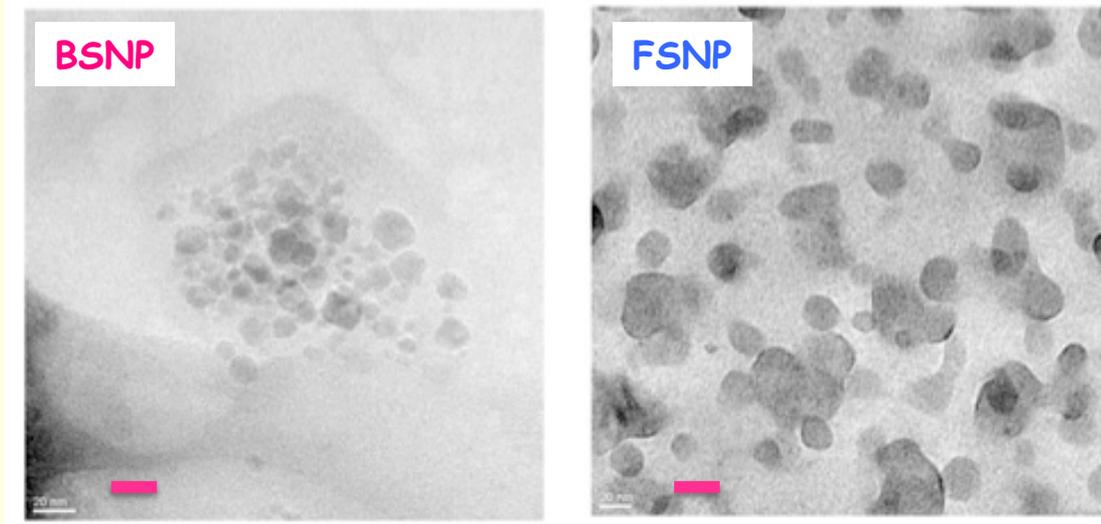
Structure and some properties



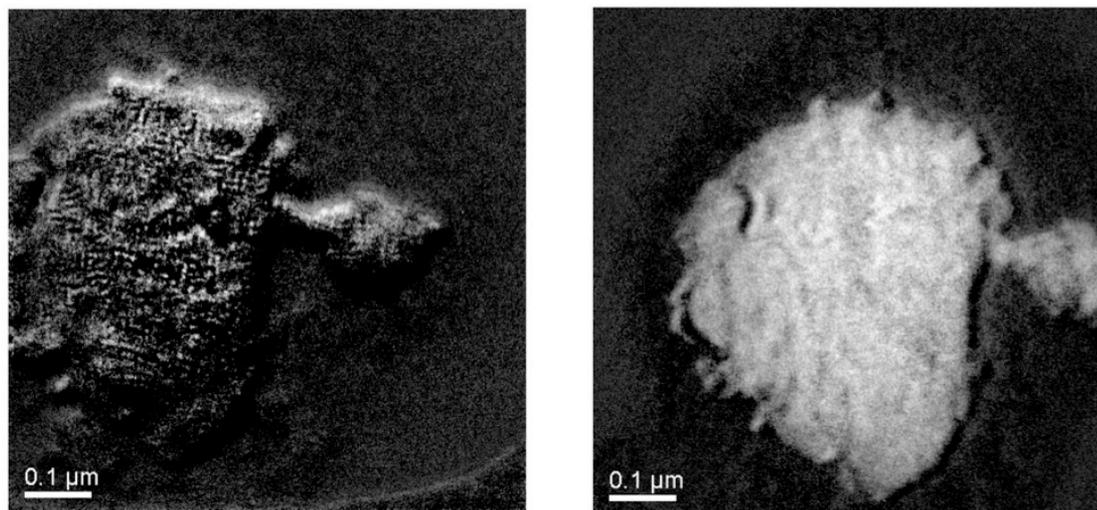
Nominal mole fraction
 $x = 1.00, 0.75, 0.50, 0.25, 0.00$

Polymer Chemistry, **3**, 3256-3265 (2012)

HR-TEM and EELS images and nano-structures

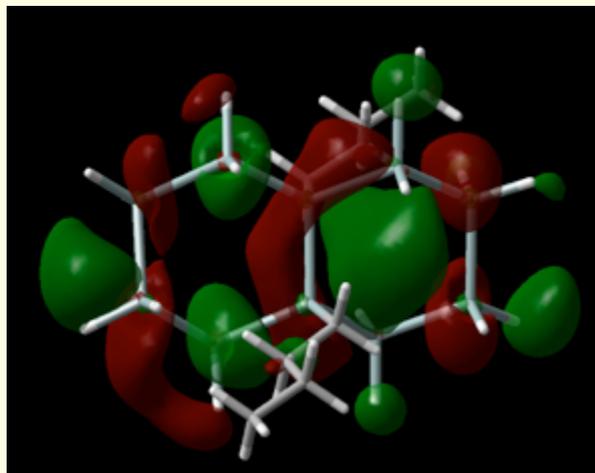


HR-TEM images of (left) **BSNP** and (right) **FSNP** cast onto a carbon micro grid (scale bar = 20 nm).



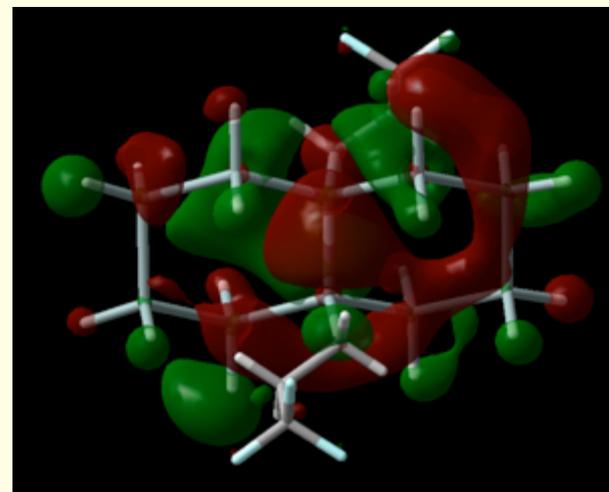
Si mapping (left) and **F** mapping (right) images in EELS of **FSNP** on a carbon micro-grid (scale bar = 0.1 μm).

Calculation (TD-DFT/3-21G)



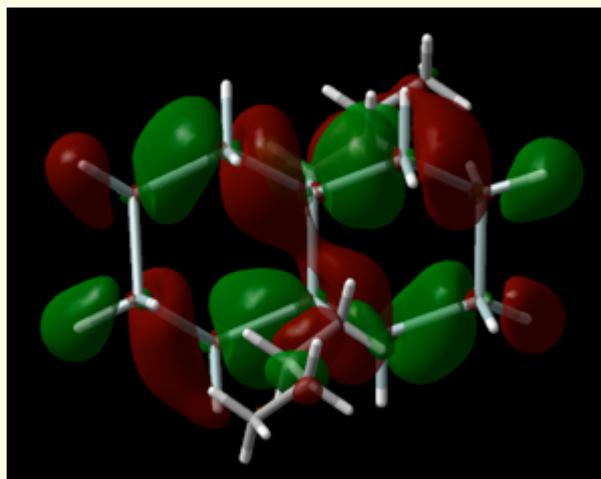
- 0.025 au

- 0.027 au



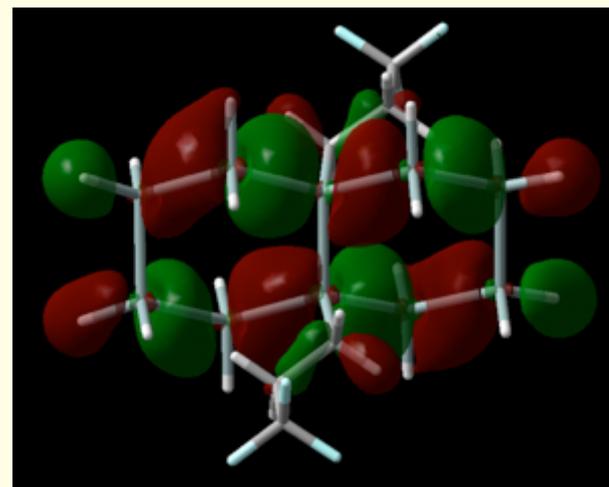
- 0.036 au

- 0.041 au



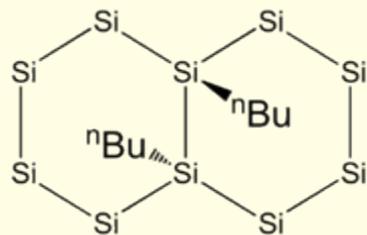
- 0.247 au

- 0.253 au

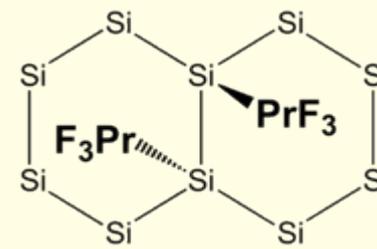


- 0.265 au

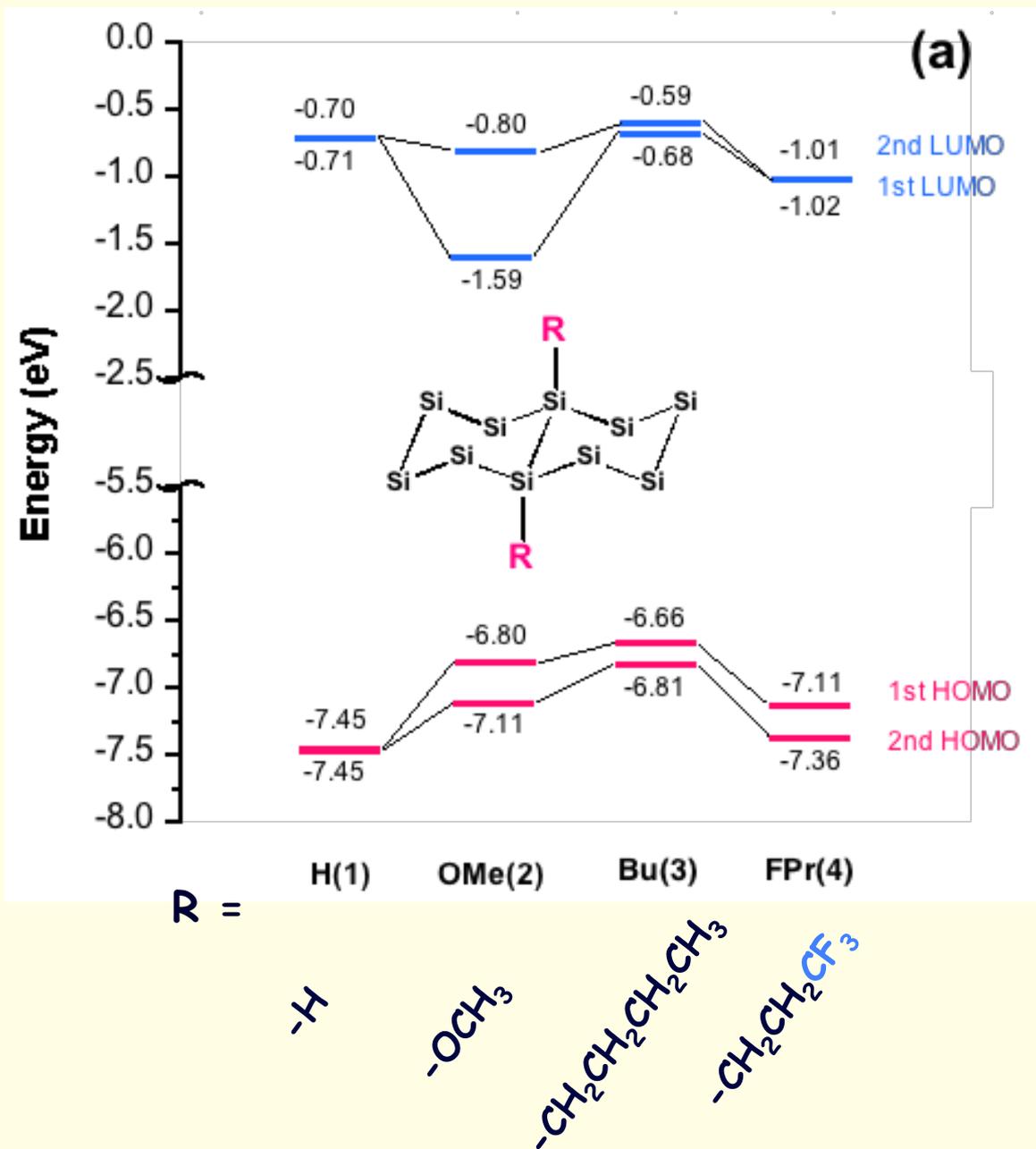
- 0.274 au



perhydro-trans-siladecaline

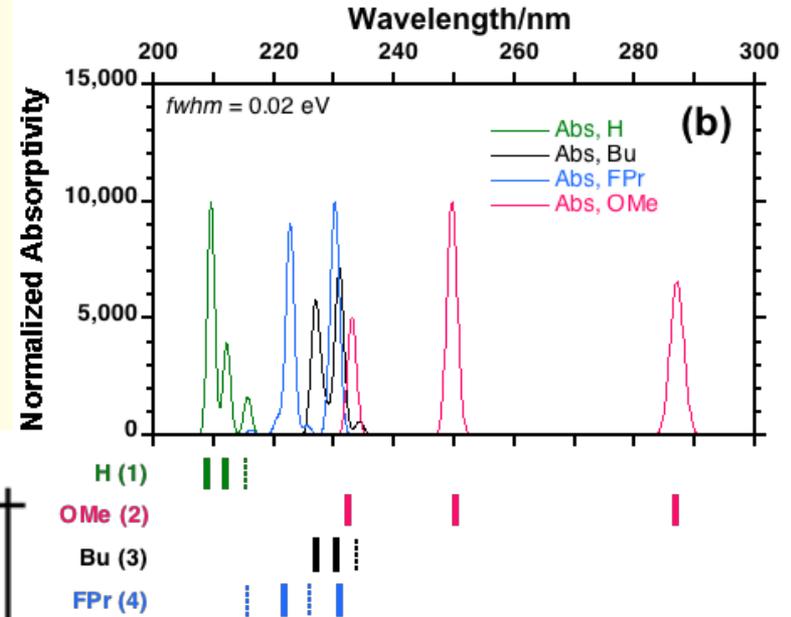
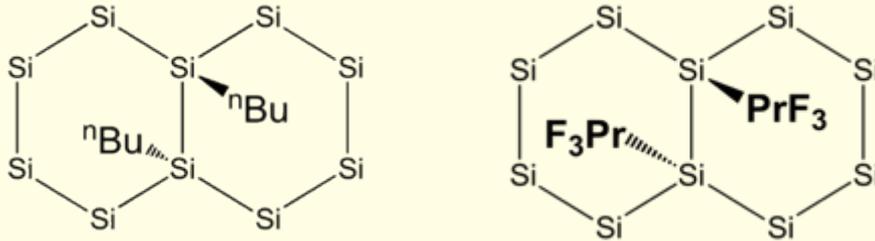


Calculation (TD-DFT/3-21G)

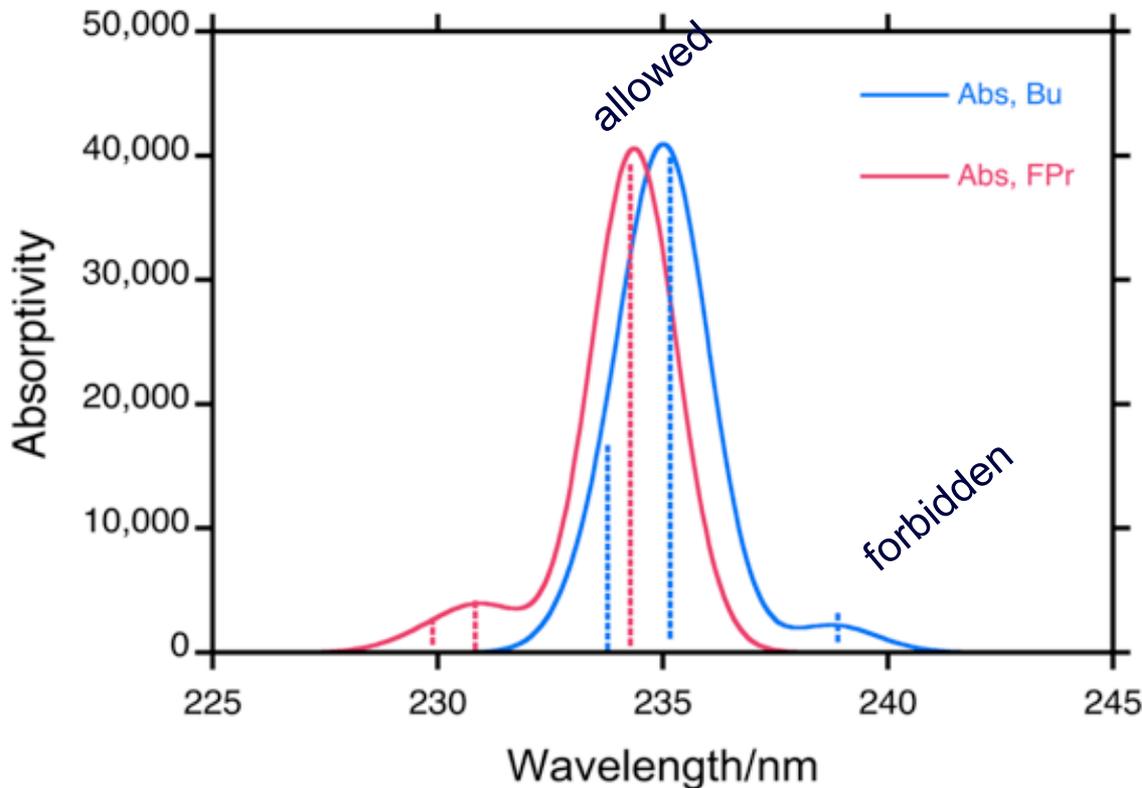


UV-Vis Calculation (TD-DFT/3-21G)

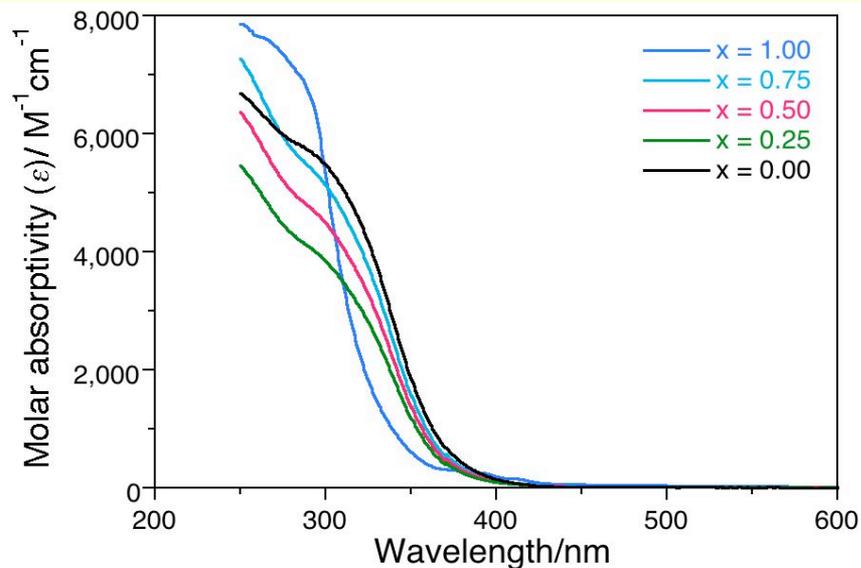
fwhm (0.025 eV)



BuSi vs FPrSi



Change in UV-Vis spectra with PL spectrum



A comparison of UV-vis absorption spectra of **FSNP**, **BSNP**, and **FBSNP** ($x = 0.25, 0.50, 0.75$) in THF at 25 °C.

Direct-type transition !

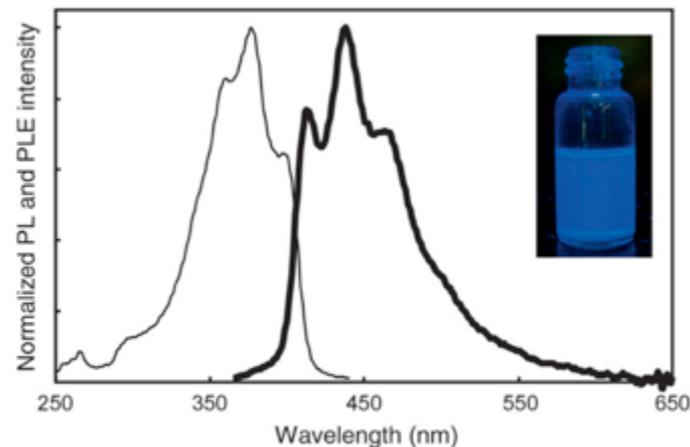
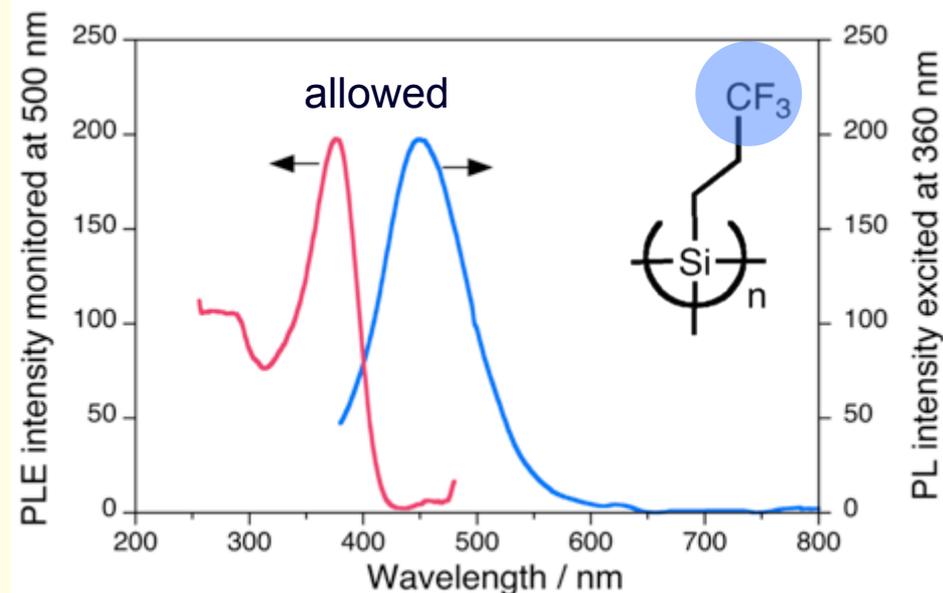
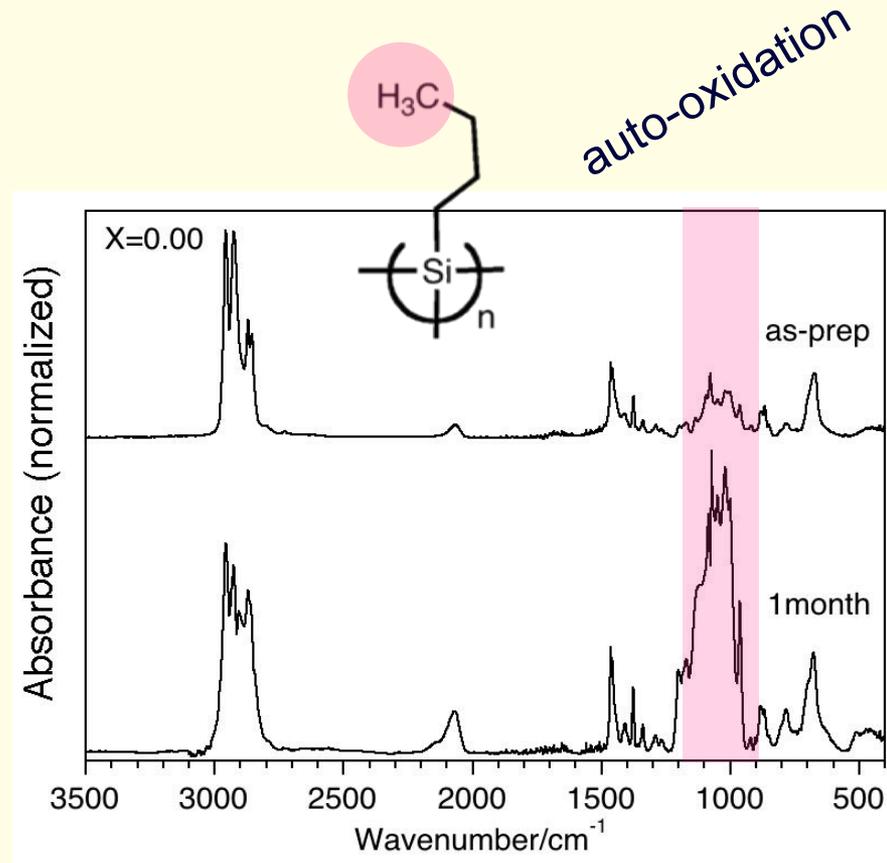
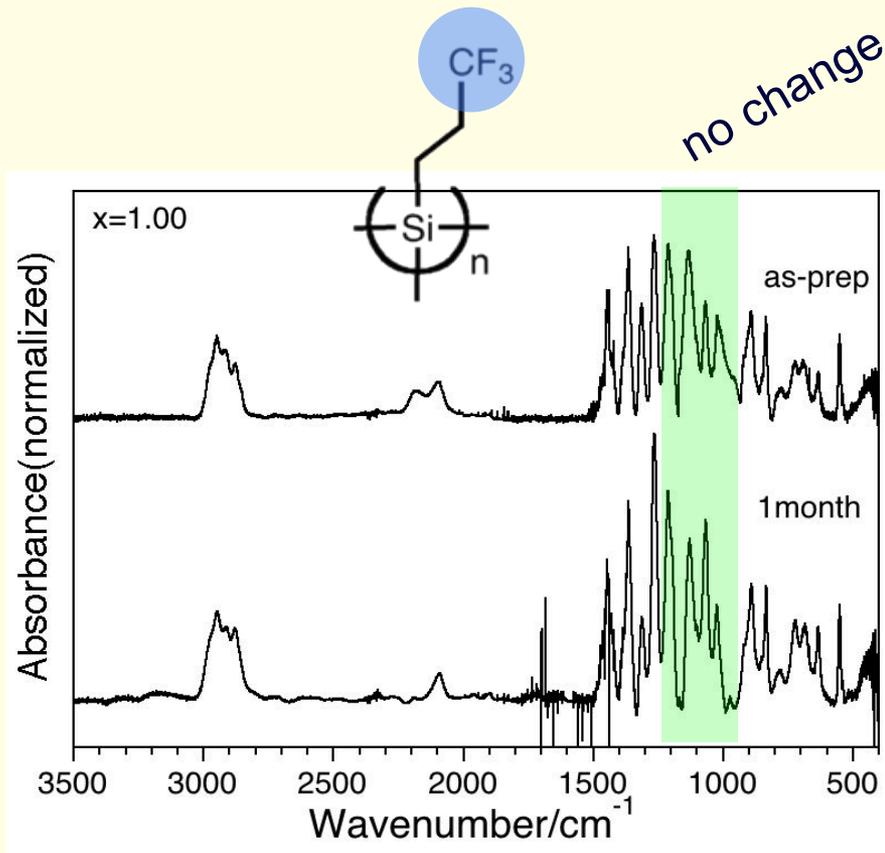


Figure 9. PL (—) and PL excitation (—) spectra of $C_{10}Si_n$ in chloroform. Excitation and fluorescence wavelengths are 350 and 450 nm, re-

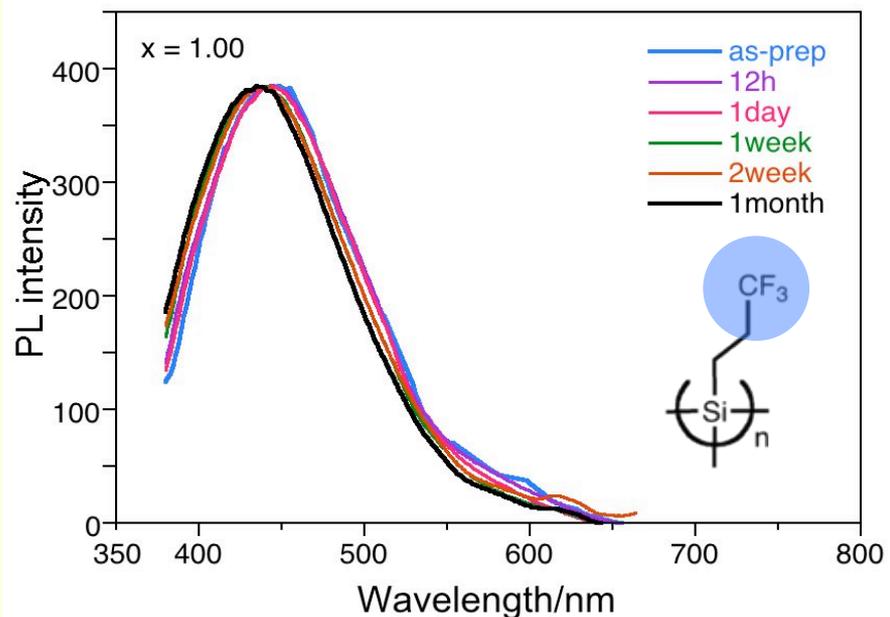
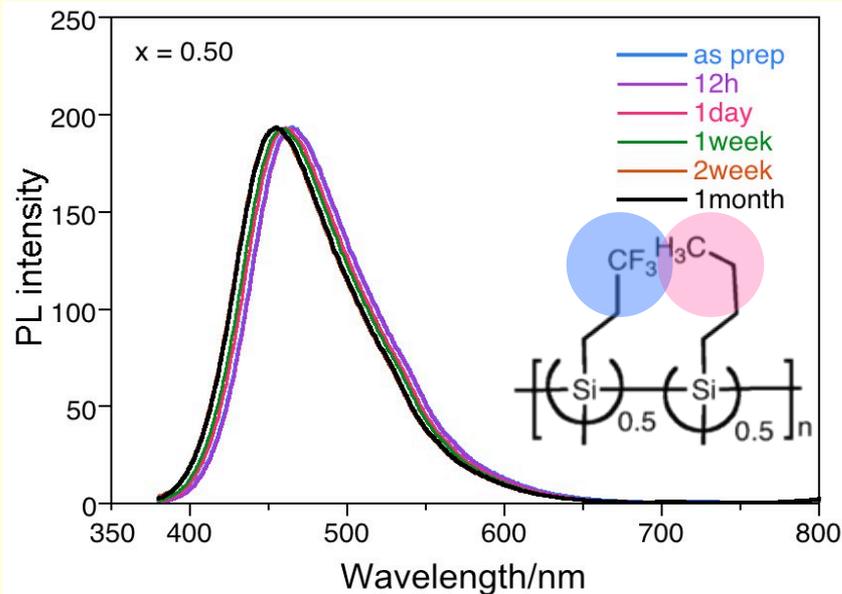
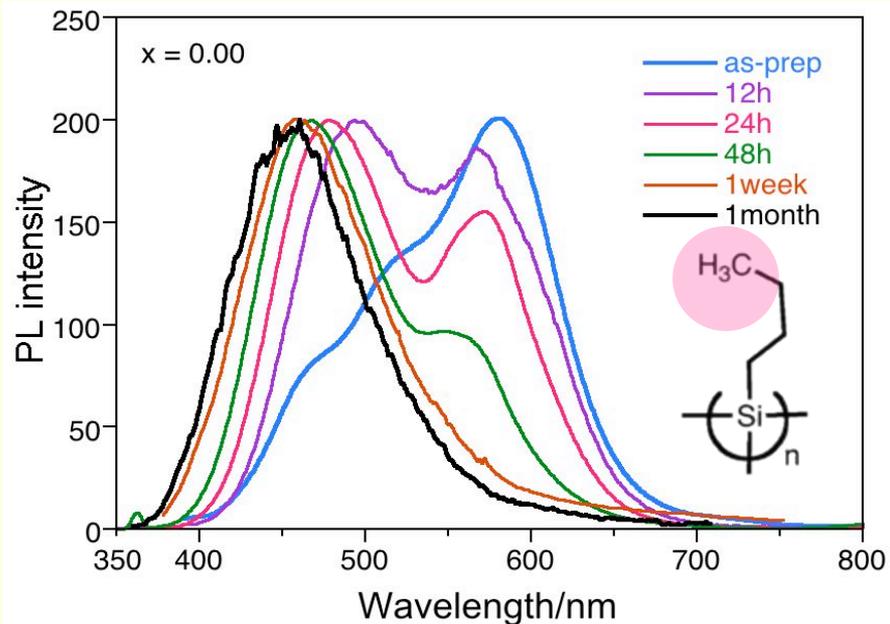
H. Okamoto, Y. Sugiyama, H. Nakano. *Chem. Eur. J.*, **2011**, 17, 9864-9887

No change in IR spectra to air exposure



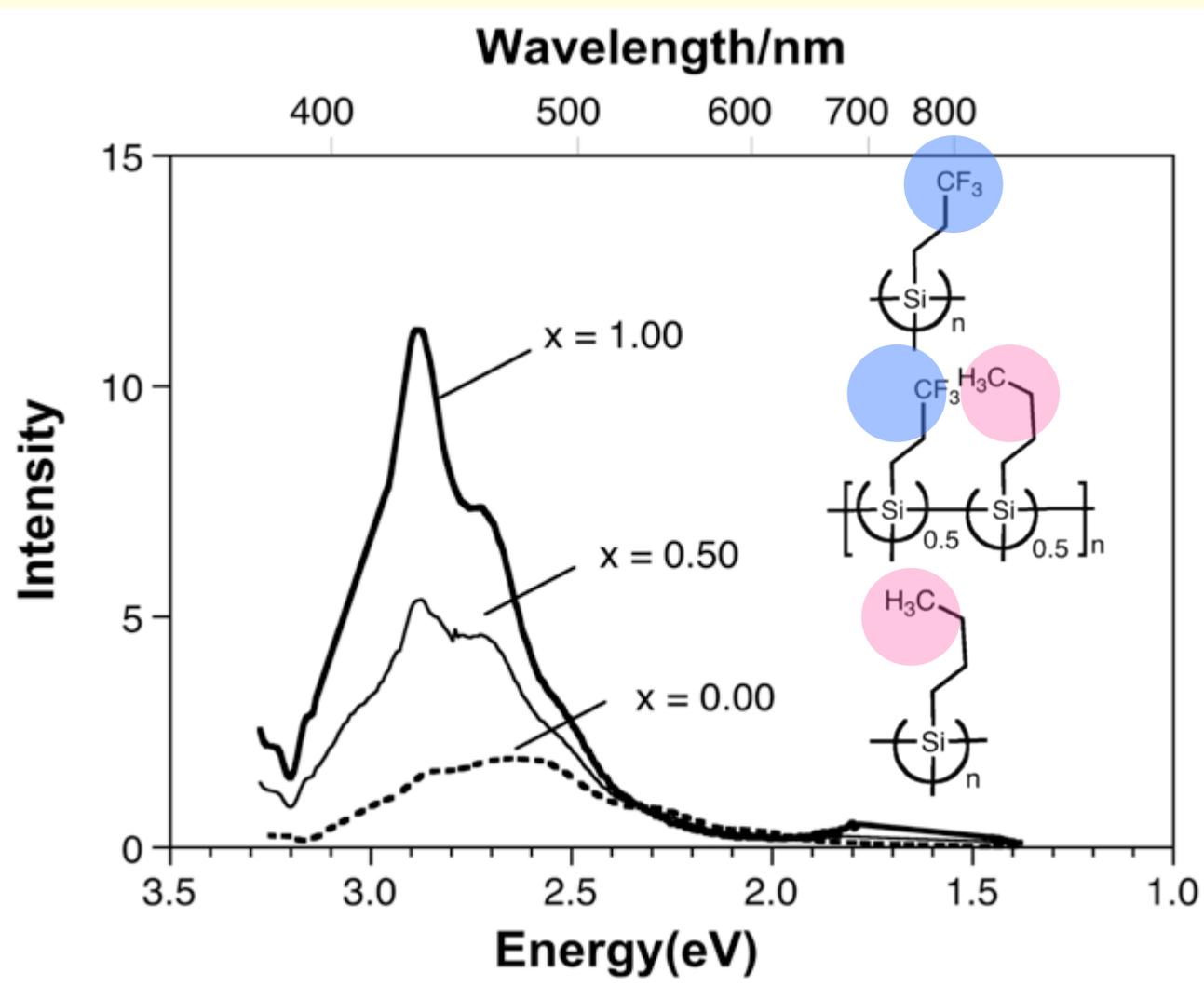
Changes in the IR spectra (3500–400 cm⁻¹) of (a) **FSNP** and (b) **BSNP** films cast onto KBr (as-prepared fresh sample and sample left in air for one month).

Change in PL spectra (Film)



Changes in the normalized PL spectra of **FSNP**, **BSNP**, and **FBSNP** ($x = 0.50$) films after different air-exposure times.

A comparison of three PL spectra (THF, RT)

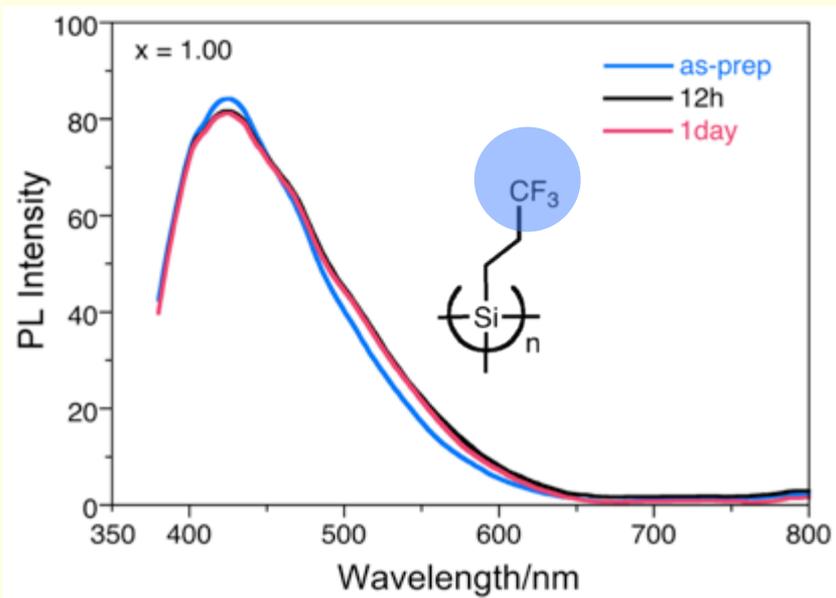
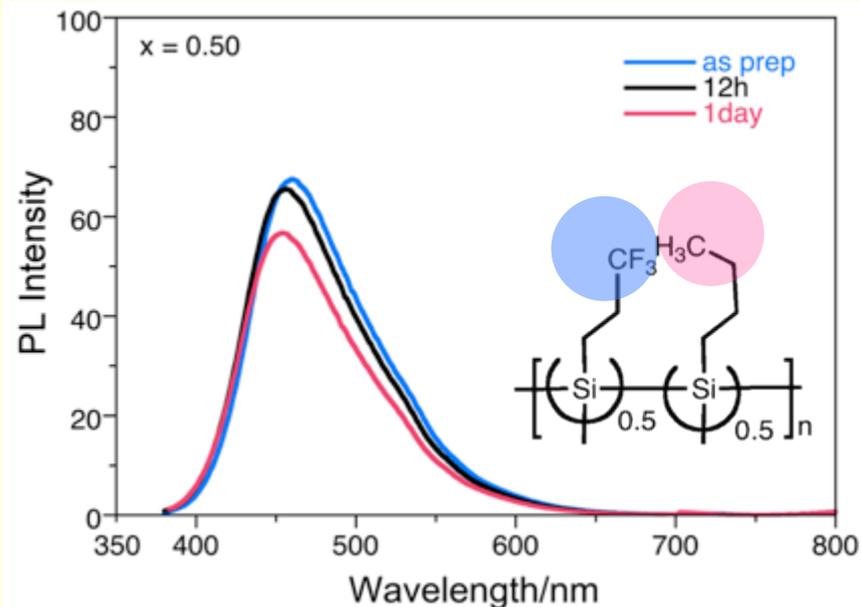
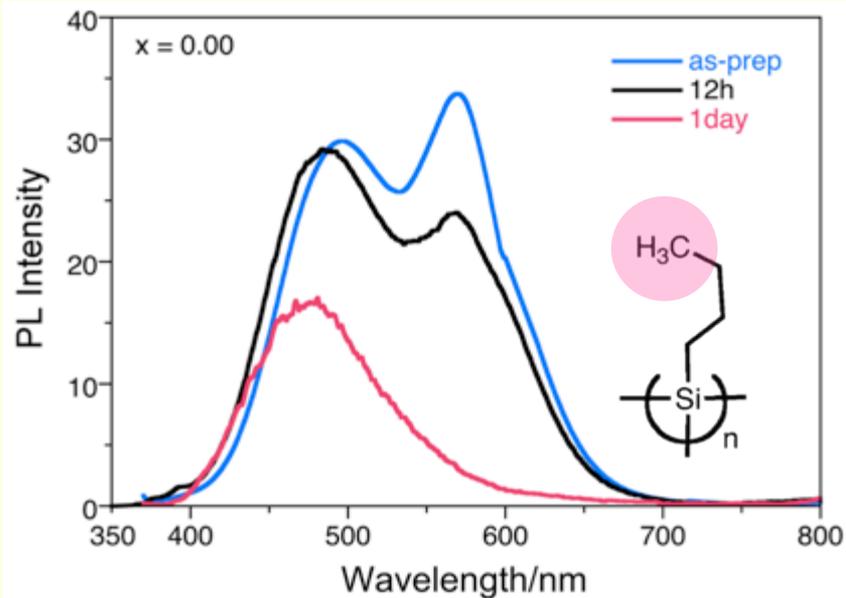


$\Phi_F / 3.0 \%$

$\Phi_F / 1.9 \%$

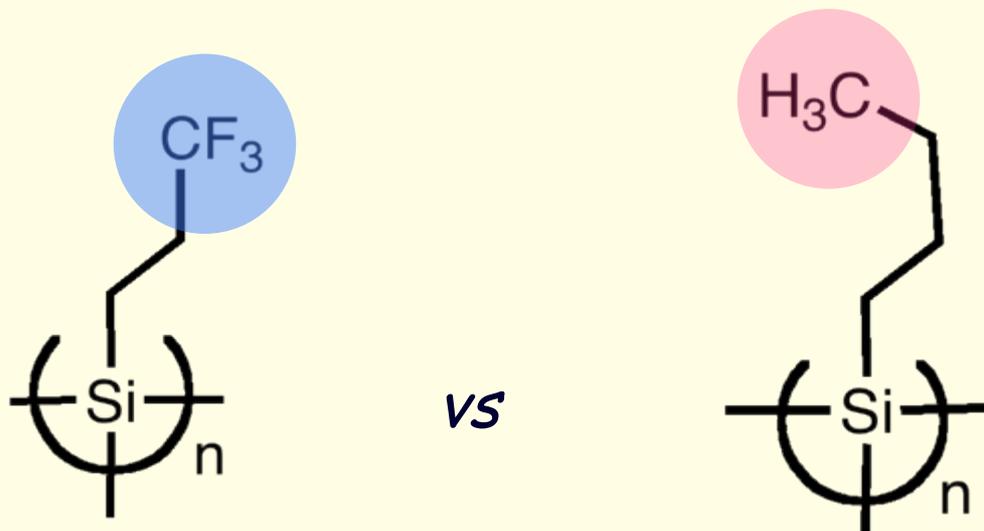
$\Phi_F / 1.0 \%$

Change in PL spectra in THF-H₂O solution



Changes in the PL spectra of **FSNP**, **BSNP**, and **FBSNP** ($x = 0.50$) in a THF-water (90/10 (v/v)) solution after different storage times.

Effects of Fluoroalkyl Groups



1. Excellent stability toward air and THF-water (film, solution) upto 300 °C from IR, Raman, PL, Calculation (TD-DFT, 3-21G, B3LYP)
2. Direct-type transition from dual indirect-and-direct transitions from UV, PL, PLE, Calculation
3. Quantum efficiency ~3% at RT (*cf.* 1% of (n-BuSi)n)
4. Loss of such the stability of pyrolytic products at 500 °C due to release of trifluoropropyl group

■環境影響最小化の取り組みプロセス

http://panasonic.co.jp/eco/products/chemical_substance/



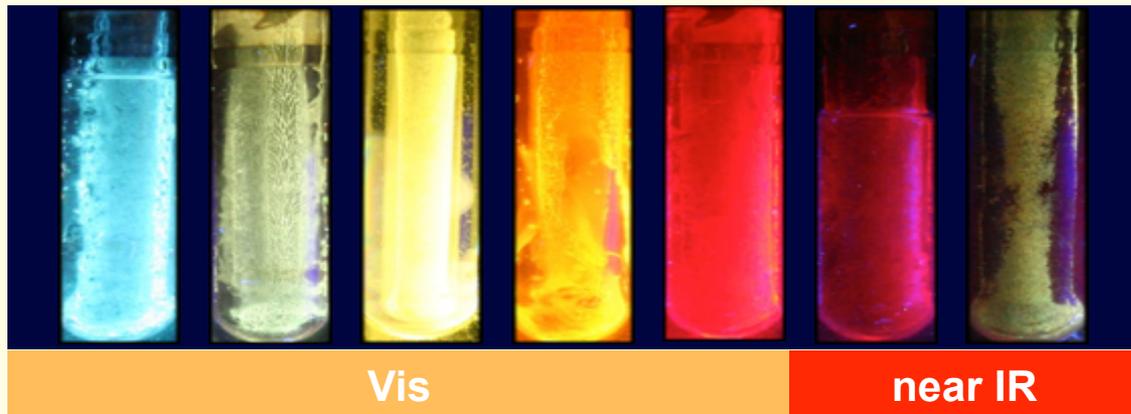
欧米では
no more new polymers
no more toxic materials

既存材料 + 新プロセス
の組合わせ技術で...

社会の動き	1989	1992	1996	2002	2006	2007	
	モントリオール 議定書発効	リオ宣言 「アジェンダ 21」	特定フロン 先進国全廃	ヨハネスブルグ サミット	RoHS指令 発効	REACH規則 発効	
パナソニック	1990	1995	2000	2005	2010		
全製品		1992 塩ビ樹脂 包装材の廃止		2003/3 鉛はんだ グローバル 廃止*2	2005/10 RoHS6物質 グローバル 廃止*2	2009/3 塩ビ内部配線 日本新製品で 廃止*2	2011/3 塩ビ内部配線 グローバル 新製品で廃止*2
個別製品	1991 水銀ゼロ マンガン 乾電池発売	1992 水銀ゼロ アルカリ 乾電池発売	1995 冷蔵庫の CFC冷媒 グローバル廃止	2002 エアコンの HCFC冷媒 廃止(日本)	2004 冷蔵庫 ノンフロン化 完了(日本)	2006 PDP(プラズマディスプレイパネル) 鉛フリー	
工場使用			1996 塩素系有機 溶剤を全廃	1997 PRTR 把握開始	1999 33/50削減 活動開始	2005 国内 使用量75%削減 排出・移動量62%削減	2010グローバル 2005年度比 重点削減物質 排出・移動量46.3%削減

Conclusion

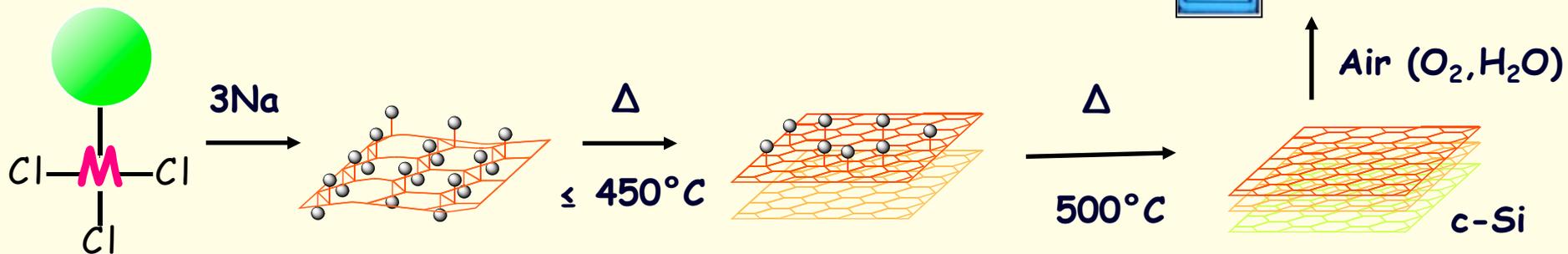
λ_{ex} 365nm, 1.0 mW/cm² (77K)



λ_{ex} 365nm,
1.0 mW/cm² (RT)



$E_g = 3 \text{ eV}$



Si



アルキル



フッ化アルキル

Ge



アルキル