

DE LA RECHERCHE À L'INDUSTRIE



DIRECT BONDING MECHANISM : FROM ADHESION TO ADHERENCE.

Frank Fournel

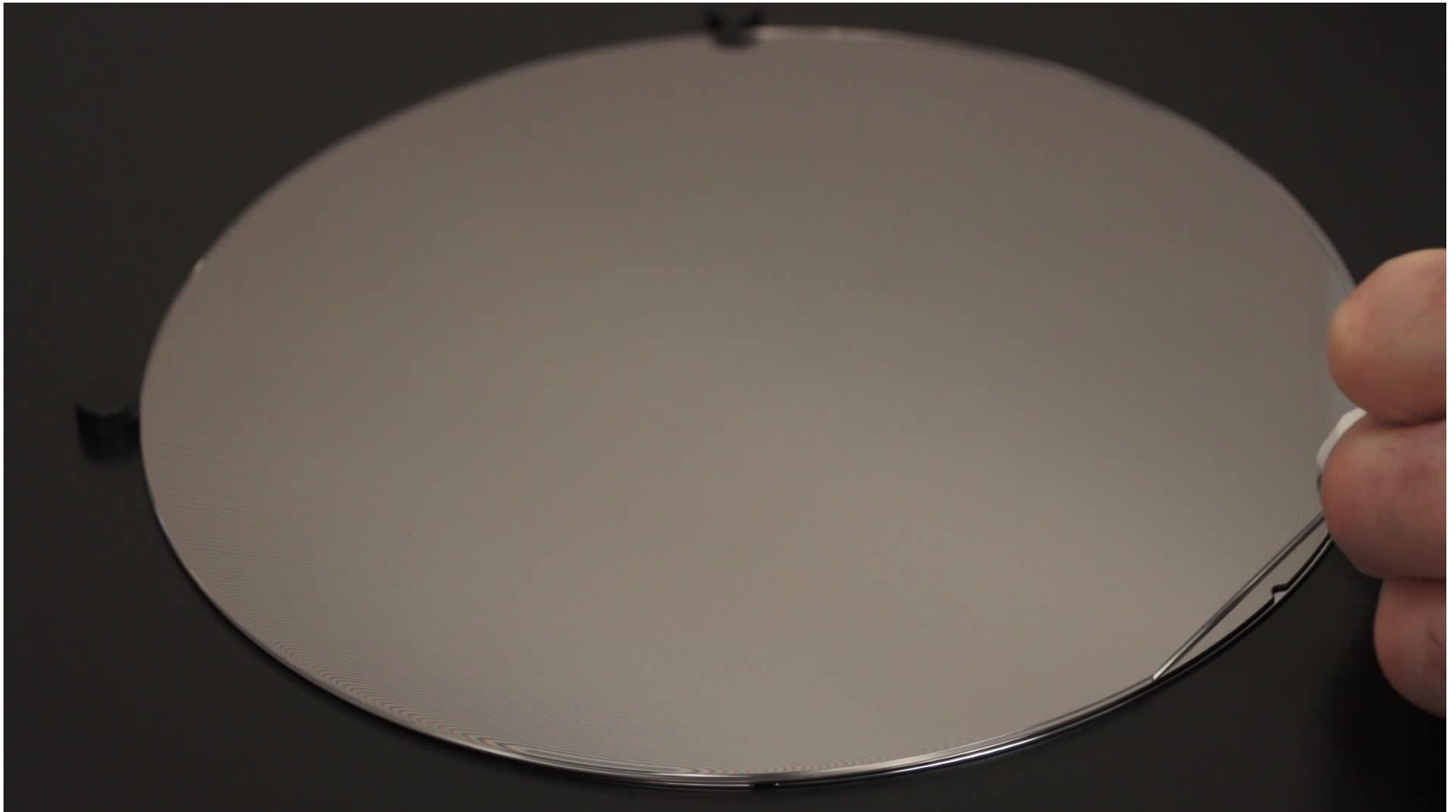
F. Rieutord, H. Moriceau, V. Larrey, C. Morales, C. Bridoux, G. Mauguen, C. Martin Cocher, L. Sanchez, B. Imbert, L. Di Cioccio, V. Balan, C. Euvrard, Y. Exbraya, C. Lecouvey, M. Rabarot.

SOITEC : I. Radu, D. Landru...

PhD students:

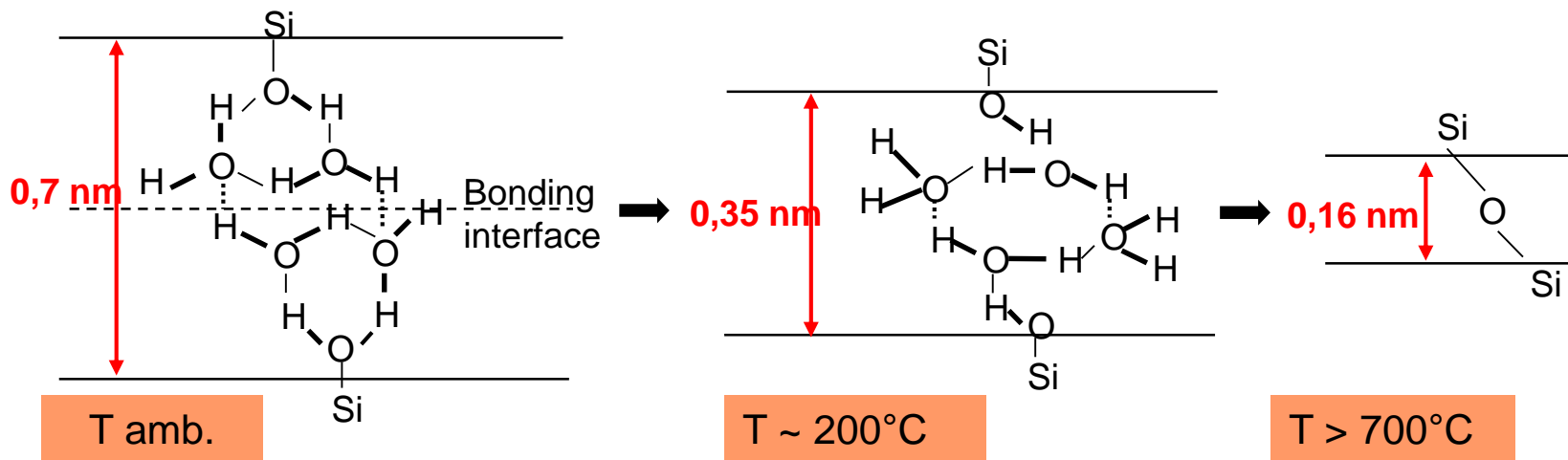
P. Noel, M. Dautriat, Q. Lomonaco, A. Calvez, M. Tedjini, E. Beche, J. Desomberg, P. Gondcharton, T. Tabata, Y. Beilliard, D. Radisson, E. Navarro, C. Rauer, F. Baudin, S. Vincent, R.M. Taibi, P. Gueguen, C. Ventosa, S. Sollier, A. Bavard, O. Rayssac, C. Lagahe...

*Spontaneous bonding without "thick" liquid material
(usually at room temperature and ambient pressure)*

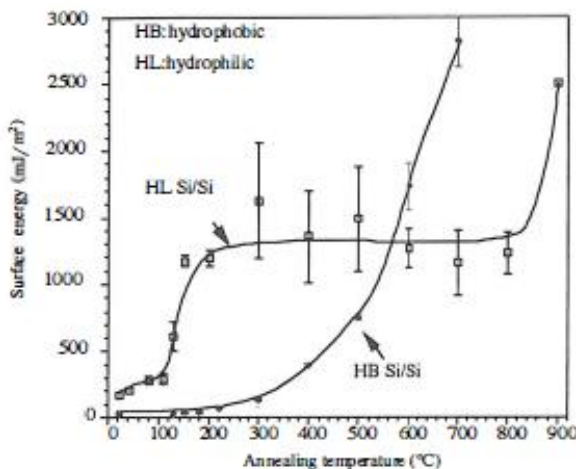


Stengl Model : hydrophilic Si bonding

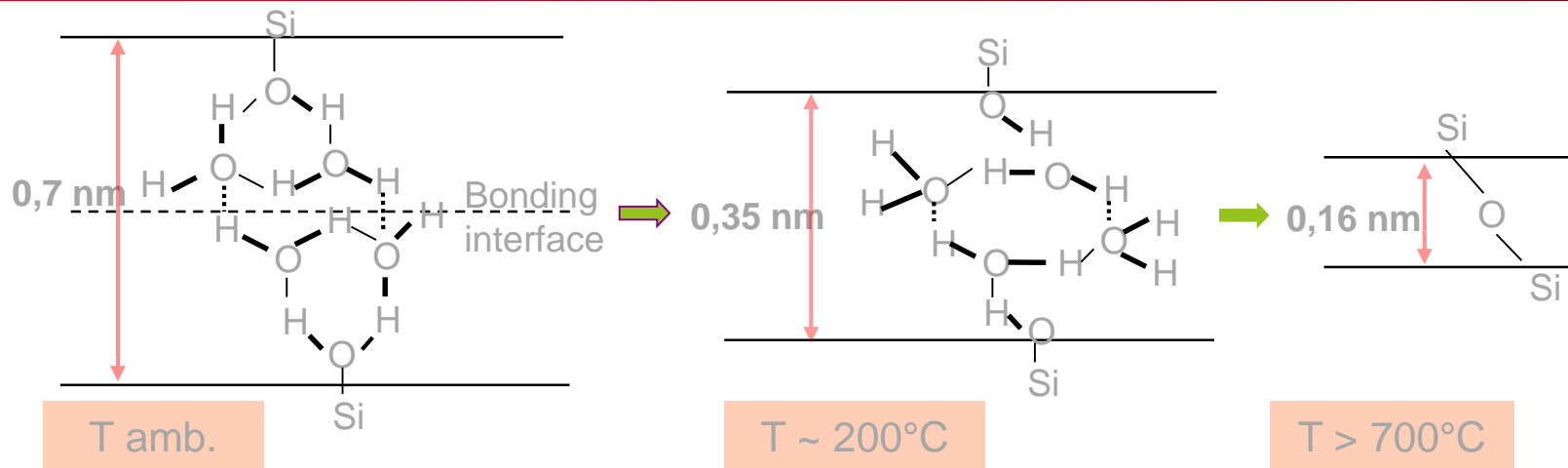
Based on infrared spectroscopy and bonding energy measurement..



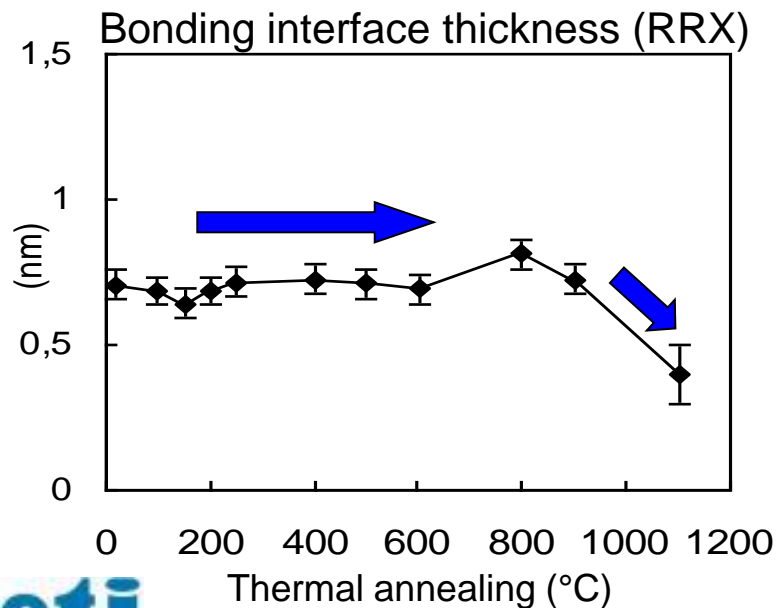
R. Stengl et al., *J. J. Appl. Phys. Lett.* (1989)



Q.Y. Tong, U. Gosele, "SemiConductor Wafer Bonding: Science and Technology", John Wiley Sons Inc (1998)



R. Stengl et al., J. J. Appl. Phys. Lett. (1989)



RRX => Constant interface thickness

→ Model has to be optimized

Hertz model (RT Bonding)

$$\sigma^{*2} = \sigma_1^2 + \sigma_2^2$$

$$\frac{1}{E^*} = \frac{1-\nu_1^2}{E_1} + \frac{1-\nu_2^2}{E_2}$$

Greenwood et al., Proc. Roy. Soc., A295, 300 (1966).

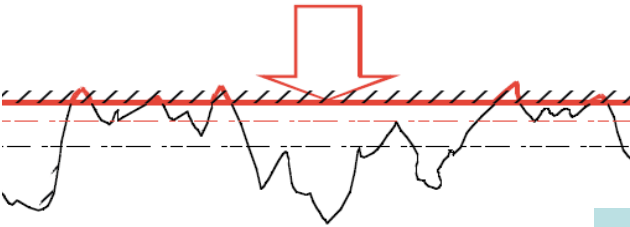
Number of asperities in contact $N = N_0 F_0(d/\sigma^*)$

Surface area in contact

$$A = A_0 (N_0 R \sigma^*) \pi F_1(d/\sigma^*)$$

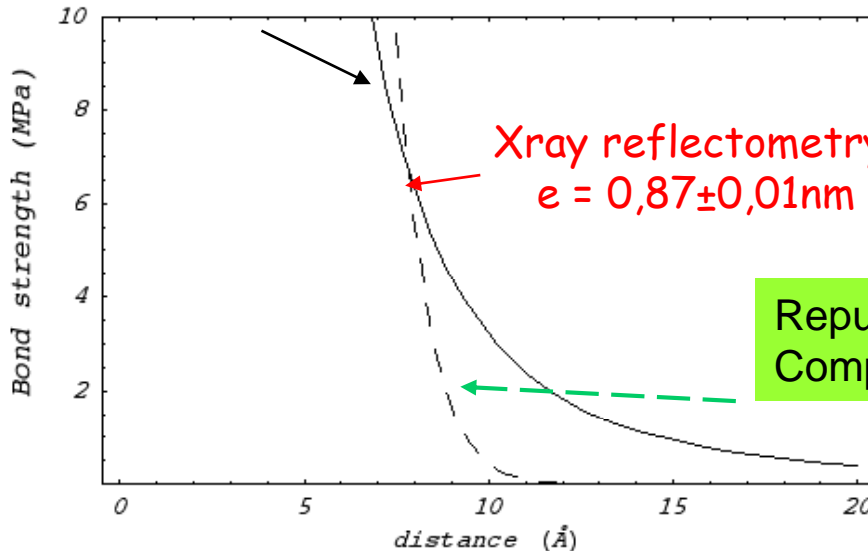
Total repulsive force

$$P = N_0 R^{1/2} \sigma^{*3/2} \frac{4}{3} E^* F_{3/2}(d/\sigma^*)$$



$$F = \frac{A}{6\pi d^3}$$

Attractive forces: Van der Waals
(Hydrophobic Si Bonding: $A = 20 \cdot 10^{-20} \text{J}$)



~1% of contacted surface

Repulsive forces:
Compressed asperities

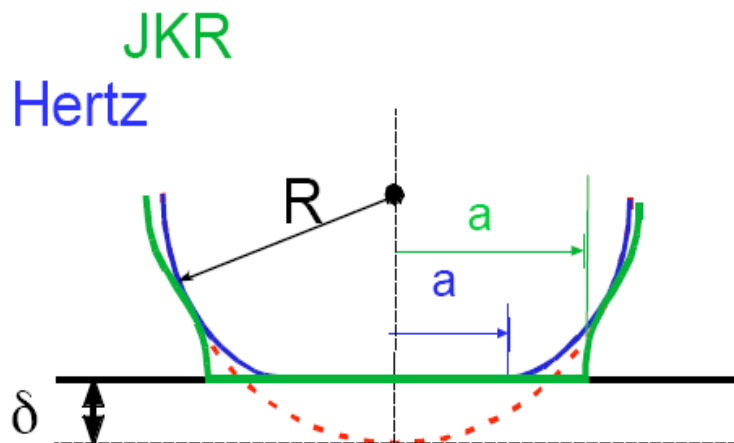
JKR Model during annealing

Johnson-Kendall-Roberts

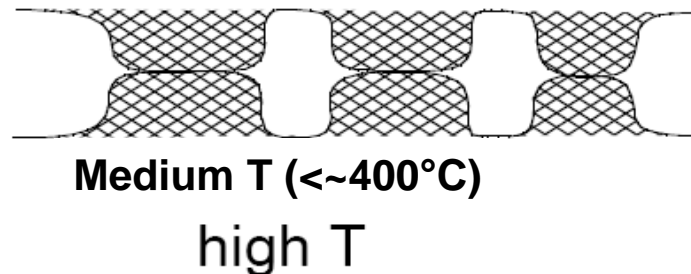
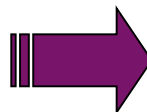
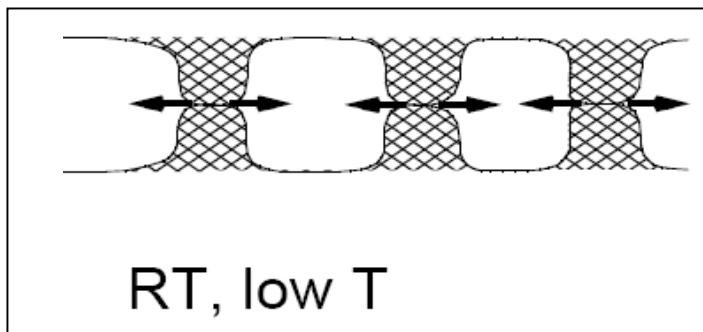
$$E_{tot}(z) = \int_z^\infty P(u)du - (wA(z) + vdW(z))$$

Elastic energy
(Asperity compression)

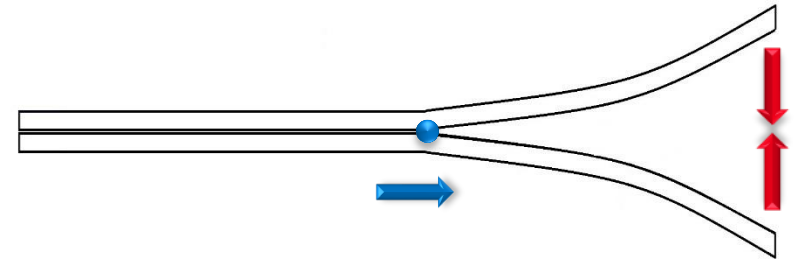
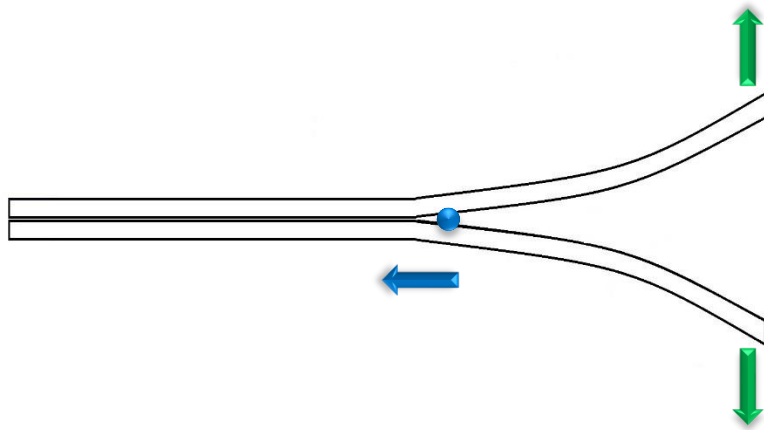
Surface energy
(Adhesion)



➤ Ziplock model



Adherence vs adhesion



Adherence Energy

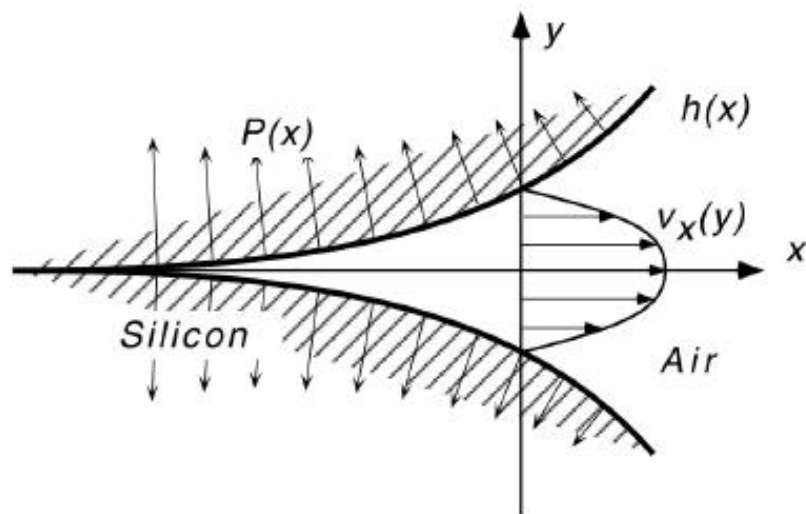
(=Bonding / Fracture energy, Fracture toughness, Critical strain energy release rate...)

- Energy needed to open the bonding
 - Chemical bonds breaking
- Measured after bonding
- Double Cantilever Beam (DCB) measurement

Adhesion Energy

- Energy needed to realize the bonding
 - Mechanical deformation
 - Hydrodynamic flow
- Measured during the bonding
- Lack of experimental data

Adhesion energy => Bonding Wave



$$U = \frac{(2\gamma)^{5/4}}{\eta t^{3/4}} \frac{\Lambda^{1/2}}{\left(\frac{E}{1-\nu^2}\right)^{1/4}} \frac{A^{3/4}}{9}$$

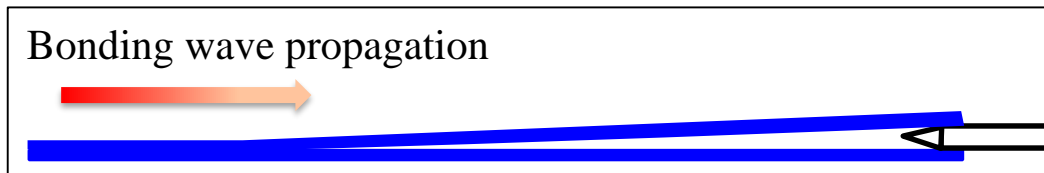
With $2\gamma = E_{\text{adhesion}}$

With $\Lambda = \text{mean free path}$, $A = \text{Numerical constant}$

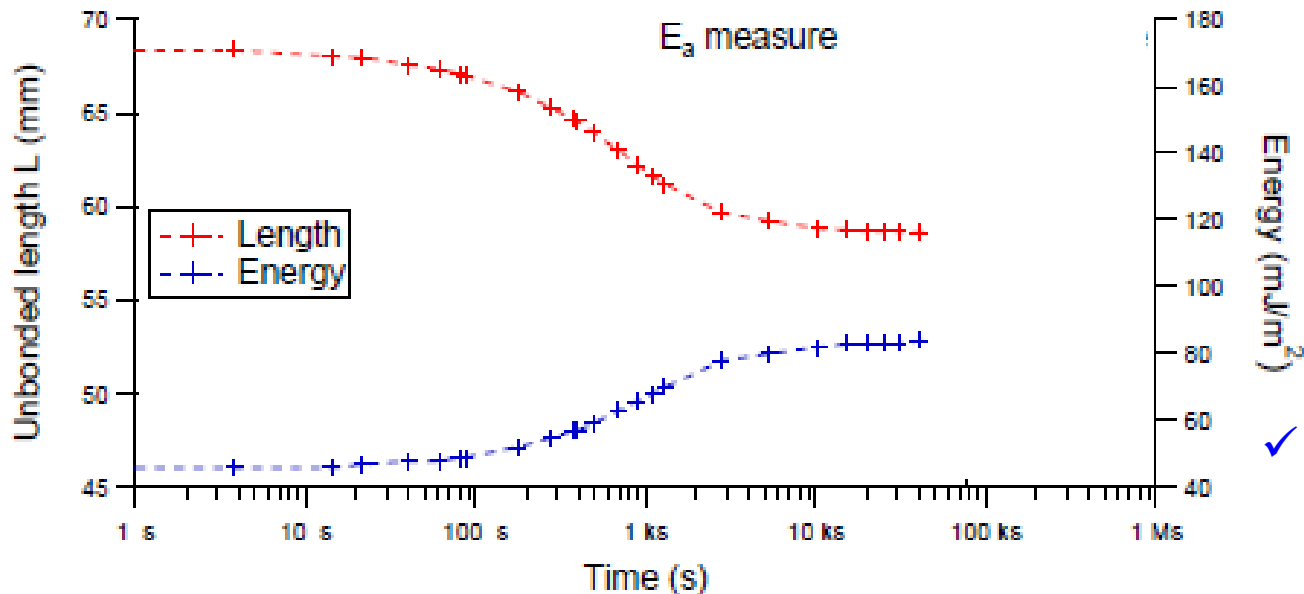


Adhesion energy measurement:

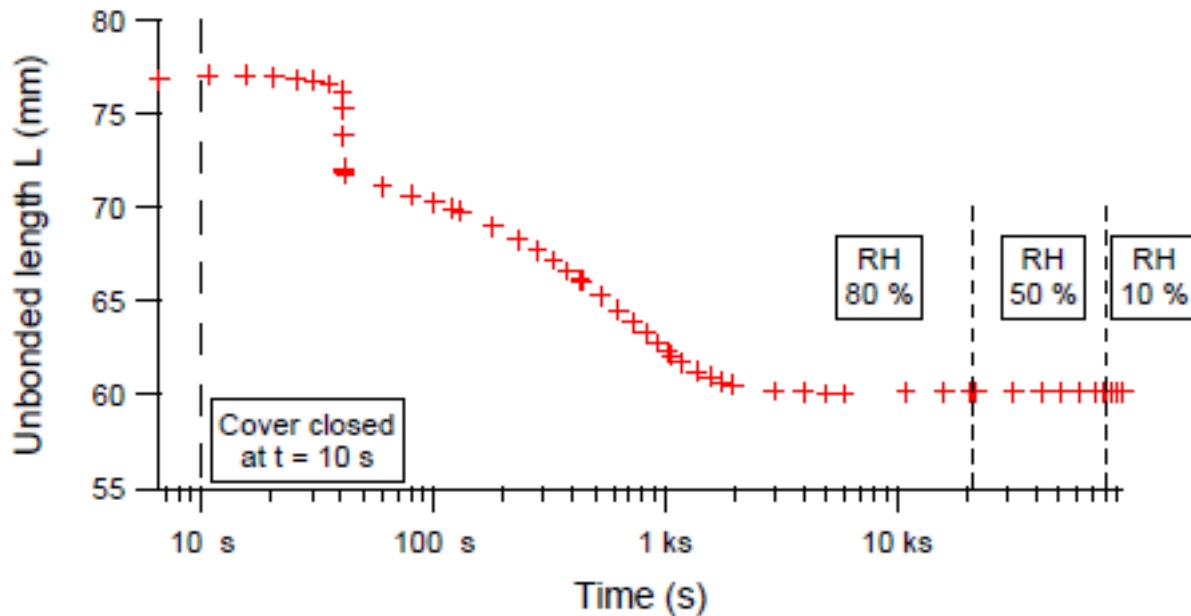
Modified DCB technique can measure the adhesion energy of chemical Si/Si direct bonding:



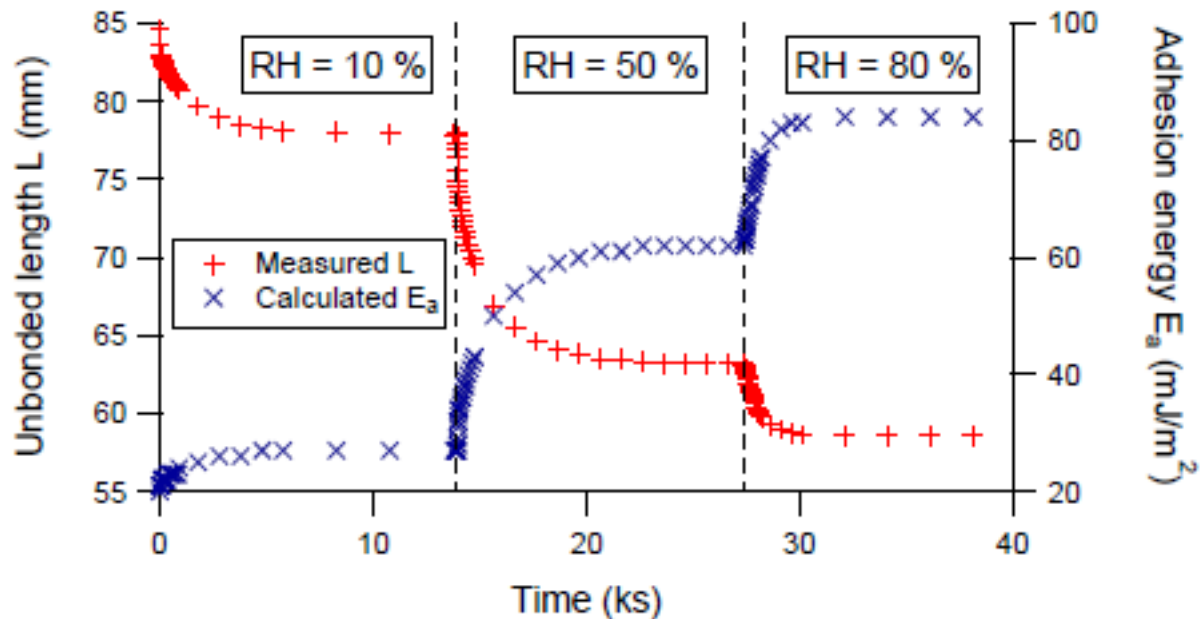
- ✓ Unbounded length
- ✓ El-Zein => Adhesion energy



- ✓ Small evolution during 4 hours!
- ? Capillarity effect ? (meniscus)

Adhesion energy measurement / Time evolution:

Time evolution is not driven by meniscus!!

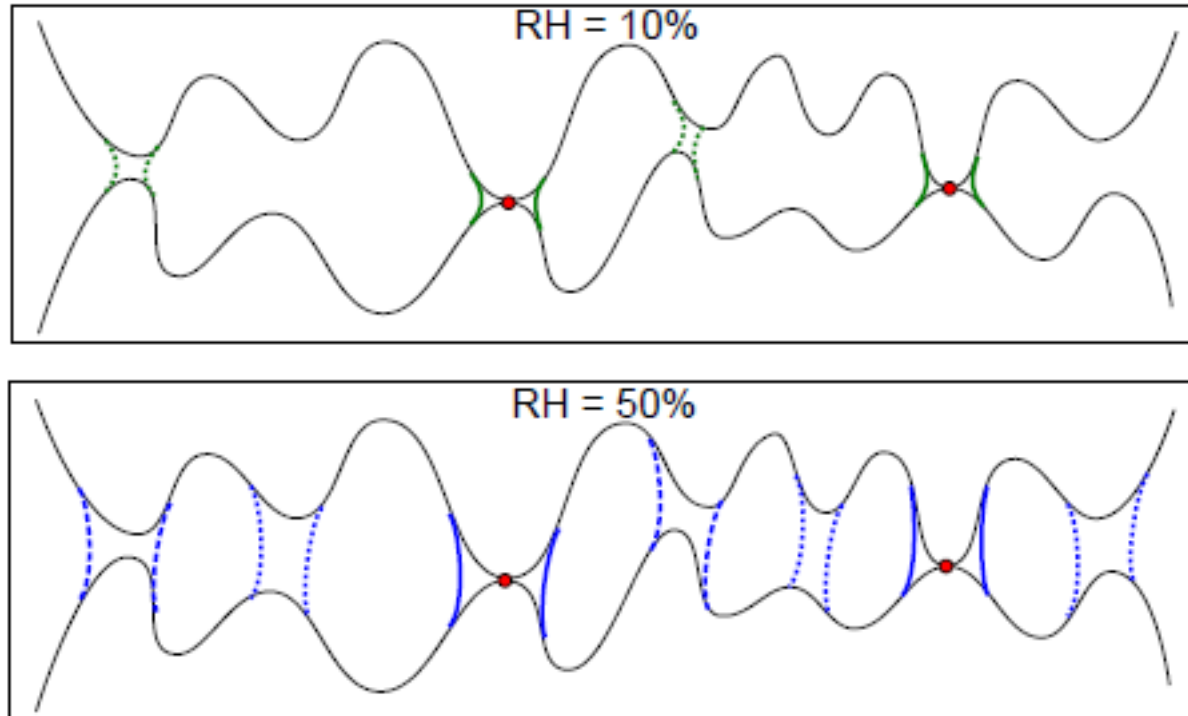
Adhesion energy measurement / Time evolution:

=> Time evolution depends of the amount of water.

=> Fast and slow evolution.

=> It is easier to bond in humid atmosphere!! 😊

Adhesion energy measurement / Time evolution:



- => Already existing bridge => fast evolution.
- => New bridge formation => slow evolution
(depends on the amount of adsorbed water)

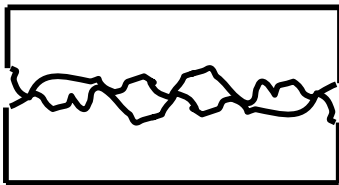
Bonding "engines" : chemistry & roughness

Attractive force:

- Van der Waals (+hydrogen bonds) + capillarity

Repulsive force

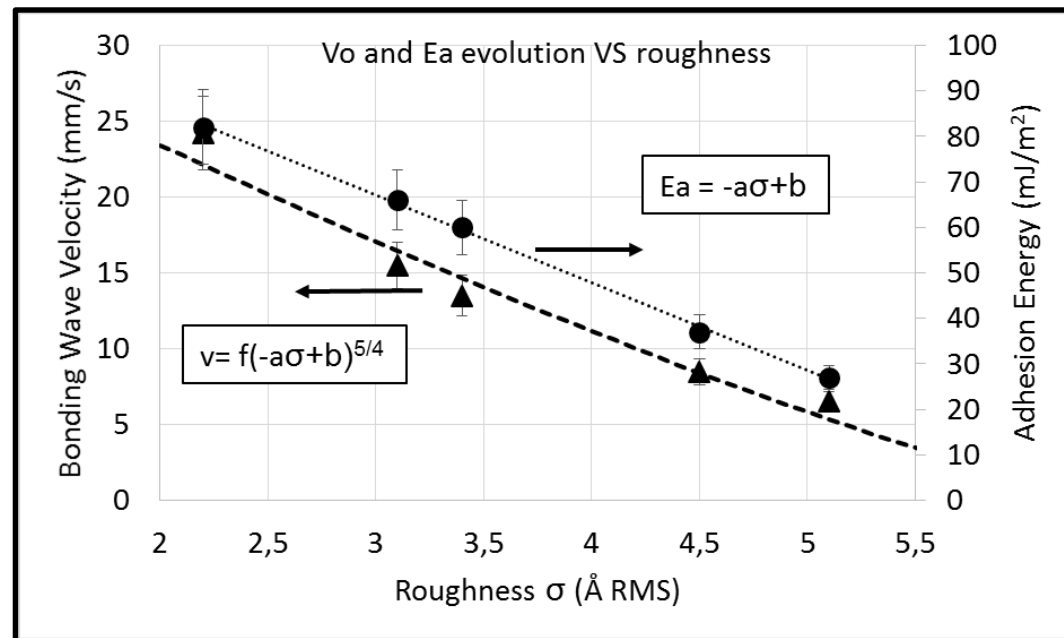
- Non adhesive contact on rough surface => Roughness acts as "accelerator pedal"



Adhesion energy versus roughness (Si/SiO₂ bonding)

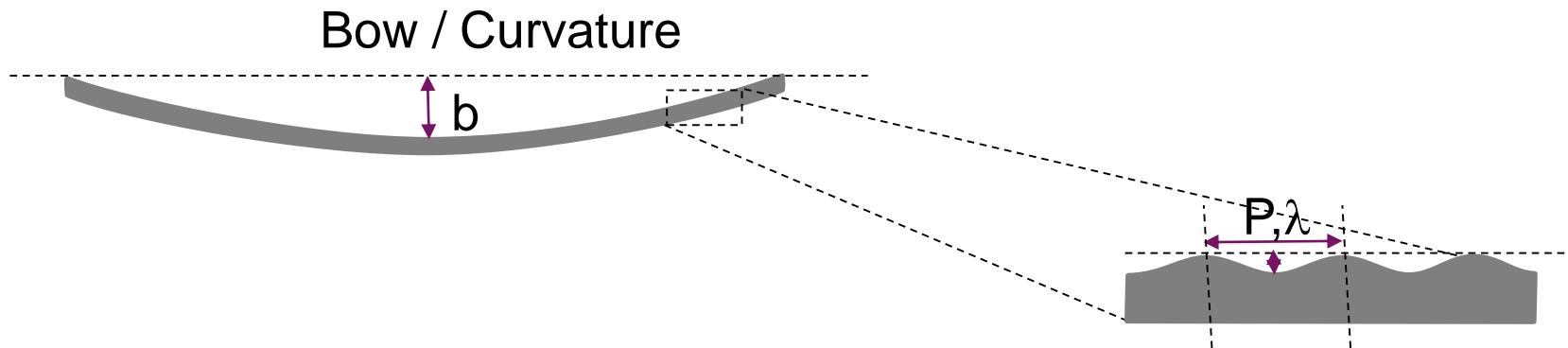
- ✓ Roughness specification : <0.6nm RMS

leti



Bonding "breaks"

➤ *Surface mechanical adaptation ("all atoms bonding")*

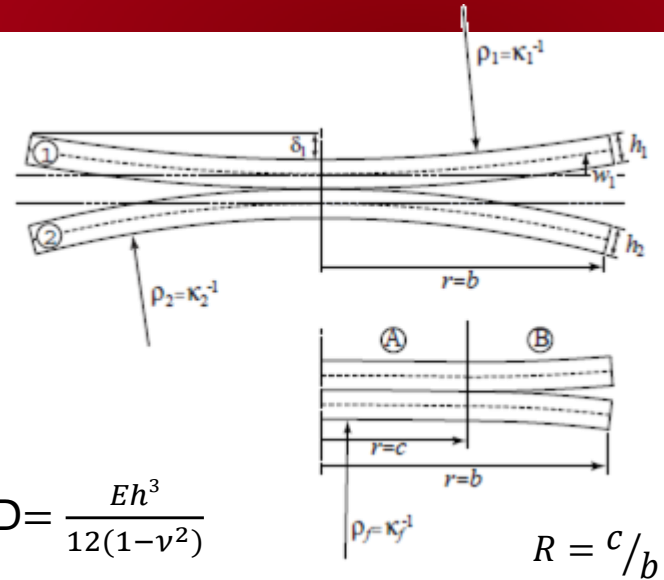


?Which criteria?

Thin plate theory

$$k_i = - \frac{\frac{\partial^2(w)}{\partial i^2}}{\left(1 + \frac{\partial(w)}{\partial i}\right)^{3/2}} \quad \varepsilon_i = \frac{z}{k_i} \quad M_i dj = \int_{-h/2}^{h/2} \sigma_i z dj dz$$

Cylindrical geometry $M_r = -D \left(\frac{\partial^2 w}{\partial r^2} + \frac{\nu}{r} \frac{\partial w}{\partial r} \right) \quad D = \frac{Eh^3}{12(1-\nu^2)}$



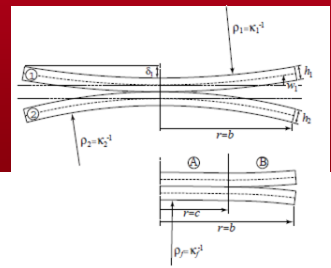
For bonded part A : $w_A = \frac{1}{2}(kf - ki)^2$

For non bonded part : Moment equilibrium without shearing force : $\frac{\partial}{\partial r} \left[\frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial w_B}{\partial r} \right) \right] = 0$

$$dU_E = -\frac{1}{2} \left(M_x \frac{\partial^2 w}{\partial x^2} + M_y \frac{\partial^2 w}{\partial y^2} \right) dx dy \quad U_E(c) = \pi D \int_0^b \left[\left(\frac{\partial^2 w}{\partial r^2} + \frac{1}{r} \frac{\partial w}{\partial r} \right)^2 - \frac{2(1-\nu)}{r} \frac{\partial w}{\partial r} \frac{\partial^2 w}{\partial r^2} \right] r dr$$

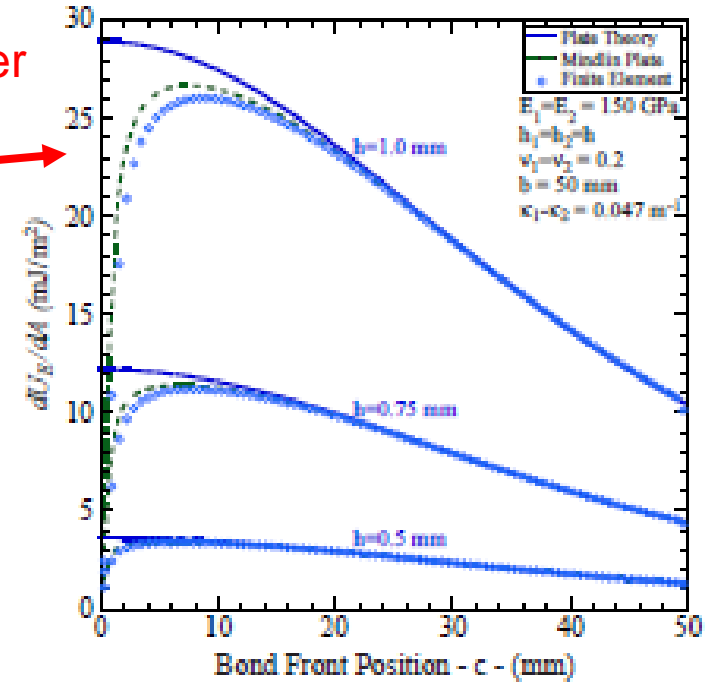
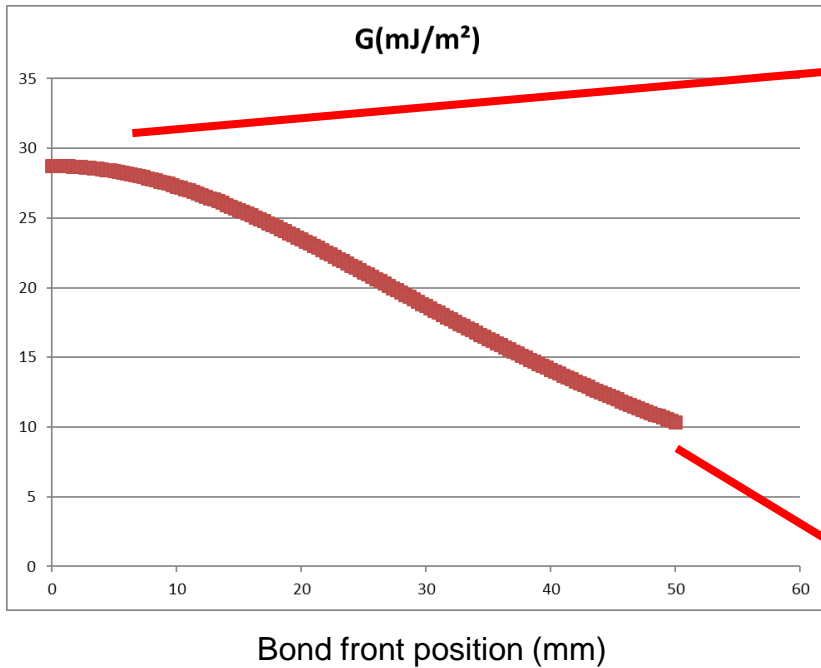
$$G = \frac{dU_E}{dA(c)} = \frac{1}{6} \frac{E_1 h_1^3}{1 + \frac{E_1 h_1^3}{E_2 h_2^3}} (k_1 - k_2)^2 \frac{1+\nu}{1-\nu} \frac{1}{[(1+\nu) + R^2(1-\nu)]^2}$$



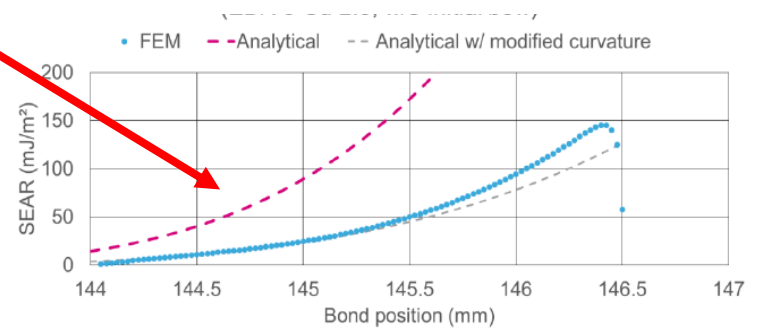


Thin plate theory :

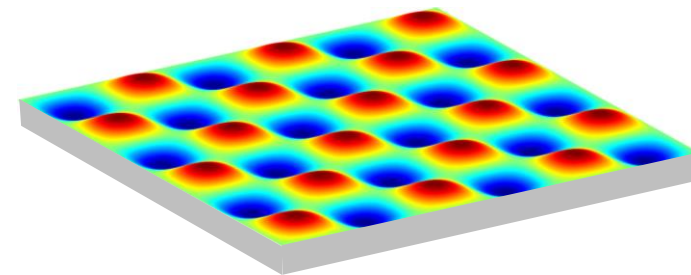
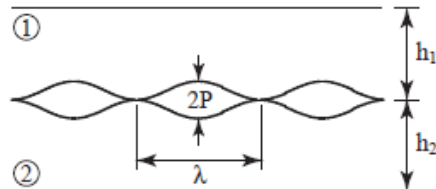
Not well accurate at the center



Neither at the edge
(with specific edge roll down)



Thin plate theory

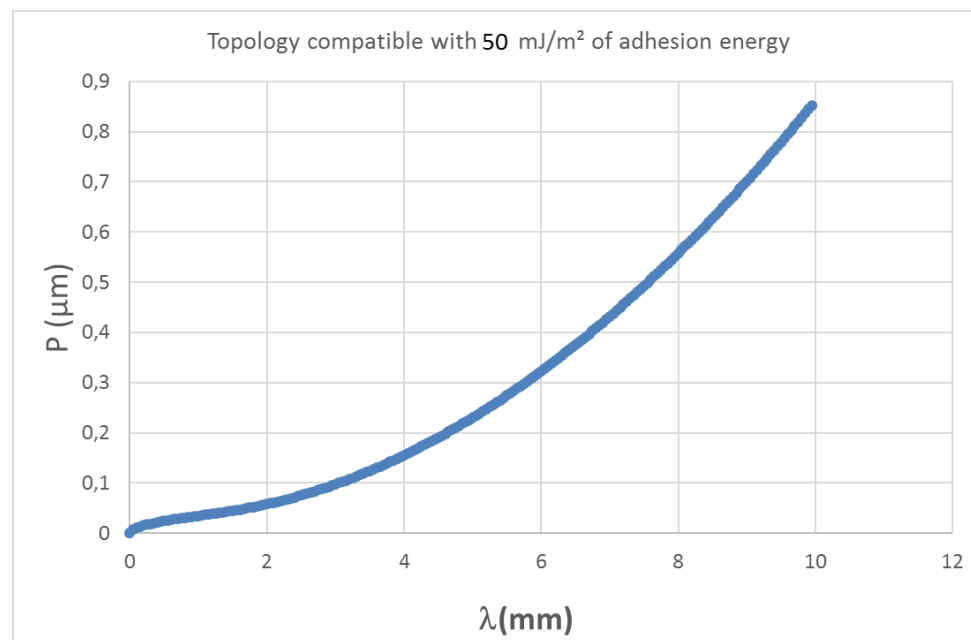


$$\text{Gap} = 2P \left[1 + \cos\left(2\pi \frac{x}{\lambda}\right) \cos\left(2\pi \frac{y}{\lambda}\right) \right]$$

$$\frac{\Delta U}{\Delta A} = \frac{\pi P^2}{4\sqrt{2} \lambda} \left[\frac{1}{\bar{E}_1 I \left(2\pi \frac{h_1}{\lambda}\right)} + \frac{1}{\bar{E}_2 I \left(2\pi \frac{h_2}{\lambda}\right)} \right]$$

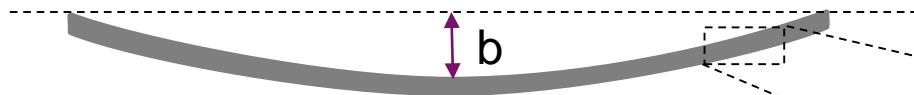
$$\bar{E} = \frac{E}{(1 - \nu^2)}$$

$$I(x) = \frac{e^{2\sqrt{2}x} + e^{-2\sqrt{2}x} - 2 - 8x^2}{e^{2\sqrt{2}x} - e^{-2\sqrt{2}x} + 4\sqrt{2}x}$$



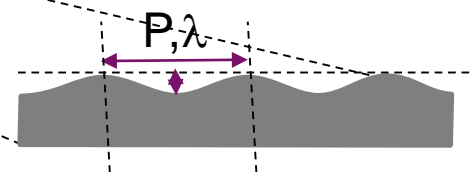
Bonding "breaks"

Bow / Curvature



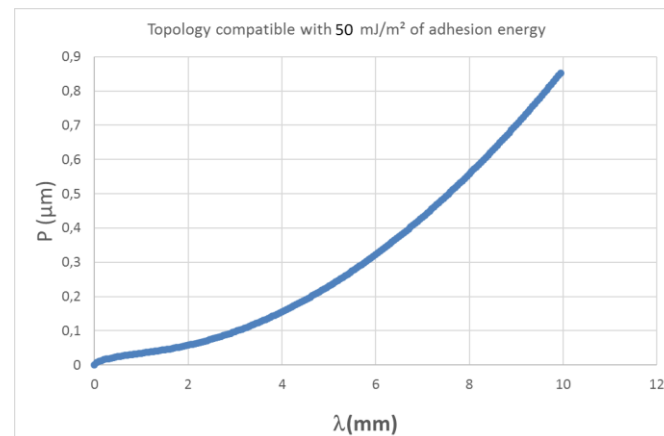
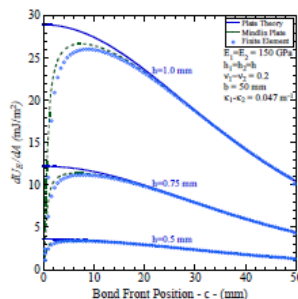
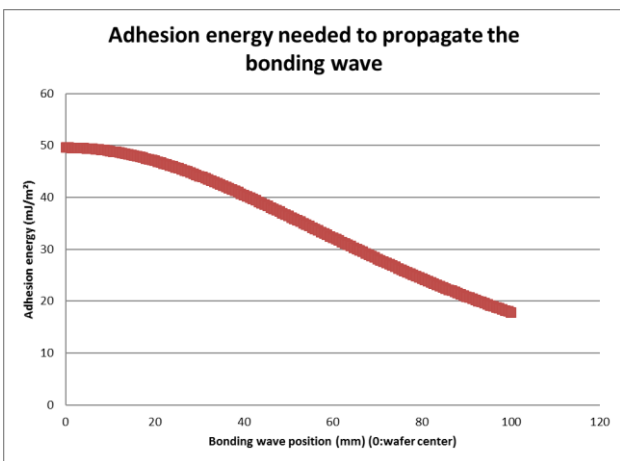
For 200mm wafer ($725\mu\text{m}$) and **50 mJ/m²** of adhesion energy

- $\Rightarrow b < 250 \mu\text{m}$
- $\Rightarrow \text{Curvature} < 0,05 \text{ m}^{-1}$
- $\Rightarrow \text{Curvature radius} > 20 \text{ m}$

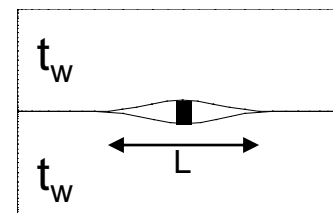
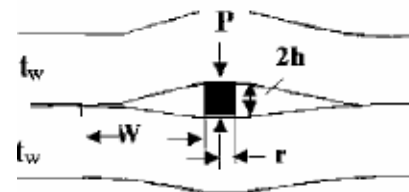
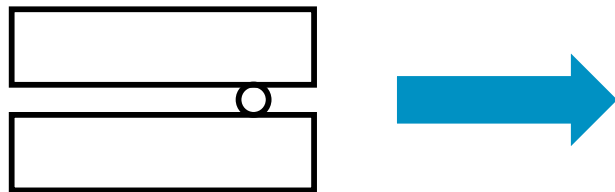


For 200mm wafer ($725\mu\text{m}$), **50 mJ/m²** of adhesion energy, $\lambda=1\text{cm}$

$\Rightarrow P < 1\mu\text{m}$

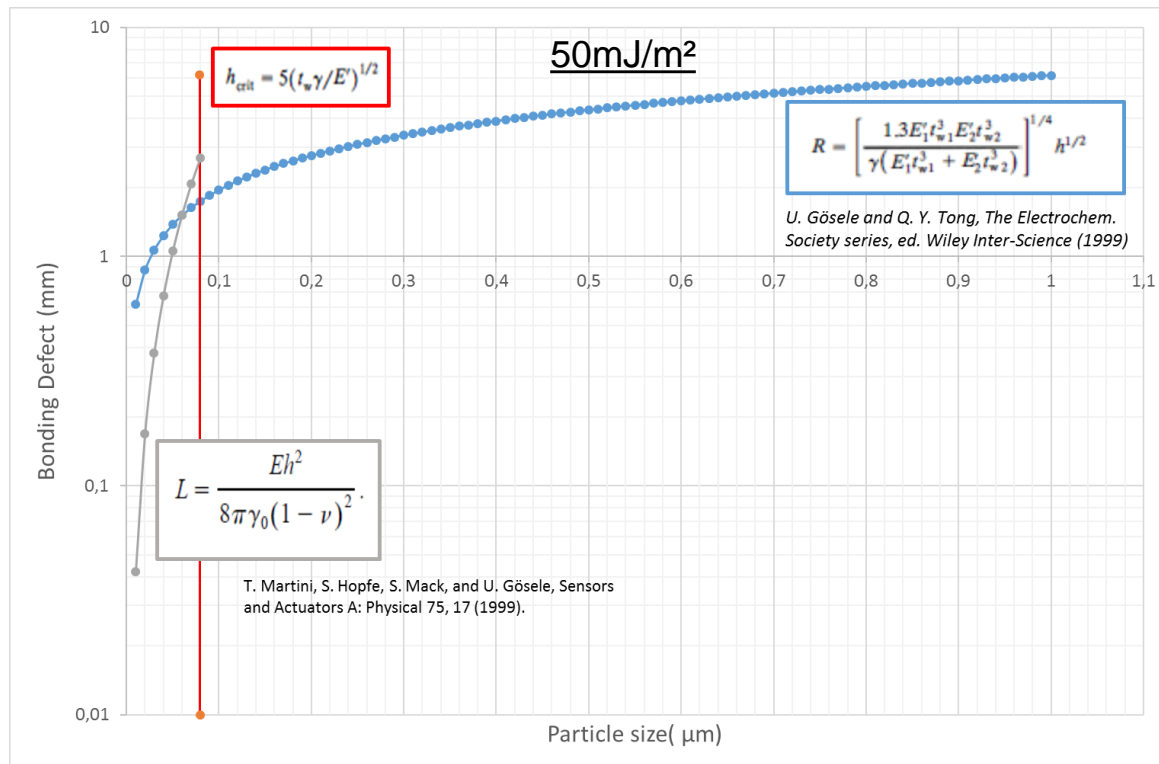


Low particle contamination



Height	500nm	1µm
Adhesion Energy mJ/m ²	80	90
Average radius	3,4mm	5,4mm

LETI 2010



Physical preparation

1. Bow, planarity (250 μ m sur 200mm & 1 μ m/1cm)
2. Micro Roughness => Adhesion energy
(hydrophilic 5 \AA RMS, hydrophobic 2.5 \AA RMS)
3. Particle contamination

Chemical preparation

4. Organic contamination
5. Surface bonds (Si-OH, Si-H...) => Adhesion energy
- (6. Surface / sub-surface modification)

⇒ The right chemistry

⇒ Particle removing

⇒ “Cleaning just before bonding”

For thick substrates:

Tensile test

Shearing test

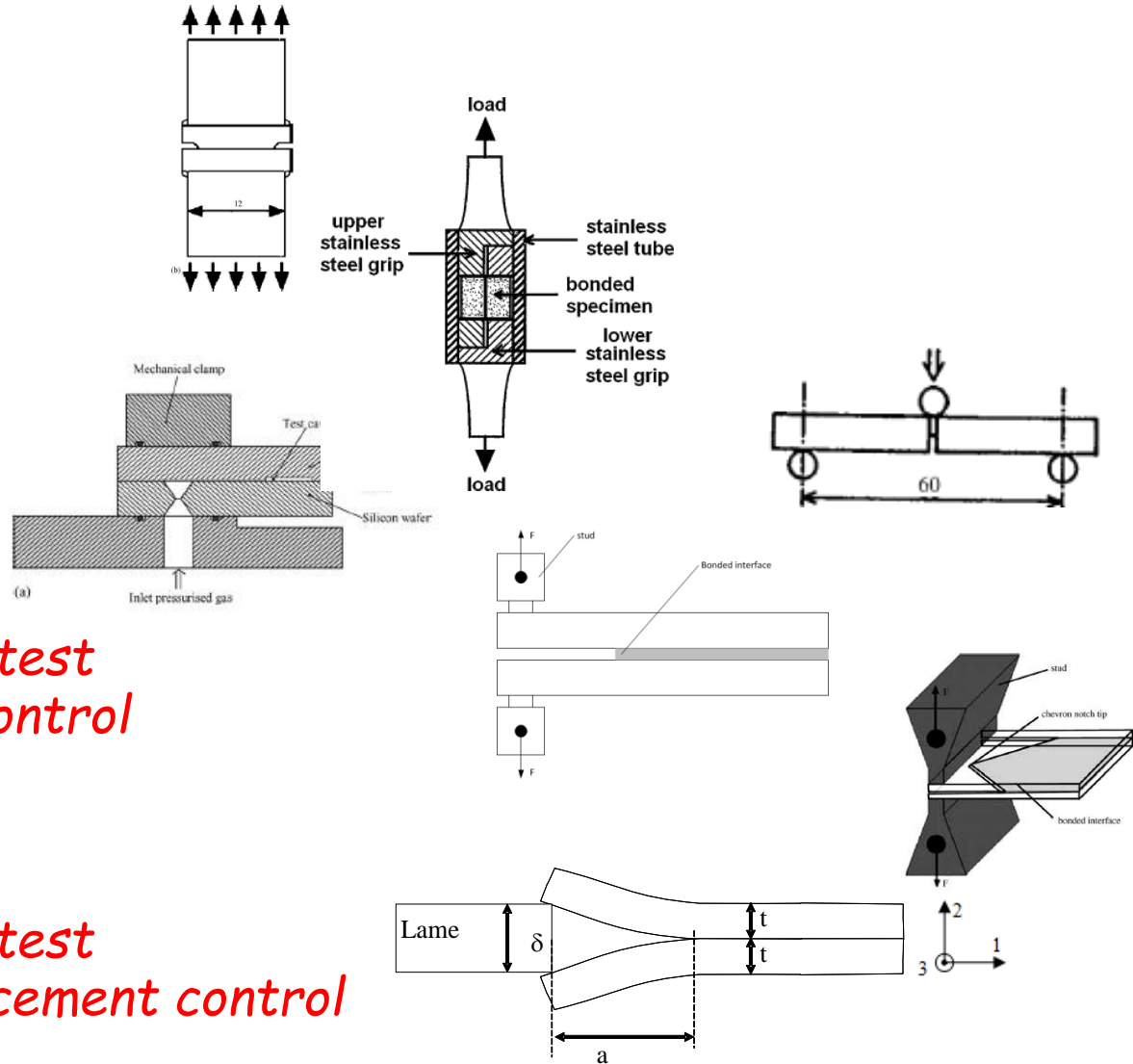
3 ou 4 bending points

« Blister » test

Double cantilever beam test
under prescribed load control

Chevron test

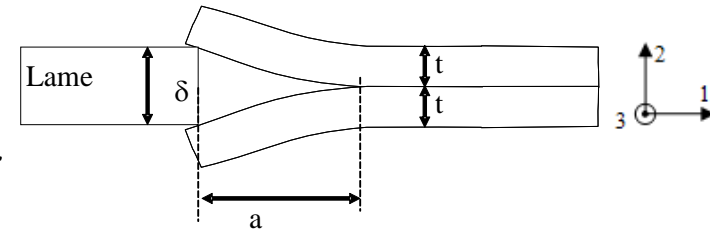
Double cantilever beam test
under prescribed displacement control



M. S. El-Zein et al., *J. of Composites Technology and Research* 10(4) pp.151-155 (1988).

Mathematic Models:

Maszara, El-Zein, Gillis, Williams, Srawley, Kanninen...



El-Zein : S_{ij} for anisotropy $\Rightarrow \beta_{ij}$ for plan strain assumption

$$\beta_{ij} = S_{ij} - \frac{S_{i3}S_{j3}}{S_{33}}$$

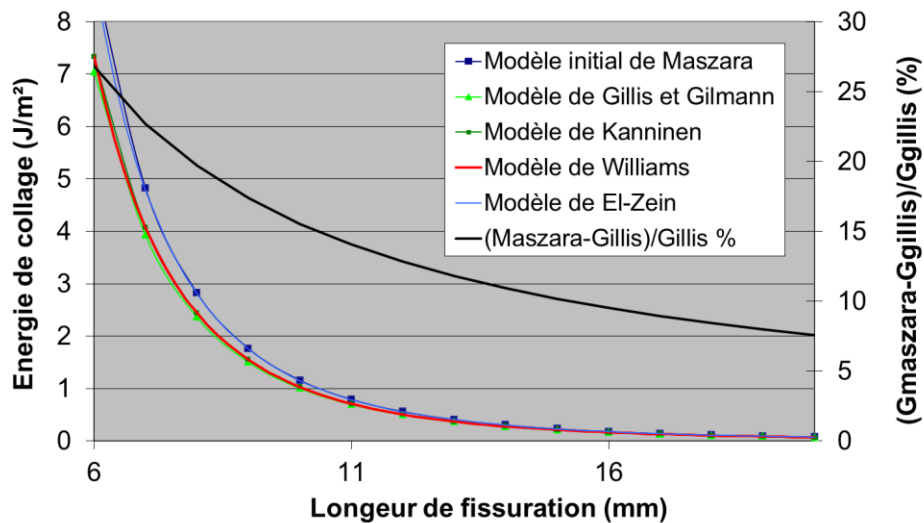
$$C_0 = \frac{24}{wt^3} \left(\frac{\beta_{11}a^3}{3} - \frac{\beta_{26}t^3}{24} \right) \quad G = \frac{3}{8} \frac{\delta^2}{a^4} \frac{\frac{\beta_{111}}{t_1^3} + \frac{\beta_{211}}{t_2^3}}{\left[\frac{\beta_{111}}{t_1^3} \left(1 - \frac{\beta_{126}t_1^3}{8\beta_{111}a^3} \right) + \frac{\beta_{211}}{t_2^3} \left(1 - \frac{\beta_{226}t_2^3}{8\beta_{211}a^3} \right) \right]^2}$$

For orthotropic materials (Si beam $\langle 001 \rangle / \langle 110 \rangle$) : $\beta_{26} = 0 \Rightarrow \sim$ Maszara:

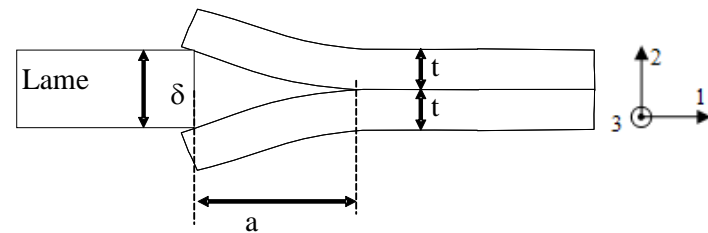
$$\frac{1}{\beta_{11}} = \frac{1}{S_{11} - \frac{S_{13}S_{13}}{S_{33}}} = \frac{1}{S_{11} - \frac{S_{13}S_{31}}{S_{33}}} = \frac{1}{S_{11} \left(1 - \frac{S_{13}}{S_{11}} \frac{S_{31}}{S_{33}} \right)} = \frac{1}{E_{11} (1 - \nu_{13}\nu_{31})} = \frac{E_{11}}{(1 - \nu_{13}^2)}$$

$$G = \frac{3\delta^2}{8a^4} \frac{E_1^* t_1^3 E_2^* t_2^3}{E_1^* t_1^3 + E_2^* t_2^3} \quad E_i^* = \frac{E_{i,11}}{1 - \nu_{13}^2}$$

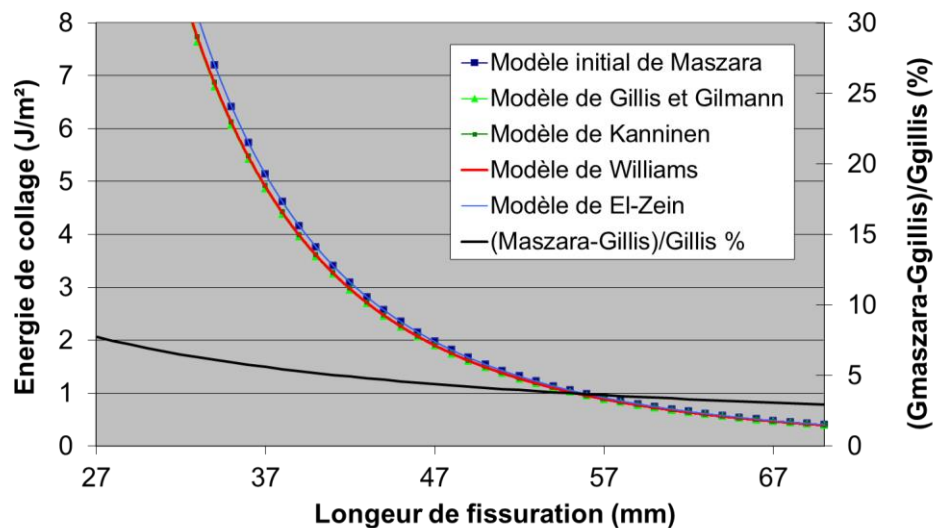
Mathematic models:



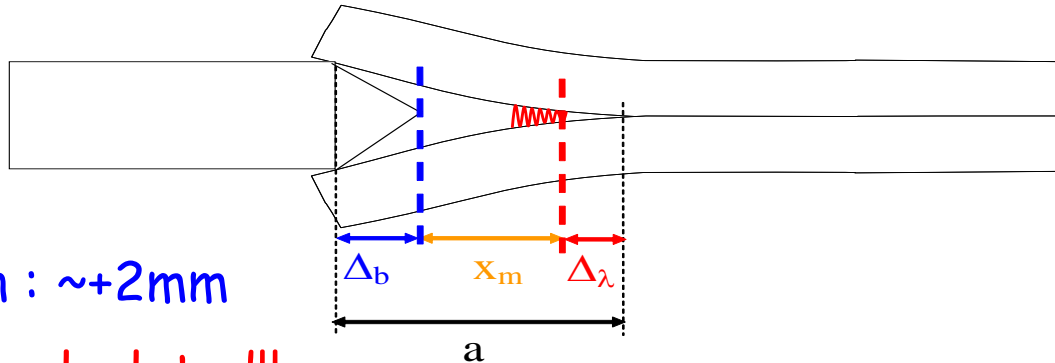
Thin blade : 50µm
Thin wafers : 525µm



Thick blade : 640µm
200mm Si wafers: 725µm



Measurement protocol:



Δ_b : known : $\sim +2\text{mm}$

Δ_λ : to be calculated!!

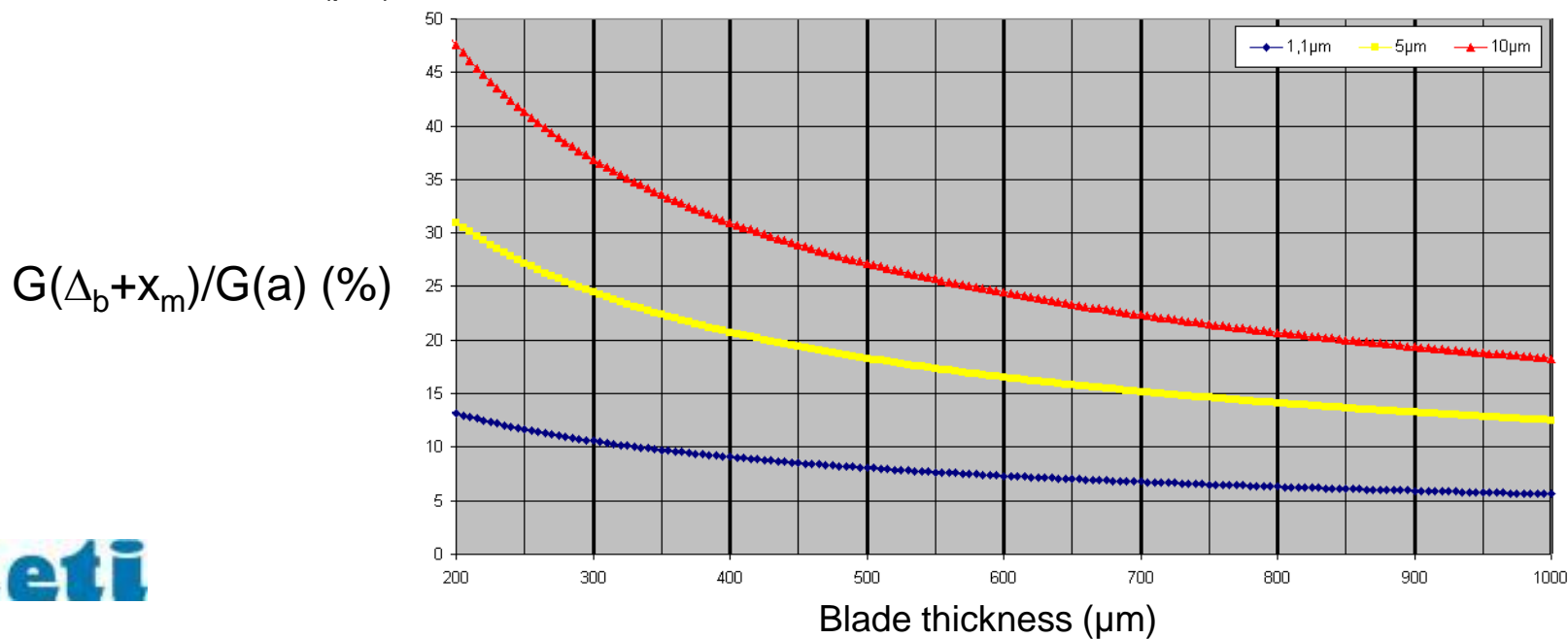
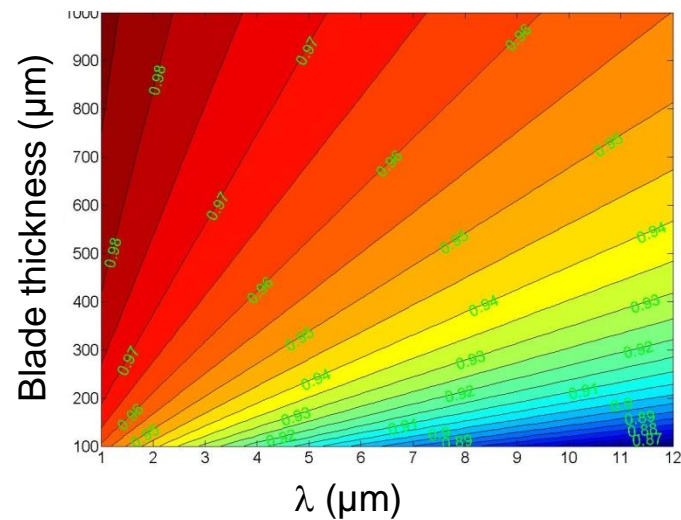
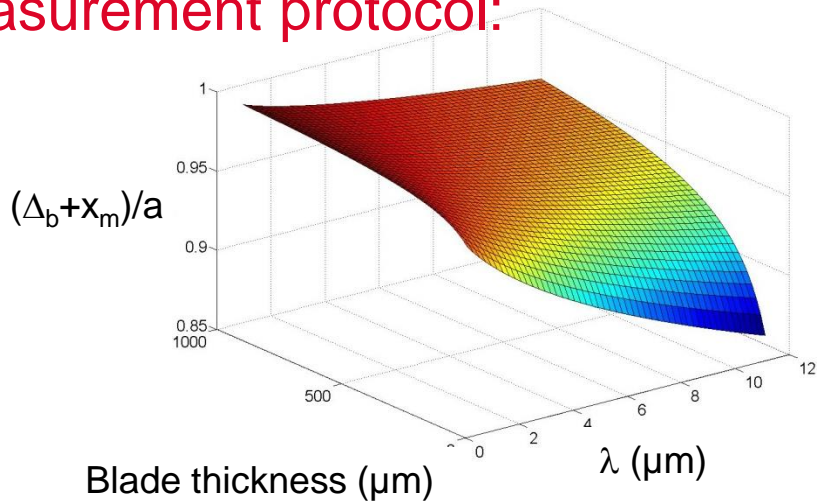
Timoshenko beam equation:

$$d_m = \frac{\delta}{4} \left[2 - \frac{3x_m}{a} + \left(\frac{x_m}{a} \right)^3 \right] = \frac{\lambda}{8}$$

El-Zein beam equation (two different anisotropic beams):

$$z^3 - \frac{3x_m^2}{4 \left(1 - \frac{\lambda}{4\delta} \right)^2} z - \frac{x_m^3}{4 \left(1 - \frac{\lambda}{4\delta} \right)^3} + \frac{x_m^3}{2 \left(1 - \frac{\lambda}{4\delta} \right)} - \frac{3x_m}{8 \left(1 - \frac{\lambda}{4\delta} \right)} \frac{\left(\frac{(\beta_{12})_1}{t_1} + \frac{(\beta_{12})_2}{t_2} \right)}{\left(\frac{(\beta_{11})_1}{t_1^3} + \frac{(\beta_{11})_2}{t_2^3} \right)} - \frac{1}{8} \frac{(\beta_{26})_1 + (\beta_{26})_2}{\left(\frac{(\beta_{11})_1}{t_1^3} + \frac{(\beta_{11})_2}{t_2^3} \right)} = 0$$

Measurement protocol:



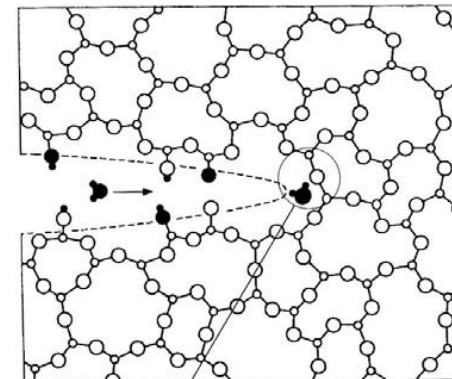
“Stress corrosion cracking (SCC) is the growth of cracks under tensile stress in a corrosive environment.”

For SiO2 (glass, silica...):

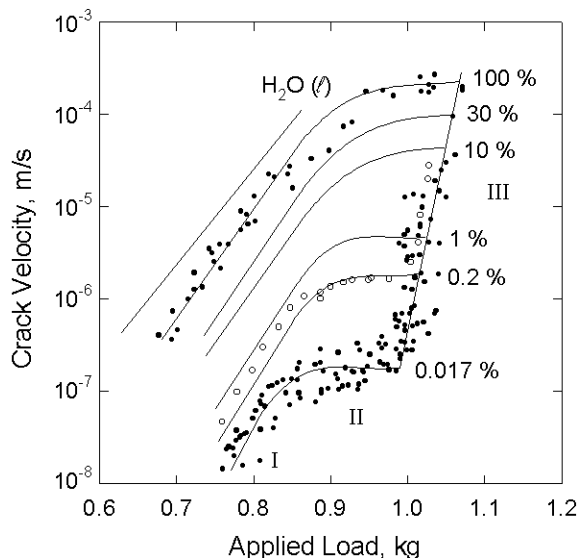
1. Stress => Si-O-Si angle modification => Ionization

2. Specific chemical molecules:

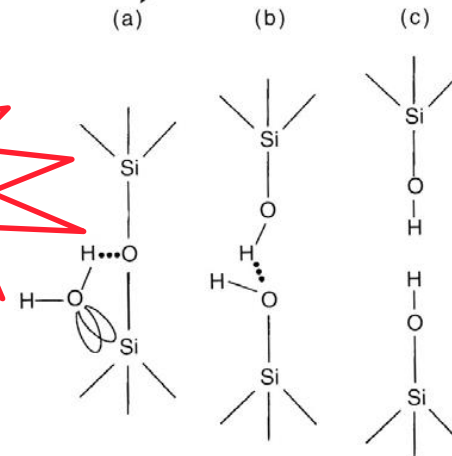
- Lewis basis (electron pair donor)
- Brönsted acid (proton donor)
- Acid-Basis distance \approx Si-O distance (0,163nm)



Example : Soda lime crack growth



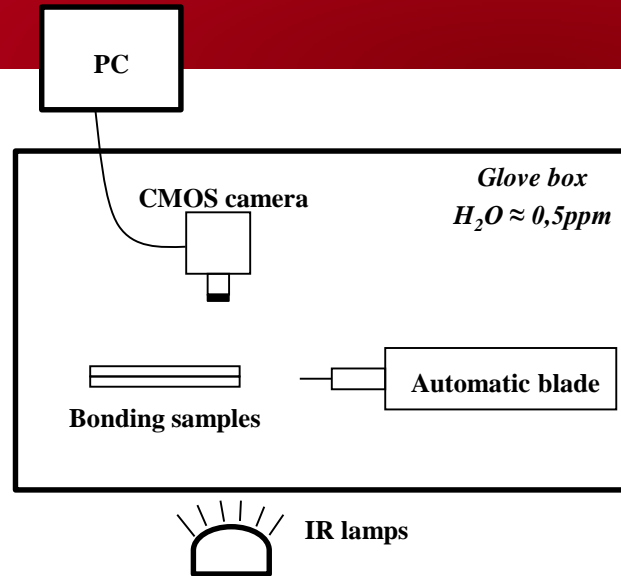
Water is the best



T.A. Michalske and B.C. Bunker, *J. Appl. Phys.* 56(10) p.2666 (1984)

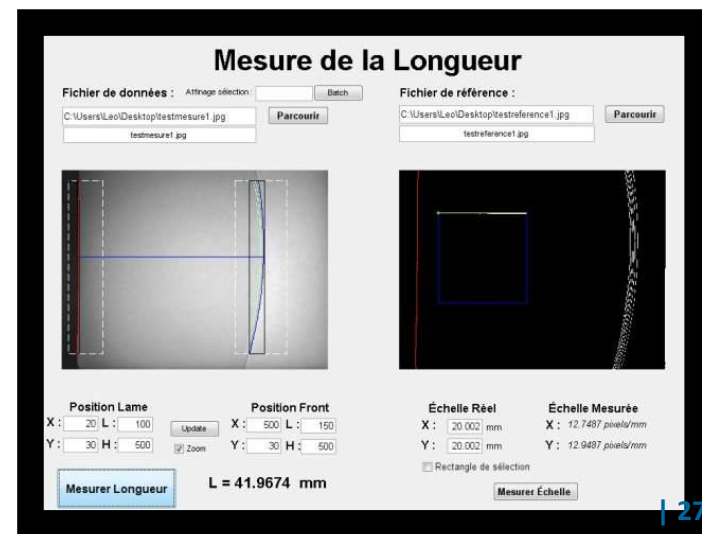
Setup:

Glove box with dessicator

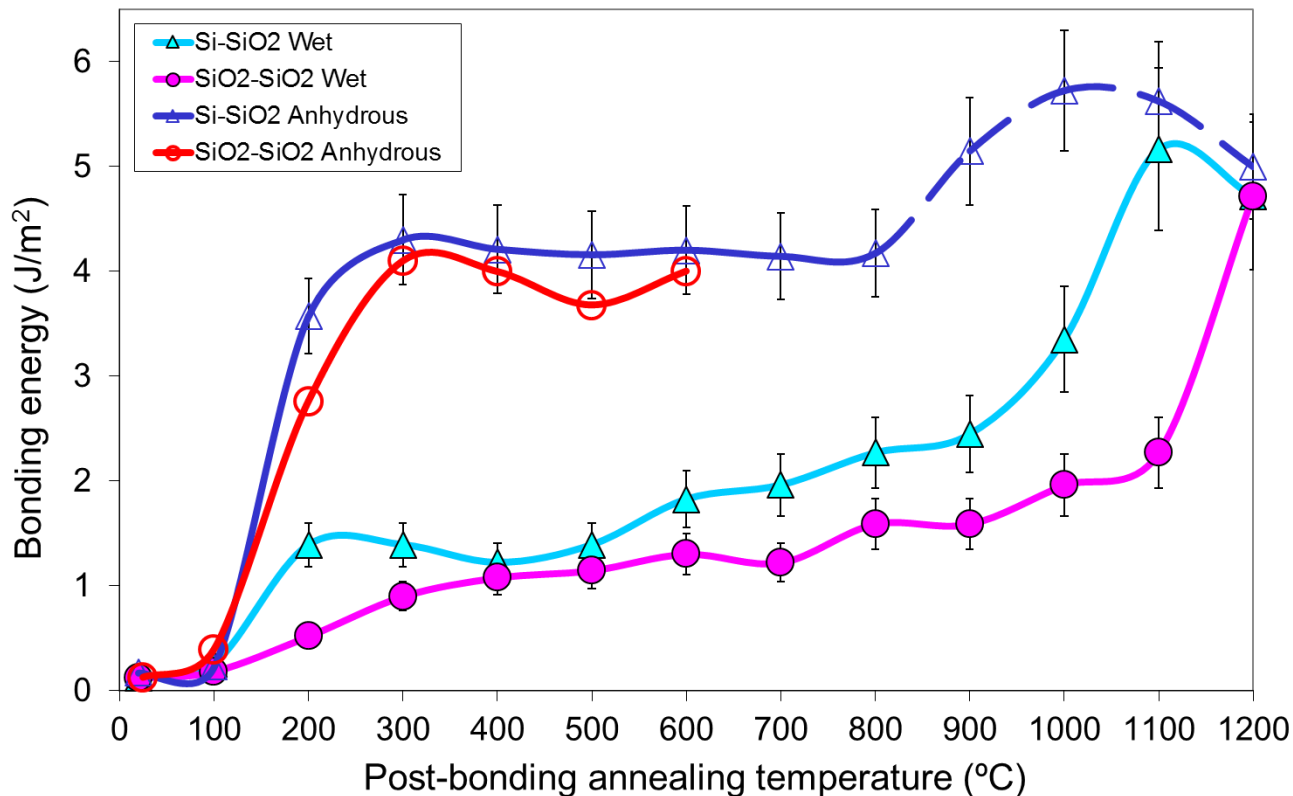


Video recording / processing
homemade software

Automatic blade insertion



Standard hydrophilic bonding



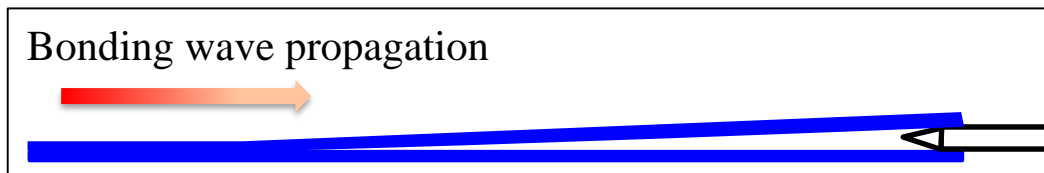
=> Anhydrous bonding energy is:

more «realistic»

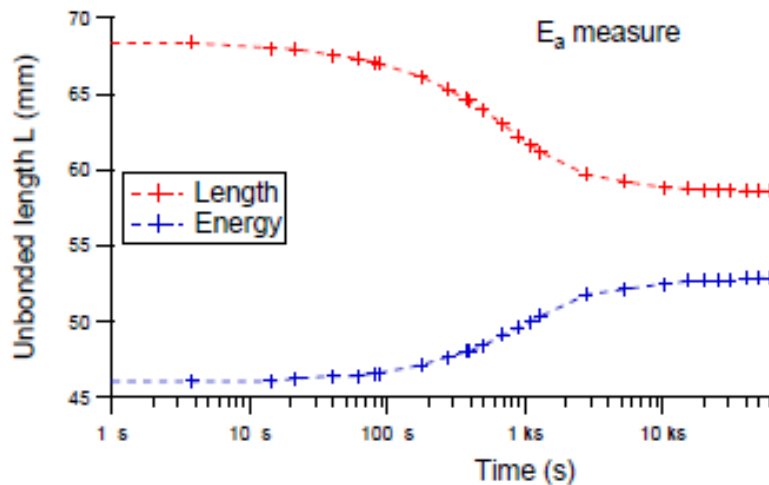
more «discriminating» for mechanism understanding

Adhesion energy measurement:

Modified DCB technique can measure the adhesion energy of chemical Si/Si direct bonding:

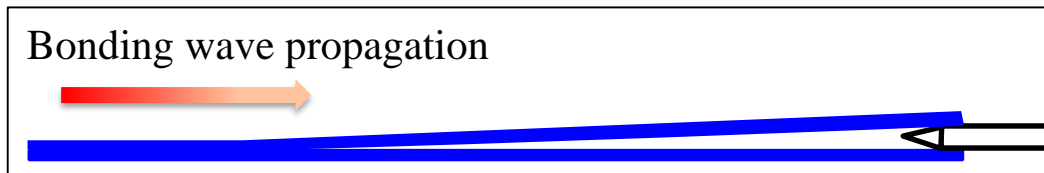


- ✓ Unbounded length
- ✓ El-Zein equation => Adhesion energy

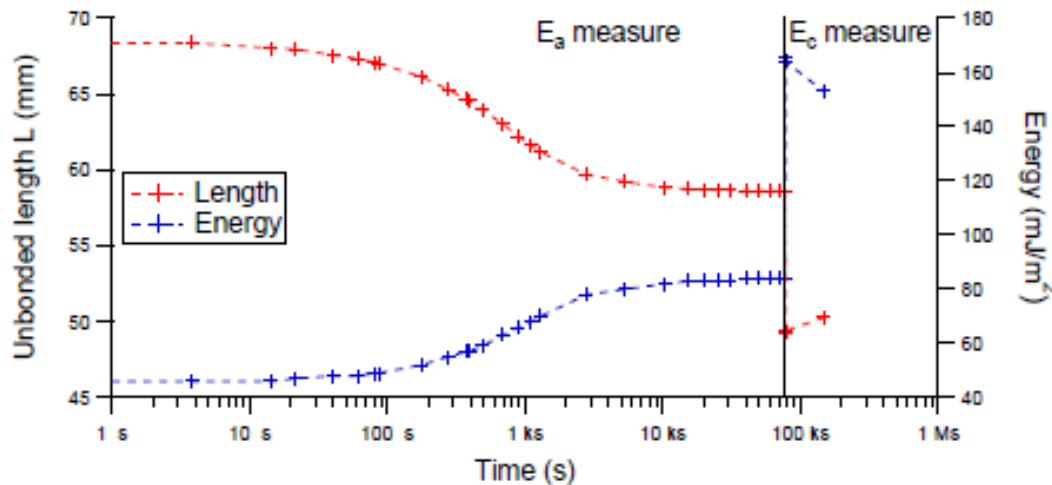


Adhesion energy measurement:

Modified DCB technique can measure the adhesion energy of chemical Si/Si direct bonding:



- ✓ Unbounded length
- ✓ El-Zein equation => Adhesion energy



- ✓ After 4 hours : bonding energy is measured by entering the blade
- => Bonding energy > Adhesion energy

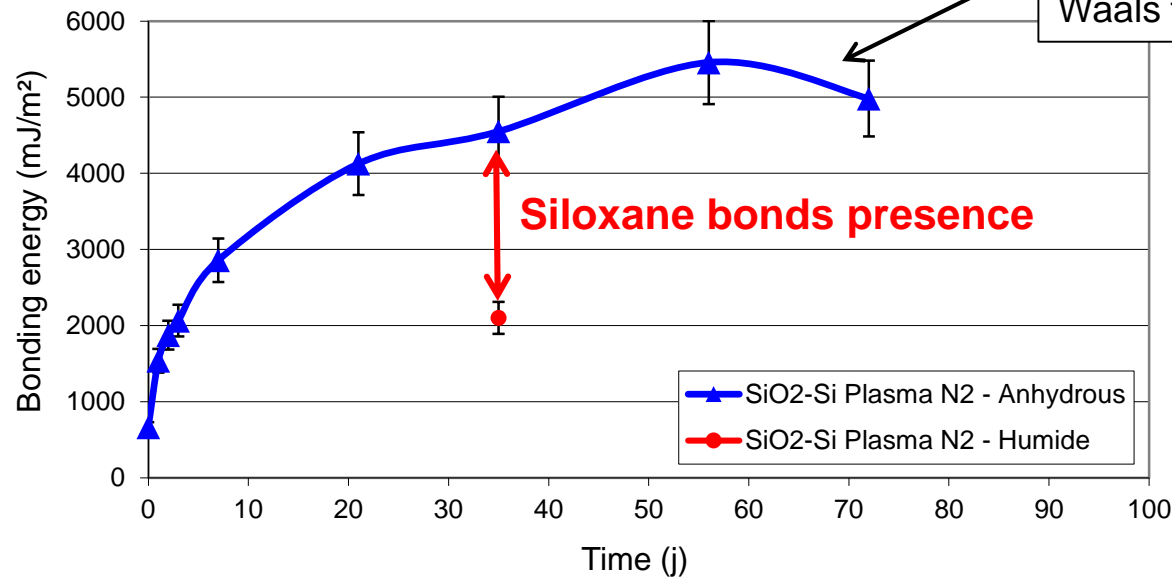
**Siloxane bonds presence @RT
for chemical bonding**

WSC and covalent bonding at room temperature:

N2 plasma Si/SiO2 direct bonding

Storage @ room temperature

Bonding energy measurement

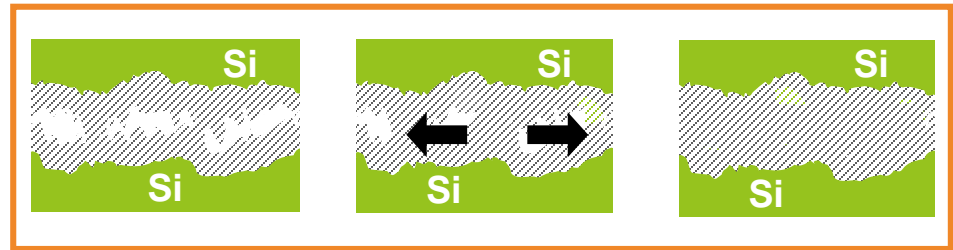
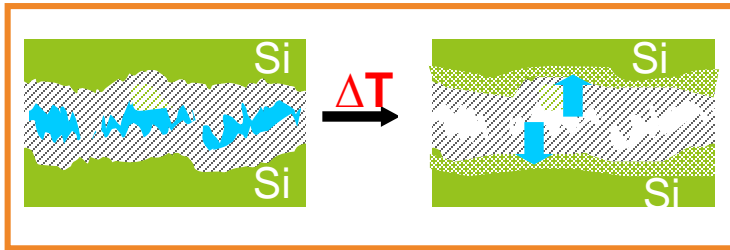
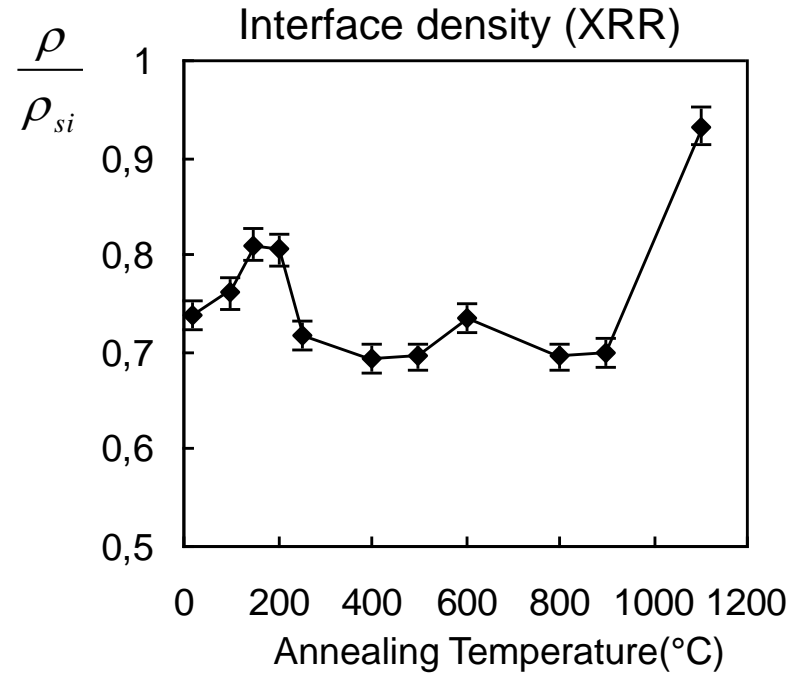
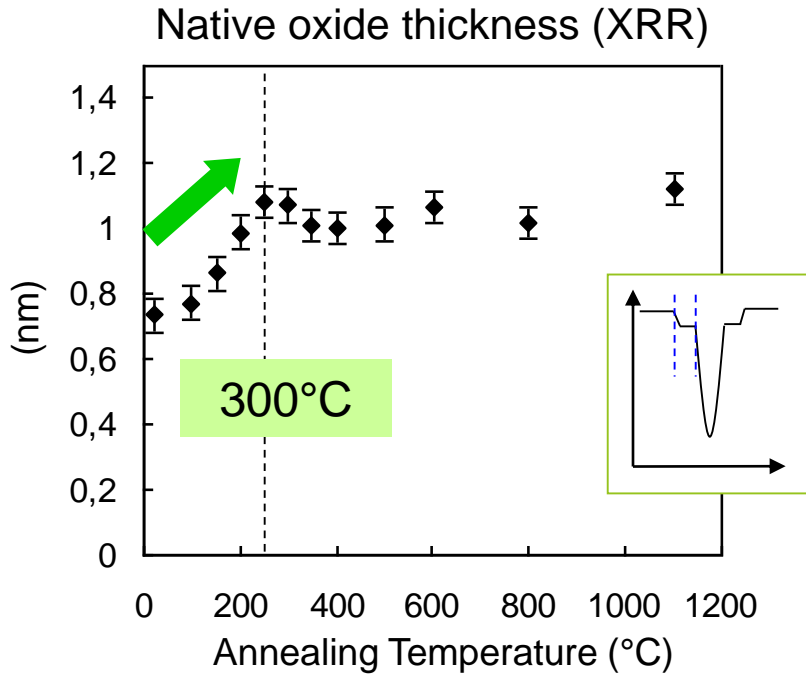


Too important bonding strength for Van der Waals forces

Siloxane bonds presence

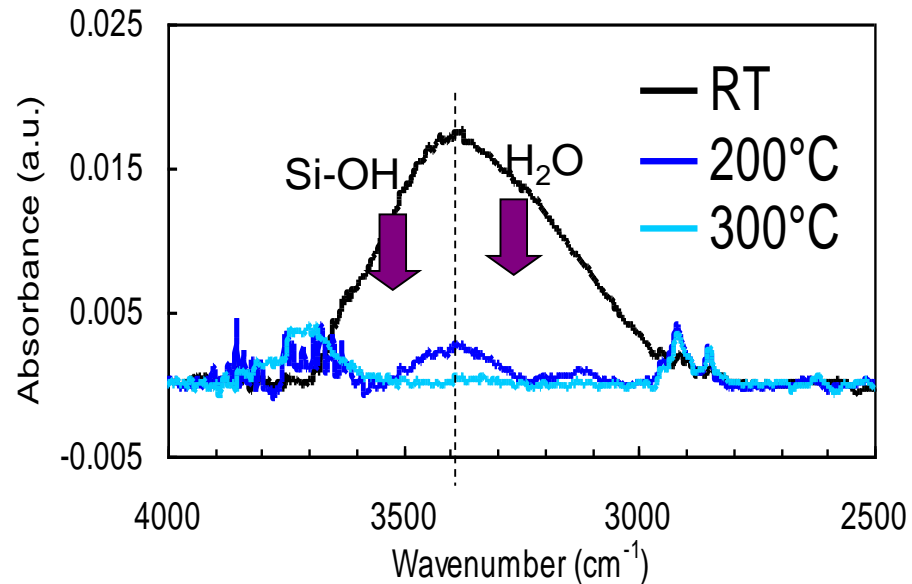
- **Siloxane bonds can thermodynamically appear at room temperature**
- **Mixt of Van Der Waals and Siloxane @RT but Siloxane hardly visible!**
 - Too few contact point?
 - Trapped water which induce internal WSC?

Si-Si hydrophilic bonding

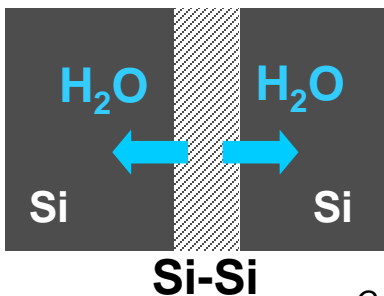


Si-Si hydrophilic bonding

FTIR-MIR: O-H absorption band



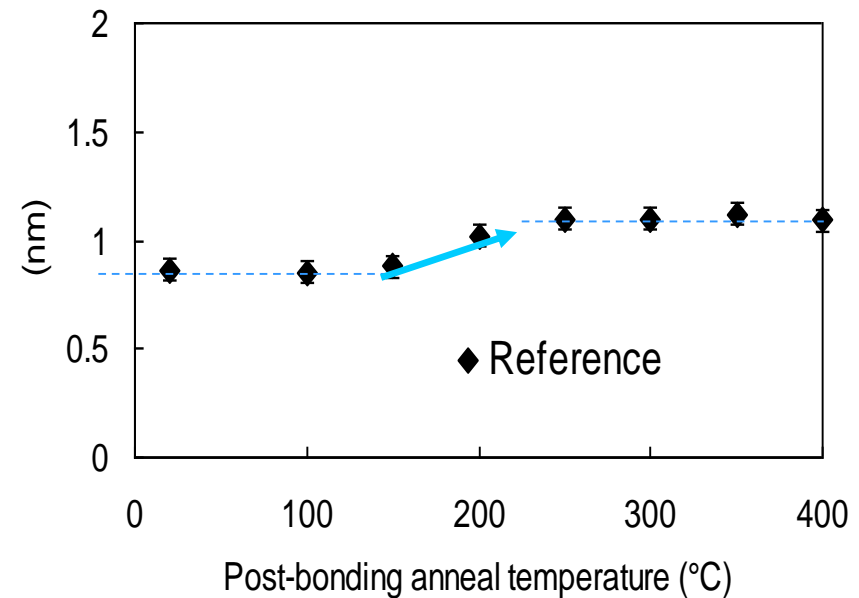
✓ Disappearing of the O-H band at 200°C and 300°C post-bonding anneal



Silicon oxidation through the reaction $\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2$

Main source of voids at the bonding interface

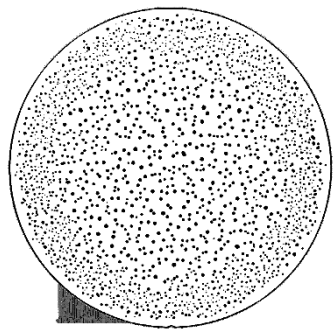
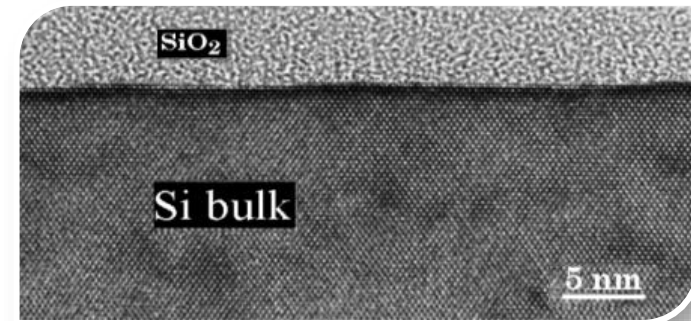
XRR: oxide film thickness



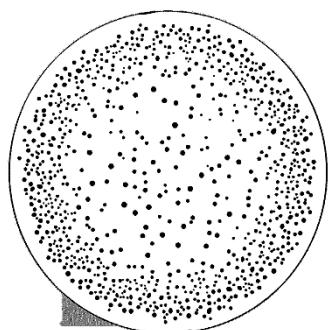
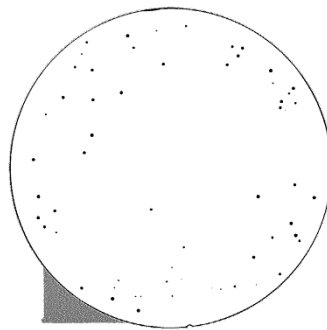
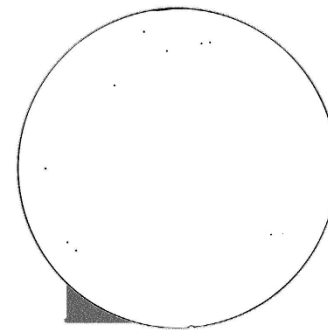
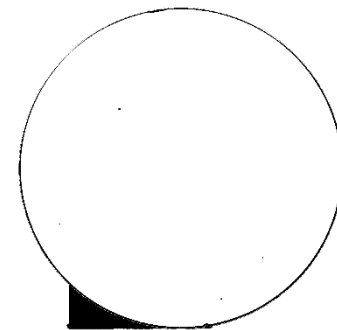
✓ Increase of oxide film thickness

Si-SiO₂ hydrophilic bonding

⇒ SiO₂ layer can store the hydrogen
... if the layer is thick enough!

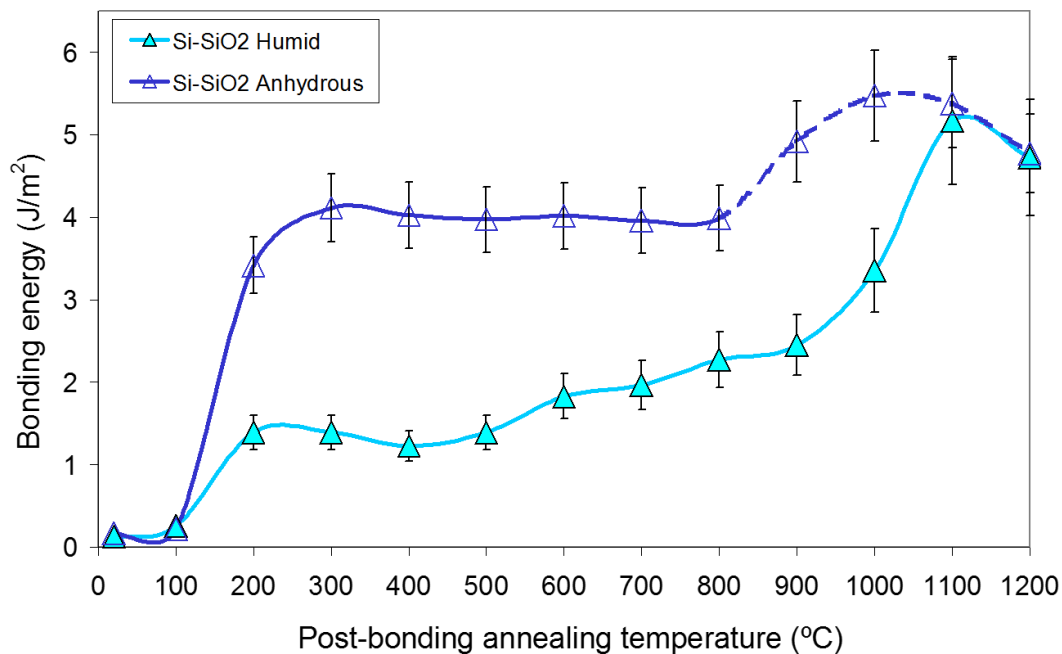
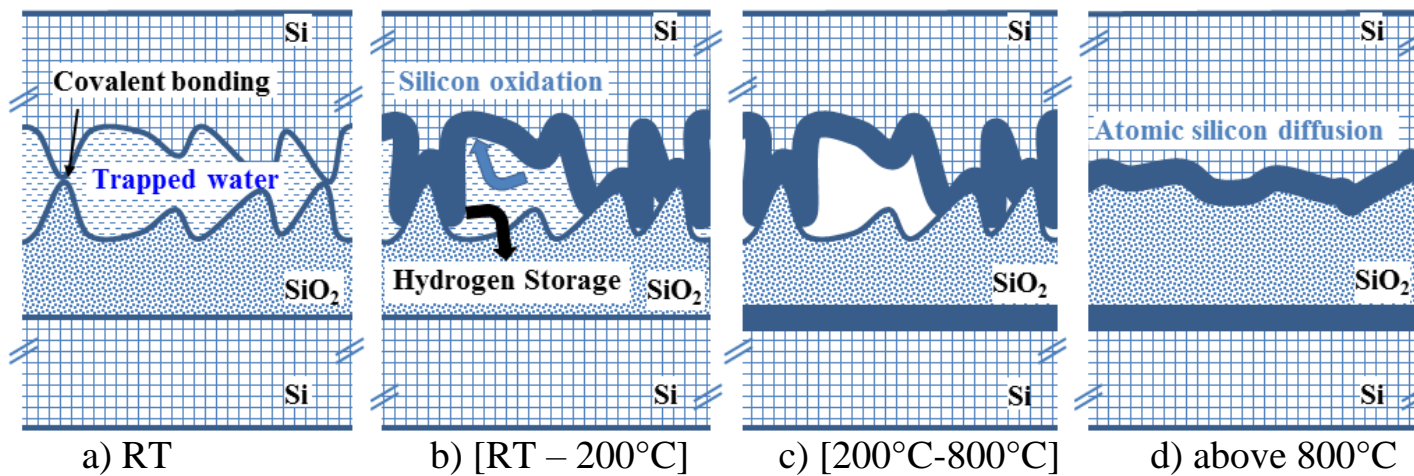


Si/Si

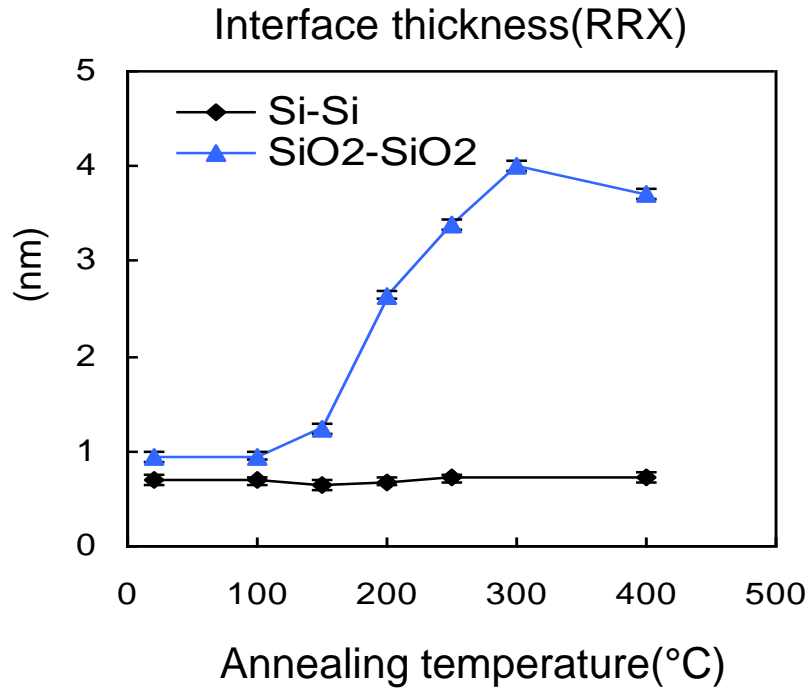
Si/SiO₂ 12nmSi/SiO₂ 25nmSi/SiO₂ **50nm**Si/SiO₂ 100nm

This bonding type is really depending of the last cleaning step

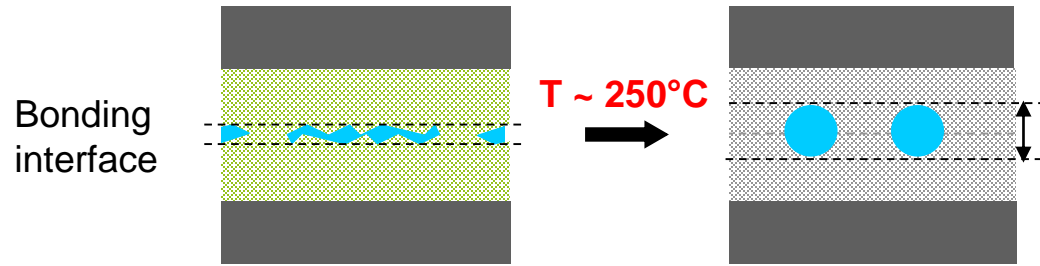
SI/SiO₂ BONDING MECHANISM



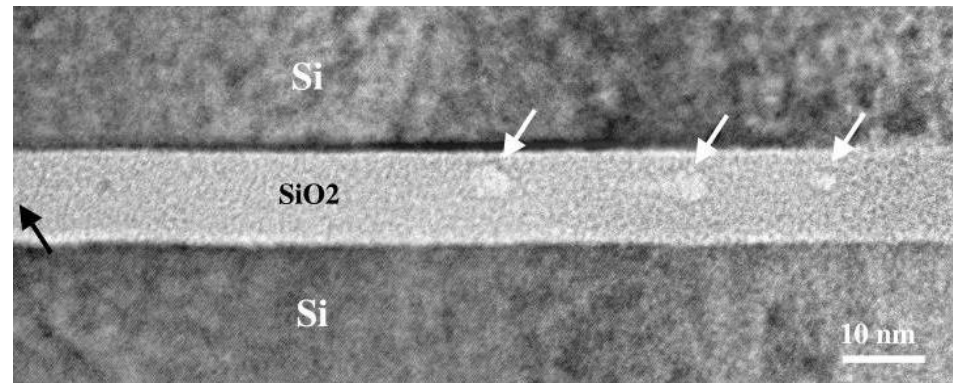
SiO₂-SiO₂ hydrophilic bonding



➤ **Oxide layer is a water barrier layer**

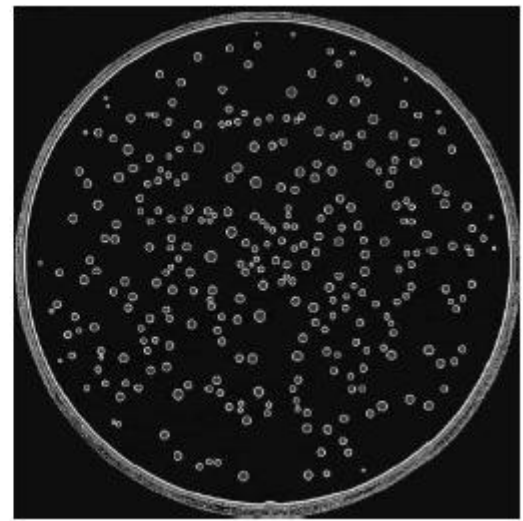
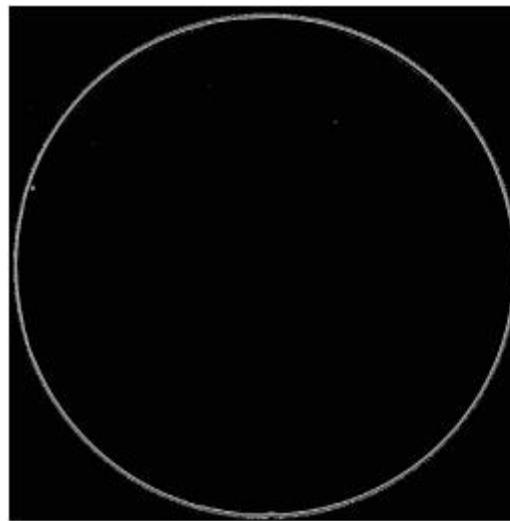


TEM : LETI/DPTS



SiO₂-SiO₂ hydrophilic bonding

Thin oxide bonding : 5nm SiO₂- 5nm SiO₂



Annealing temperature(°C) :

400°C

600°C

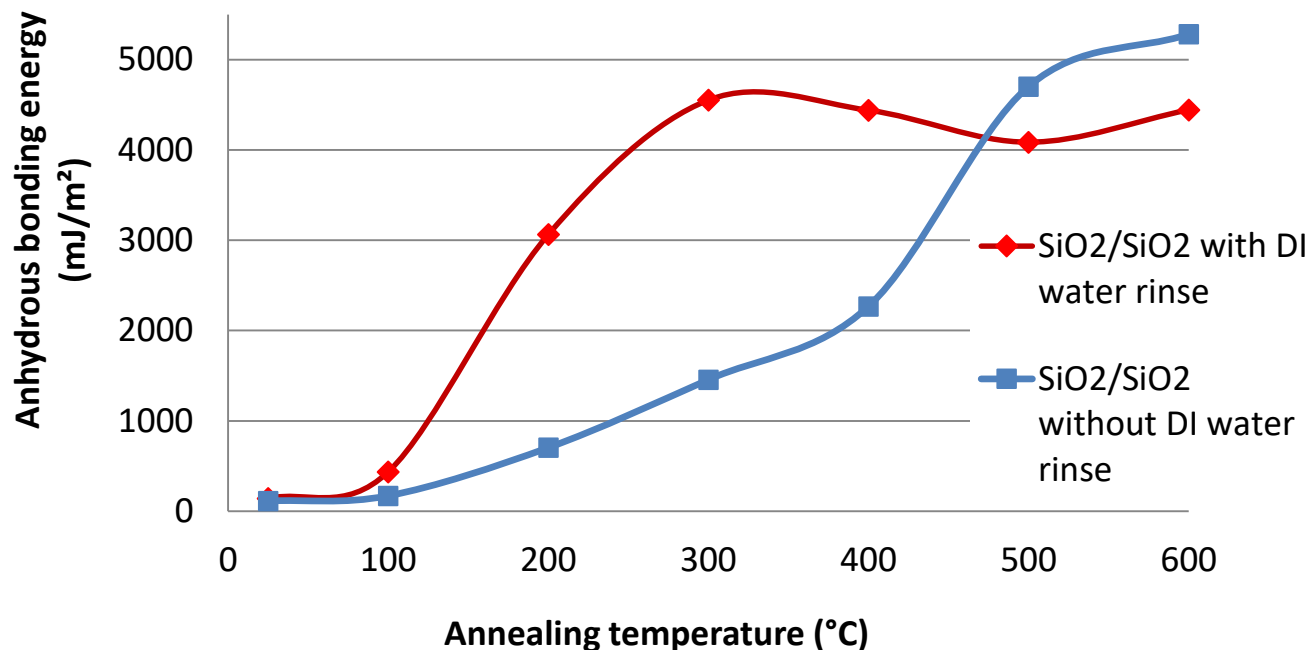
Thermal oxide is a water barrier until 600°C.

SiO₂ surface cleaning with N₂ dryer

=> "dry" SiO₂ surface

Adding DI-water rinse

=> "wet" SiO₂ surface



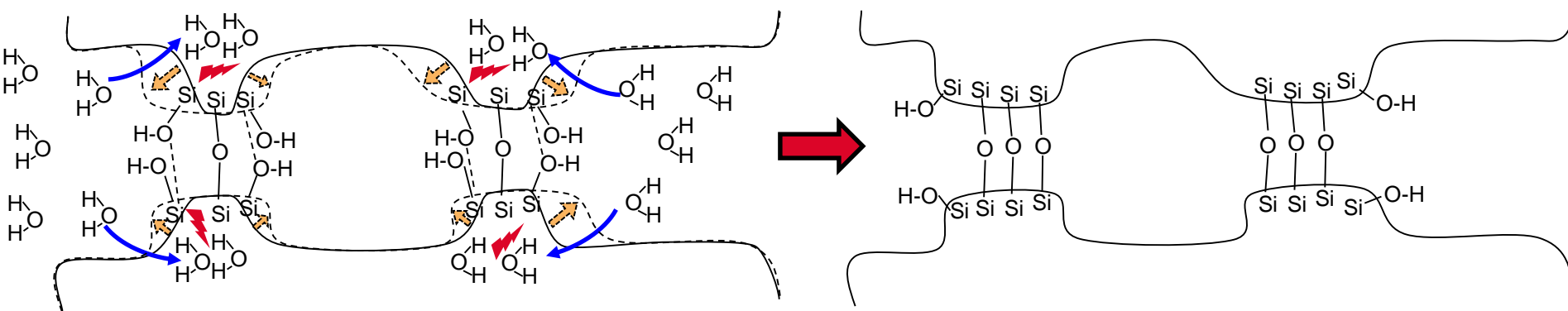
⇒ **Water is an adherence promoter**

□ Water stress corrosion during annealing:

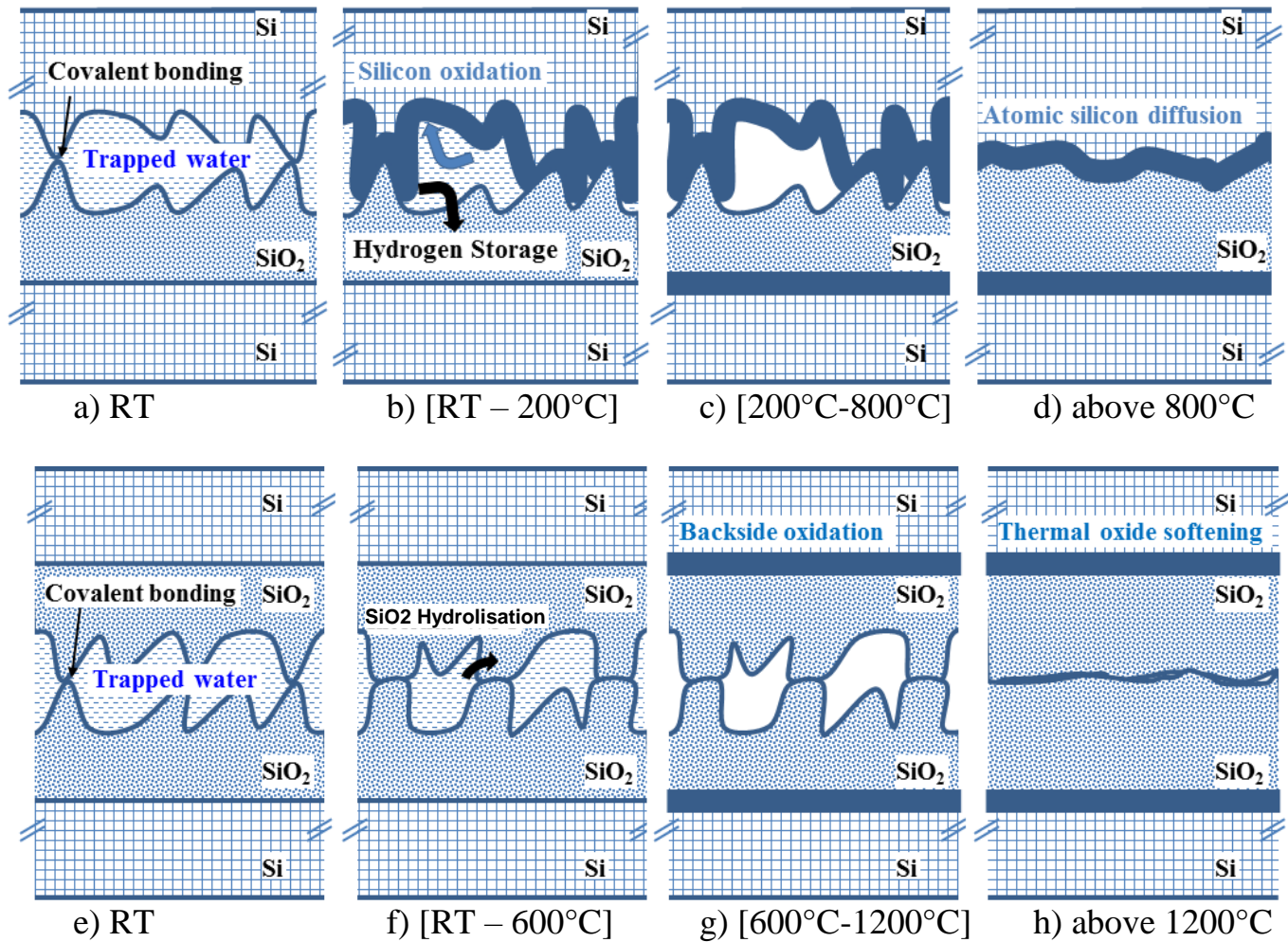
- @ RT few silanol bonds
- **With temperature** : water penetration inside SiO₂ asperity (→)
- SiO₂ Hydrolysis $\text{Si-O-Si} + \text{H}_2\text{O} \Rightarrow \text{Si-OH}$ (⚡)
- Asperity broadening (→)
- New covalent bonds formation (---)

⇒ More important contact area with covalent bonds

⇒ More important bonding energy

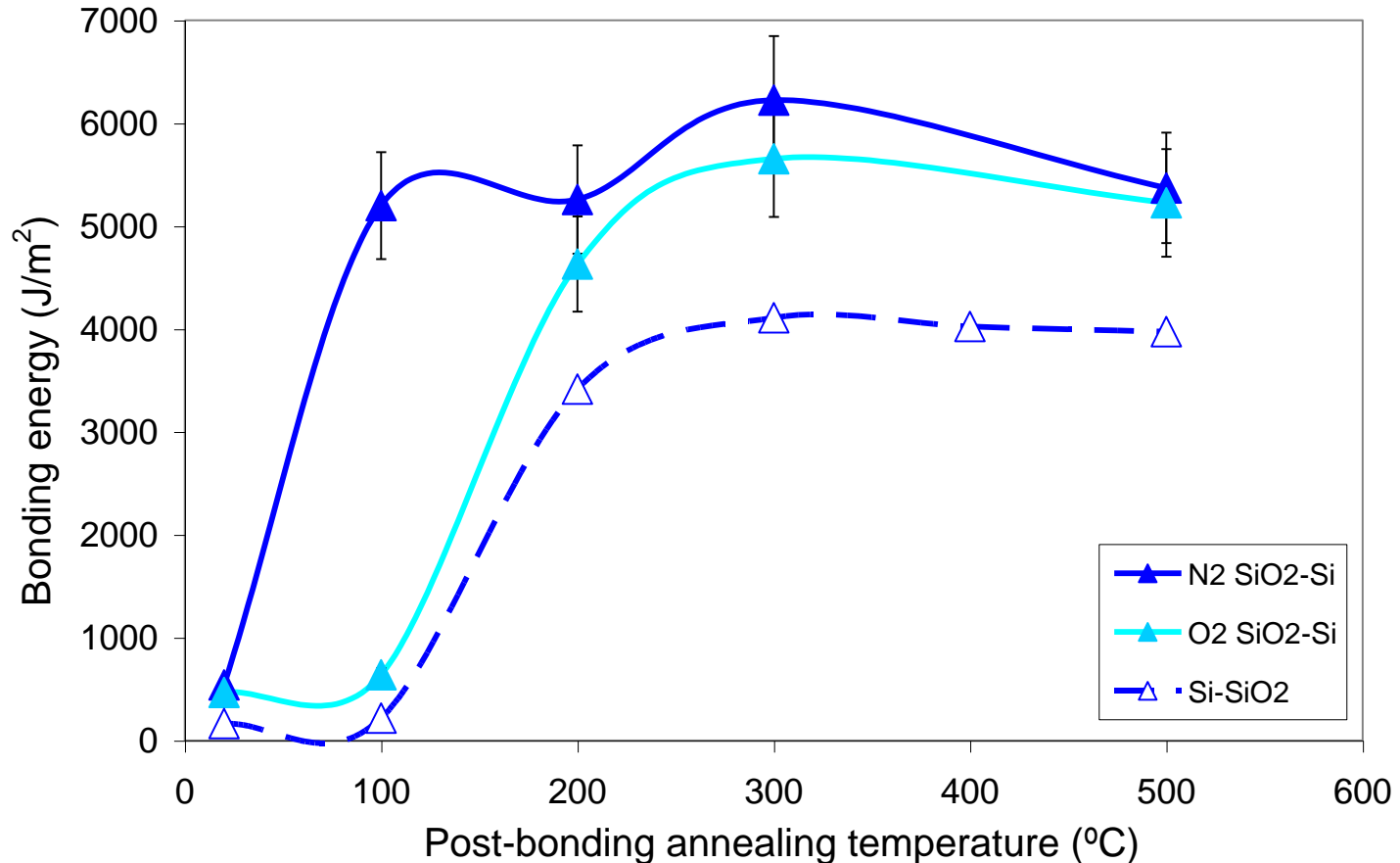


SI/SiO₂ AND SiO₂/SiO₂ BONDING MECHANISM



⇒ Water is an adherence promoter

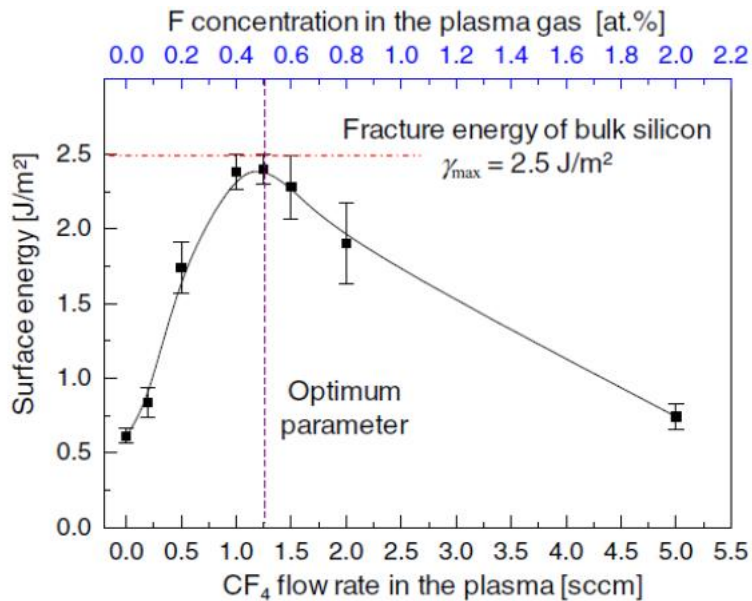
Plasma bonding Si-SiO₂:



=> Si-SiO₂ Plasma N₂ : 5J/m²@100°C

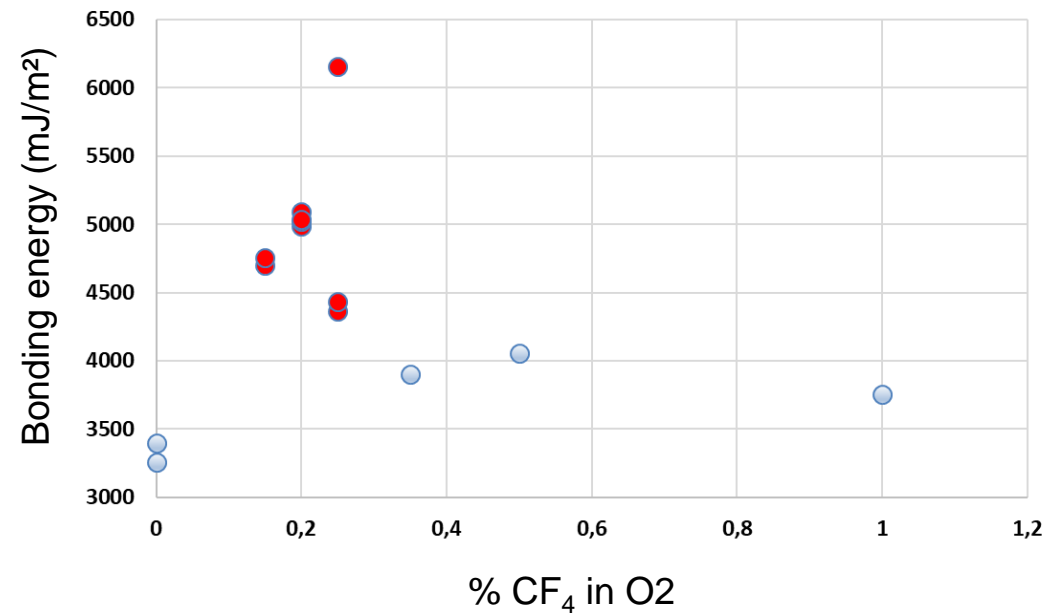
=> Plasma N₂ > Plasma O₂

Fluorine plasma



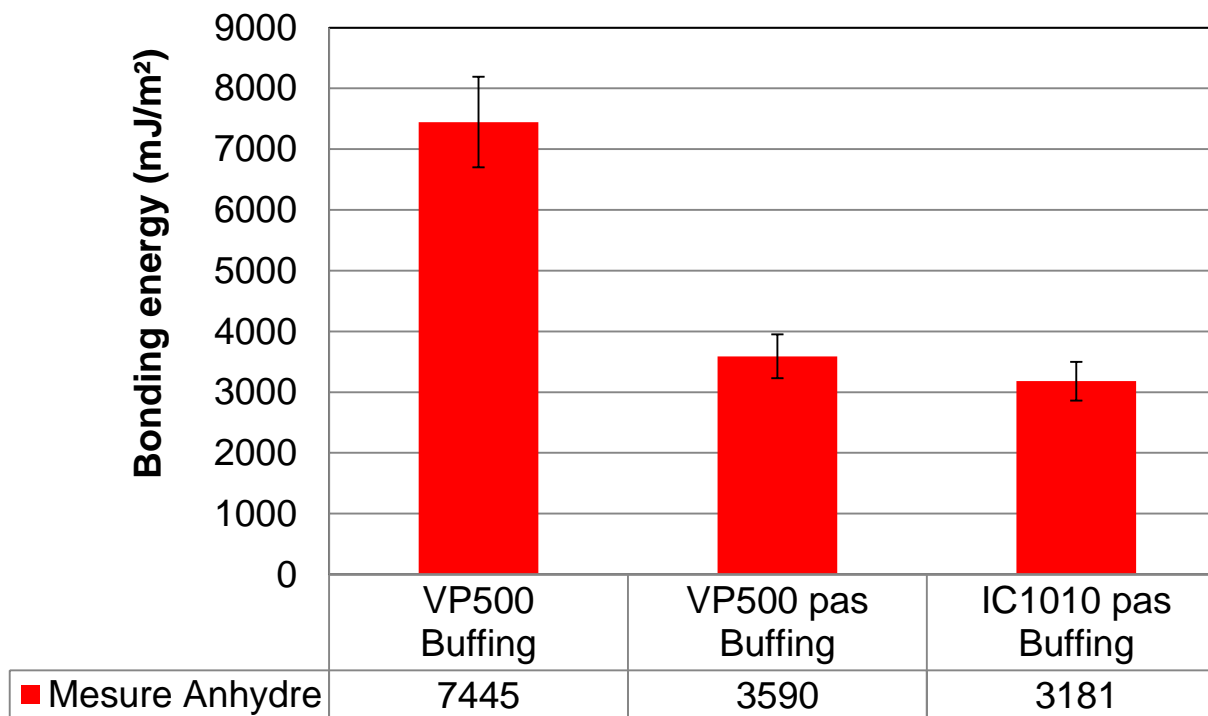
*Wang, C, et al. « Low-Temperature Direct Bonding of Silicon to Quartz Glass Wafer via Sequential Wet Chemical Surface Activation. », *5th LTB-3D conference*, IEEE, Tokyo, Japan, 2017; pp 21–21. <https://doi.org/10.23919/LTB-3D.2017.7947417>.

Annealing temperature : 190°C / 1h

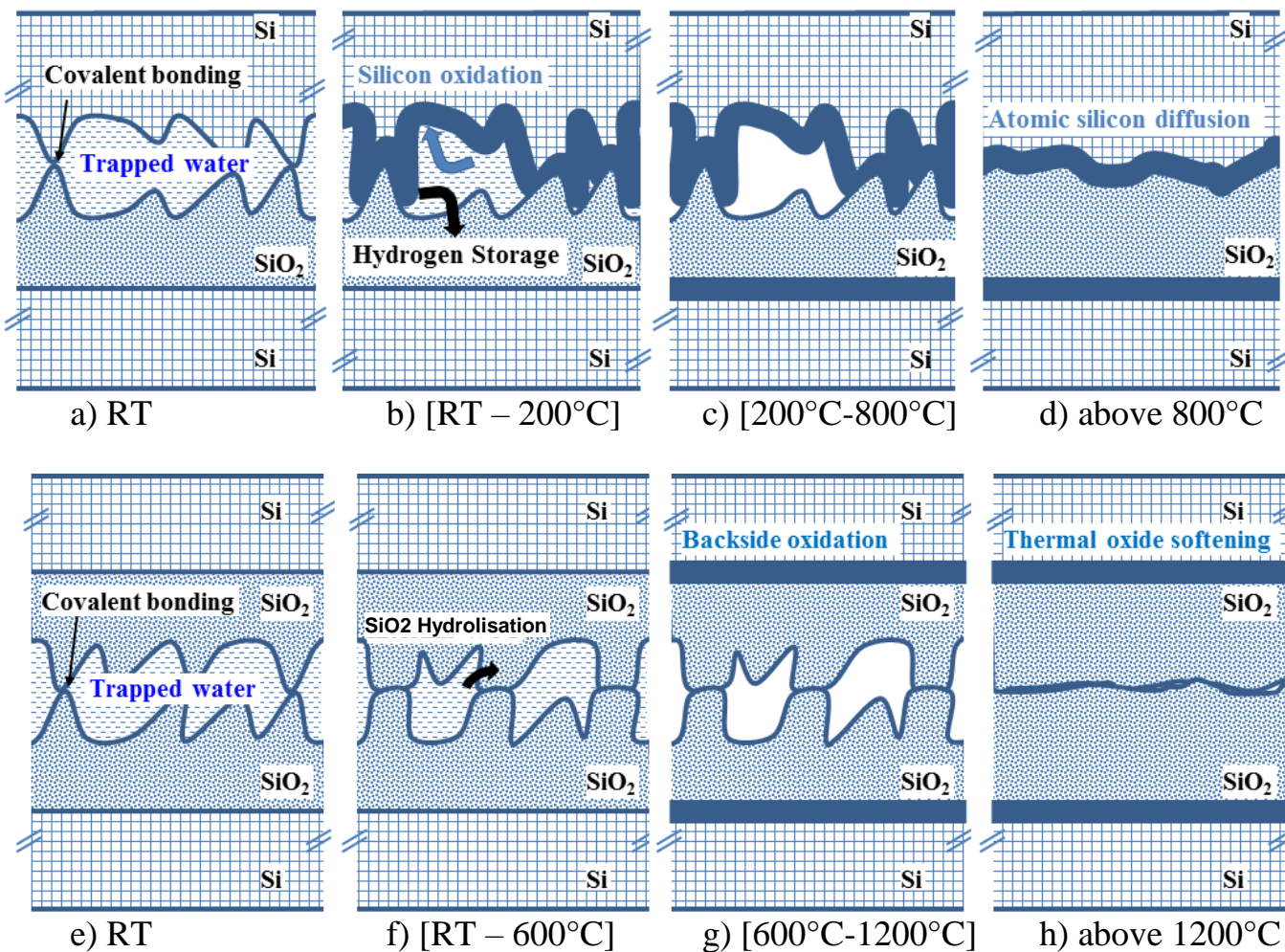


=> HUGE adherence at low temperature

CMP SiO₂//SiO₂:

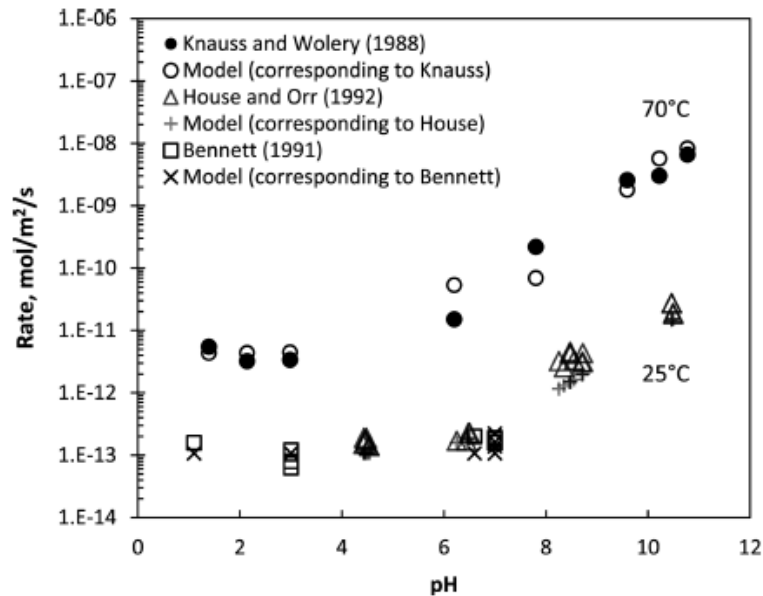


SI/SiO₂ AND SiO₂/SiO₂ BONDING MECHANISM

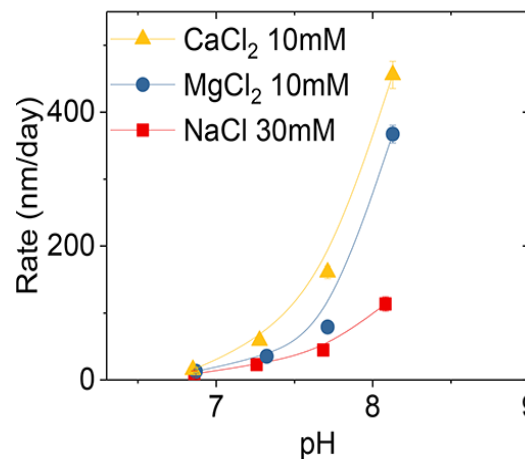


⇒ Water is an adherence promoter

Silica dissolution in basic solution

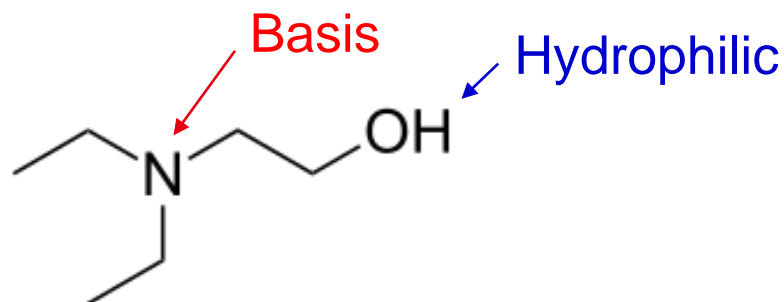


F.K. Crundwell et al., ACS Omega 2, 1116 (2017).

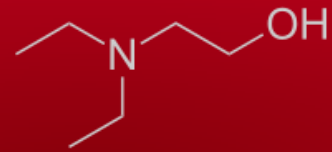


Yoon Kyeong Lee, et al. ACS (9), 49 42633-38 (2017).

N,N-diethylethanolamine (DEAE)



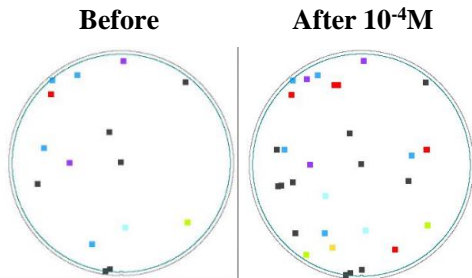
Dissolution is enhance @ high pH
=> Hydrolisation is enhanced @ high pH



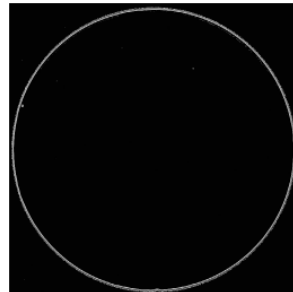
Basic molecule (DEAE):

Deposition on silicon surface

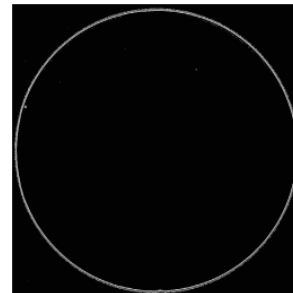
SP2 surfscan @90nm



After annealing

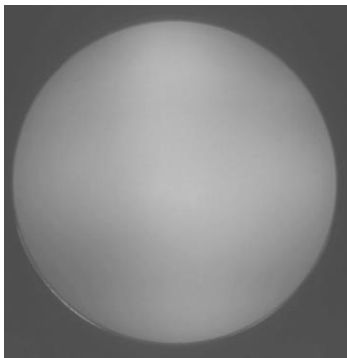


Si//SiO₂ @400°C



Si//SiO₂ @1100°C

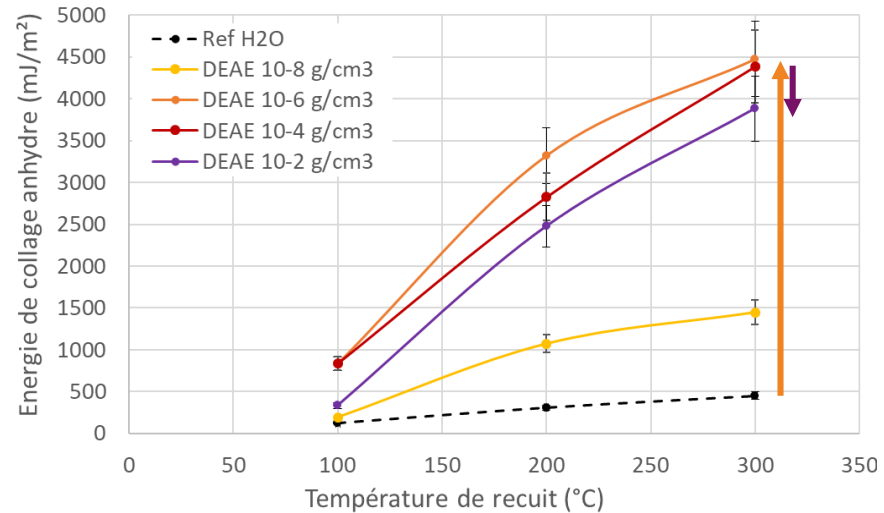
No adhesion impact



leti

⇒ No impact on defectivity
(small amount of molecule)

Adherence with DEAE in SiO₂//SiO₂



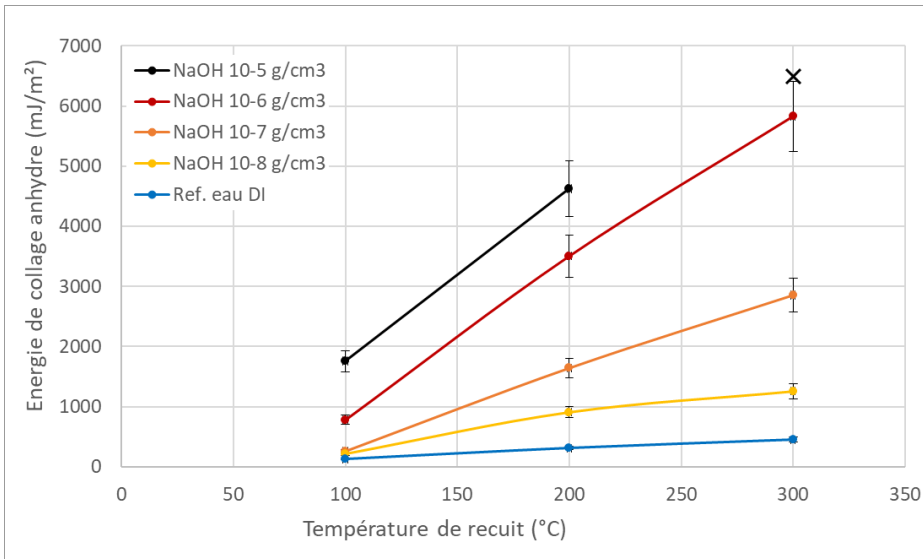
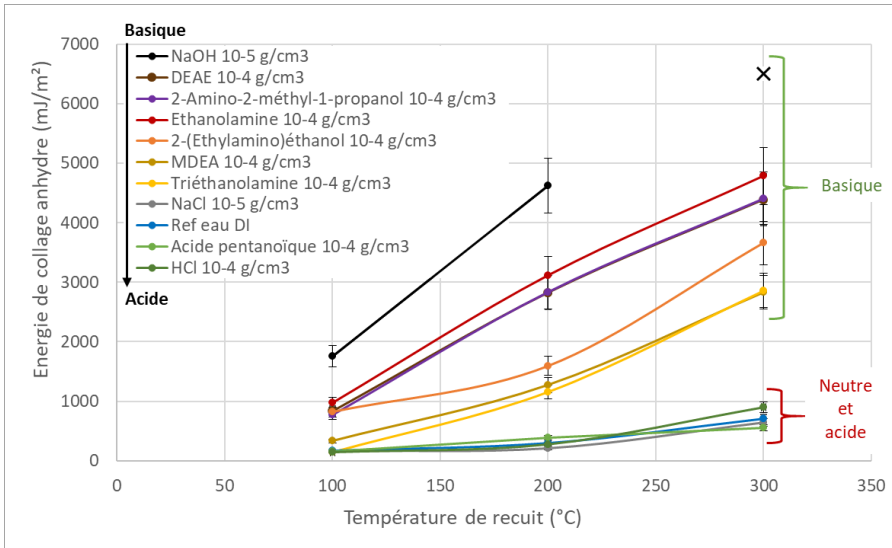
Huge impact on Adherence
⇒ 10⁻⁵ (g/cm³) (~10⁻⁴ M) seems to be a save optimal concentration

*Fournel, F, et al., *ECS Trans.* **2020**, 98 (4), 3.

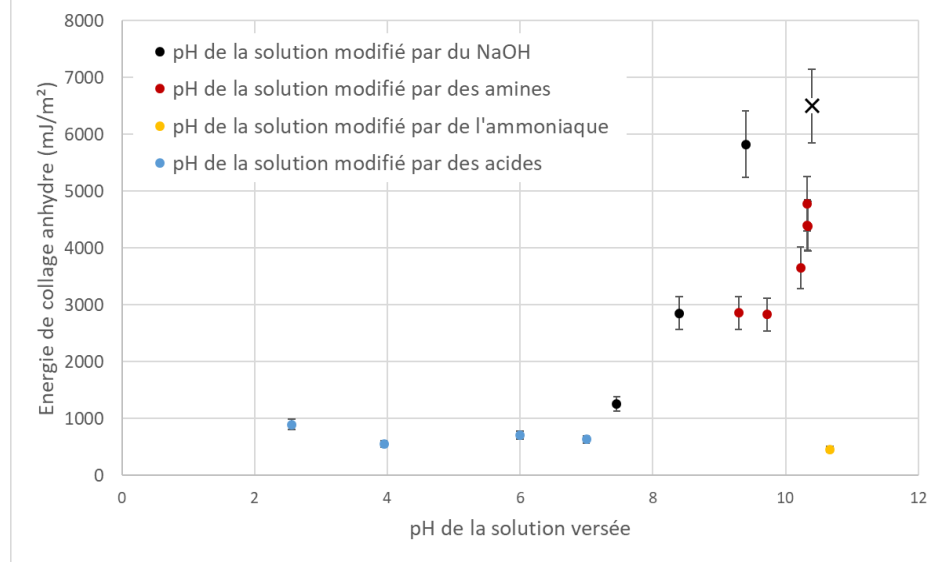
<https://doi.org/10.1149/09804.0003ecst>.

*Calvez, A., et al., *ECS J. Solid State Sci. Technol.* **2021**, 10 (6), 064005. <https://doi.org/10.1149/2162-8777/ac08d7>,

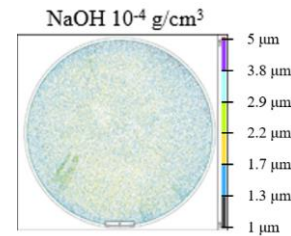
Different molecule (SiO₂//SiO₂)



Adherence @ 300°C post bonding annealing



pH seems to be the key parameter



Not anymore bondable

NaOH is the best one... for the moment 😊

Deposition model

Double electrostatic layer

- Poisson-Boltzman equation : surface charges, surface potential and ionic volume concentration

$$[Na^+]_0 = [Na^+]_\infty \exp\left(\frac{e\psi_0}{k_B T}\right)$$

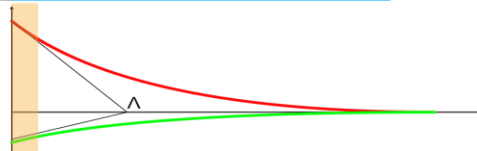
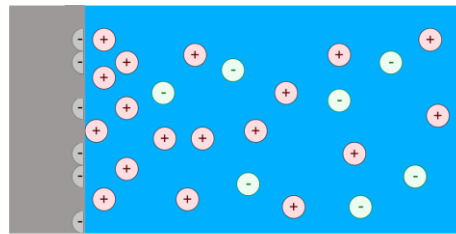
- Integration over Debye length :
Dry surface :

$$\frac{[Na^+]_0}{K} = \frac{1}{e} \left(e n_{SiOH} \frac{K_d}{K_e} \right)^{2/3} (2\varepsilon\varepsilon_0 k_B T)^{1/6} \rho^{5/6}$$

~0,883



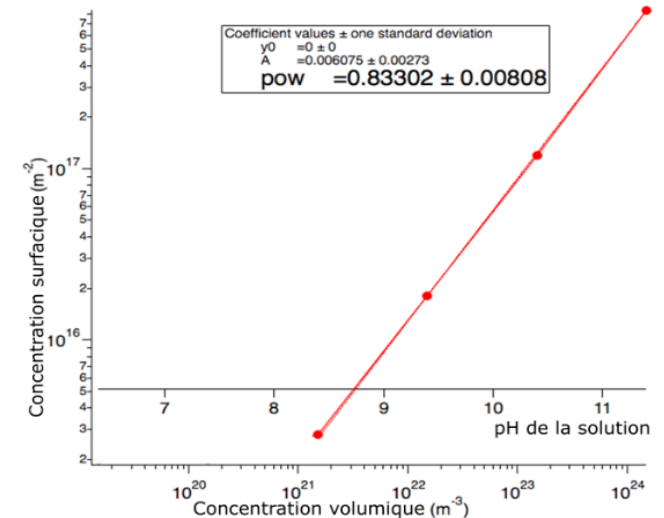
Partially ionized Silica surface



TXRF

Dispensed solution	Na ⁺ concentration on wafer surface (at/cm ²)
H ₂ O	< 2x10 ¹¹
NaOH 10 ⁻⁸ g/cm ³	< 2x10 ¹¹
NaOH 10 ⁻⁷ g/cm ³	2.8x10 ¹¹
NaOH 10 ⁻⁶ g/cm ³	1.8x10 ¹²
NaOH 10 ⁻⁵ g/cm ³	1.2x10 ¹³
NaOH 10 ⁻⁴ g/cm ³	8.4x10 ¹³

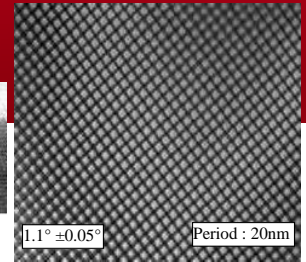
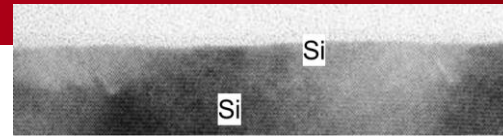
< 1/100 ML



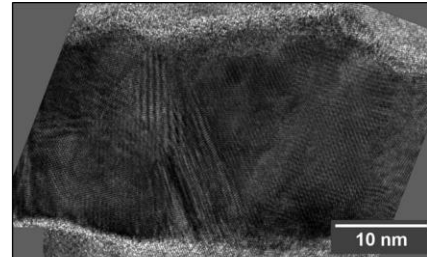
- ❑ Direct bonding mechanism based on Rough Surface model
- ❑ Adhesion energy to perform the bonding
(not only van der Waals but also capillarity bridges)
- ❑ Adherence energy for the bonding strength
(covalent bonding are already @ RT)
- ❑ Adherence measurement impacted by WSC
=> DCB in Anhydrous atmosphere
- ❑ SiO₂ adherence mechanism based on silica hydrolisation
- ❑ CMP or Plasma are adherence booster (fluorine plasma)
- ❑ Chemical molecule can be as good as plasma (NaOH)

OTHER DIRECT BONDING TYPE

- ❑ Hydrophobic bonding (Si/Si...)
- ❑ Polymer bonding (even with direct bonding 😊)



- ❑ Metallic bonding : Au/Au

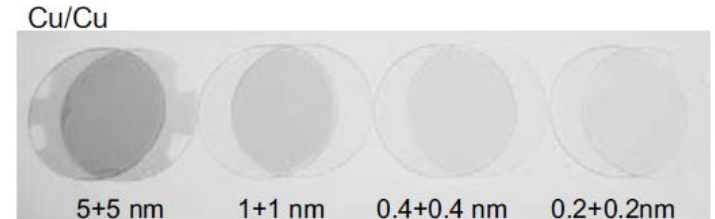
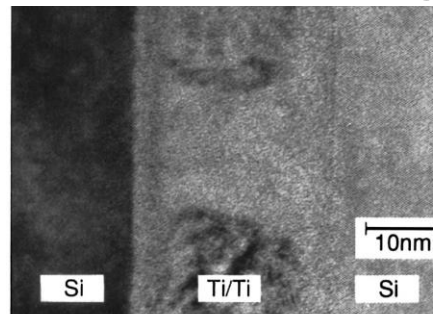
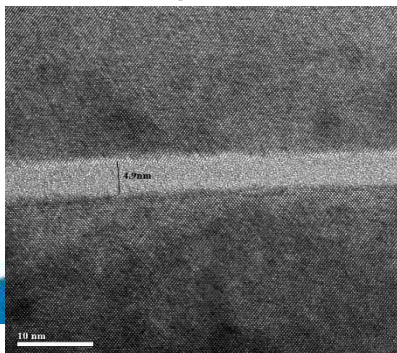


TEM cross section of RT Gold:Gold interface

- ❑ Ultra high vacuum bonding technic
Generate dangling bonds and to bond with them!

- ❑ SAB (surface activation bonding) => “etching”
- ❑ ADB (atomic diffusion bonding) => “deposition”

SAB Si bonding
Without annealing –
4,9nm amorphous layer



Merci pour votre attention