ToF-SIMS study of alternate polyelectrolyte thin films

Chemical surface characterization

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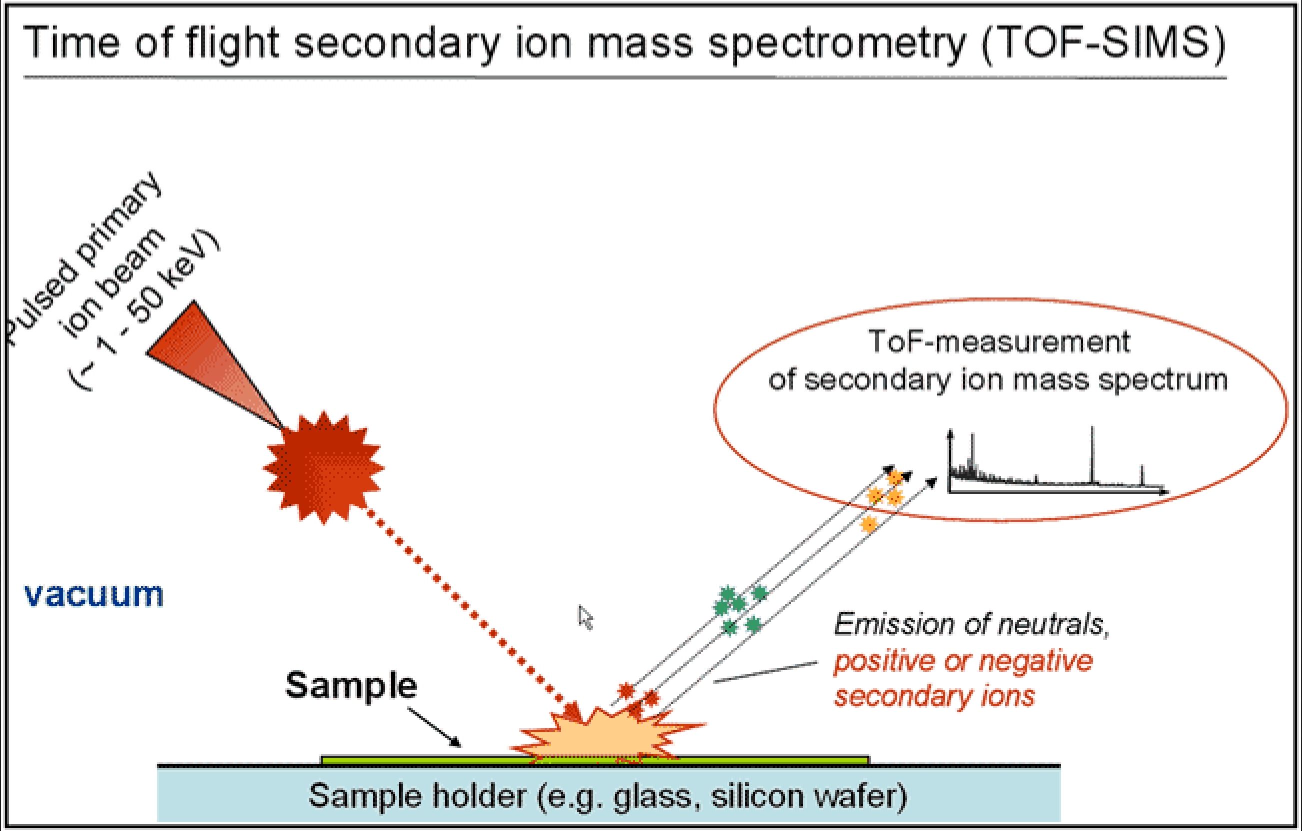
Polyelectrolytes

- Polymers – contents an electrolyte group
- Dissociate in aqueous solution (water) – form polycations, polyanions
- Elelectrolytical and polymer properties (polysalts)
- Solutions – electrically conductive, viscous
- Strong polyelectrolytes – dissociates completely in solution
- Weak polyelectrolytes – dissociates partially – not fully charged
- DNA, polypeptides, glycosaminglycans,...

SIMS (Secondary Ion Mass Spectrometry)

- Chemical surface characterization
- Compared with AES, XPS, ..
- Secondary particles : electrons, neutrals, **ions**...
- The ionization probability is strongly affected by the electronic properties of the sample matrix
- Only a small portion of secondary particles (~ 1% of total secondary particles) are ionized



ToF (Time of Flight)

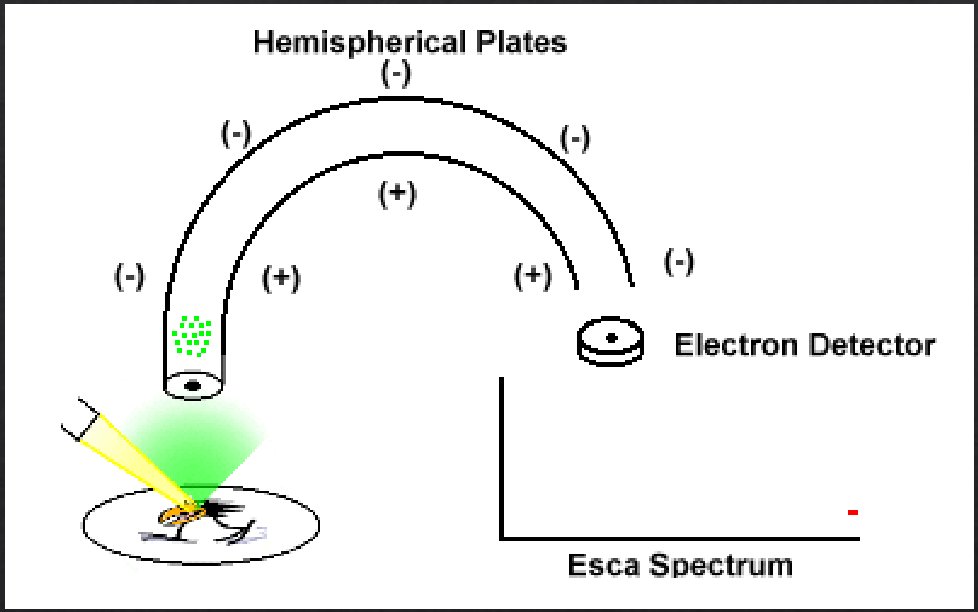
- Mass analyser - the most widely used analyser in static SIMS
- Parameter for measurement: the flight time of ion
- When ions are obtained with a constant kinetic energy from an acceleration potential (V) of 3 – 8 kV, the flight time of ions through a distance (L) of flight tube to reach a detector is calculated.

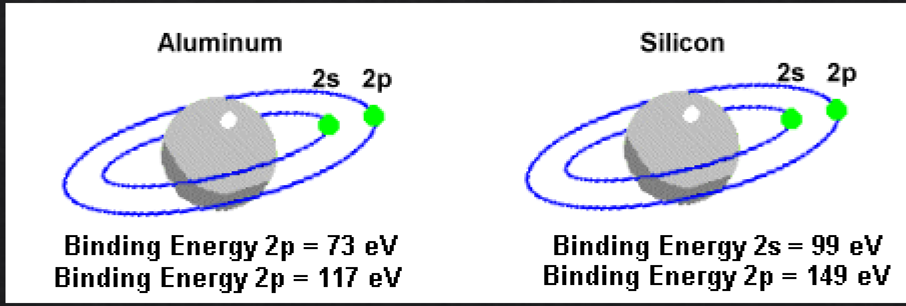
$$t = L(2V)^{-1/2}\left(\frac{m}{z}\right)^{1/2}$$

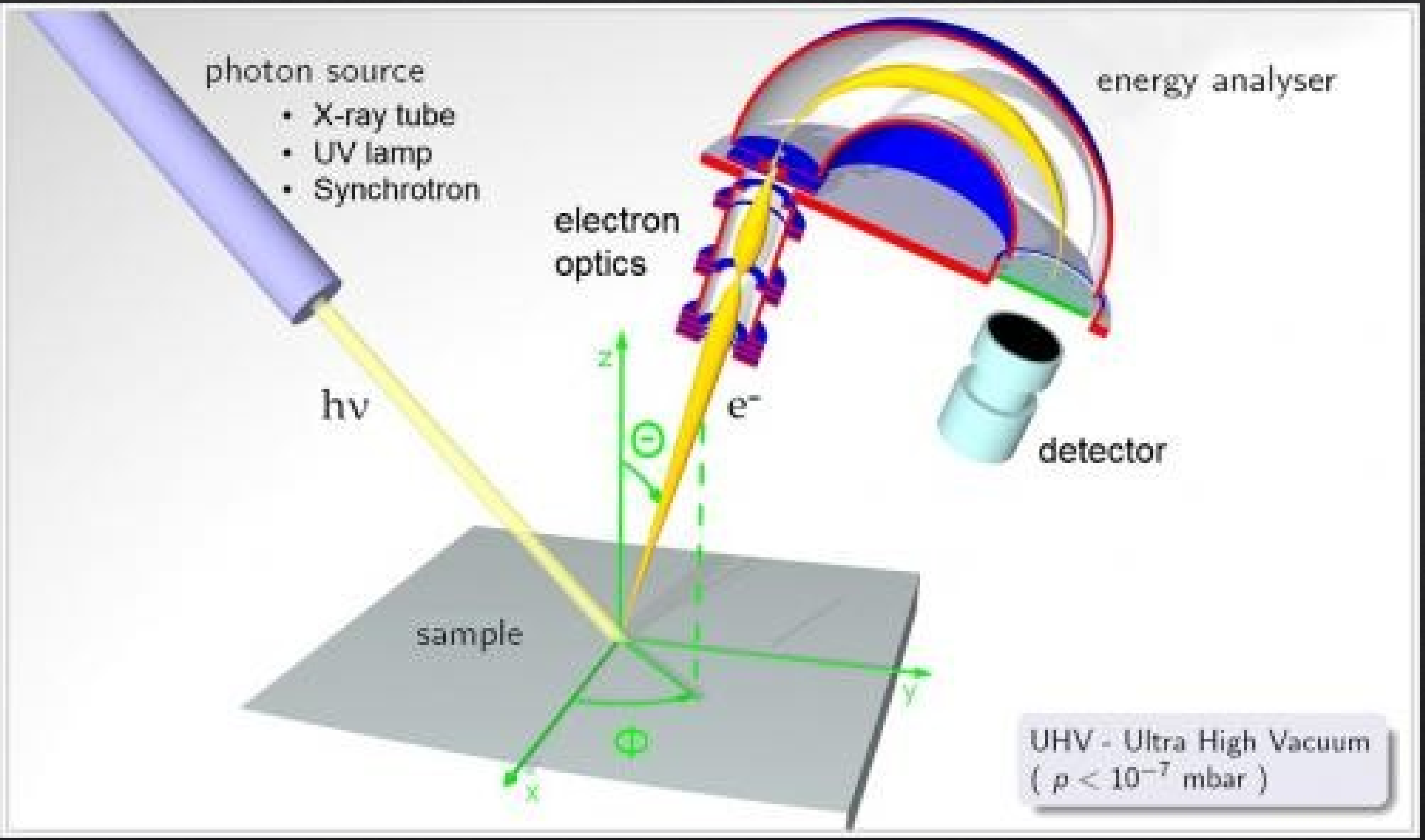
- Pulsed primary ions are used for precisely measure
- Initial kinetic energy of secondary ions will affect the resolution of mass analysis

XPS (X-ray photoelectron spectroscopy)

- Surface-sensitive quantitative spectroscopic technique
- Can be applied to a broad range of materials and provides valuable quantitative and chemical state information from the surface of the material
- Irradiates the sample surface with a soft (low energy) X-ray
- X-ray excites the electrons of the sample atoms
- if their binding energy is lower than the X-ray energy, they will be emitted from the parent atom as a photoelectron
- The kinetic energy of the electron is the incident energy (1486 eV from the X-ray) minus the binding energy






photon source
• X-ray tube
• UV lamp
• Synchrotron
energy analyser
electron optics
hν
e⁻
Θ
detector
z
sample
y
Φ
x
UHV - Ultra High Vacuum
($p < 10^{-7}$ mbar)

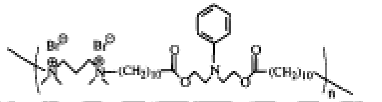
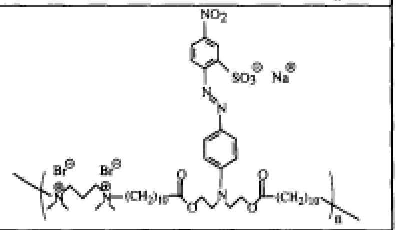
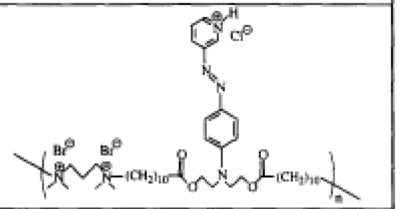
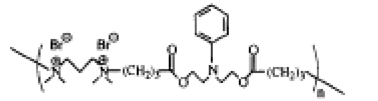
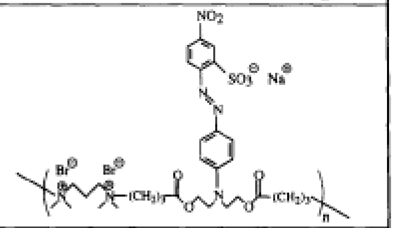
Experiment

- 3 types of multilayers with different thicknesses
- Synthesize by dipping charged silicon wafers into solutions of polyelectrolytes of opposite charge

Table 2
Different characterization techniques used for the analysis of the multilayered assemblies

Multilayer assembly	ToF-SIMS	XPS/ARXPS*	XR reflectivity	AFM
bare silicon	X	X*	X	
(6)	X	X		
(6)/(7)	X	X	X	
(6)/(7)/(1)	X	X		
(6)/(7)/(2)	X	X	X	
(6)/(7)/$(2)_2$	X	X/X*	X	
(6)/(7)/$(2)_3$	X	X*		
(6)/(7)/$(2)_4$	X	X		
(6)/(7)/(3)	X	X	X	
(6)/(7)/$(3)_2$	X	X/X*	X	
(6)/(7)/$(3)_3$	X	X	X	
(6)/(7)/$(3)_4$	X	X	X	
(6)/(7)/(4)	X			
(6)/(7)/$(4)_2$	X			X

Table 1
Formulae of the polyelectrolytes used for the multilayered assemblies

Polyelectrolyte	Chemical Formula
(1)	
(2)	
(3)	
(4)	
(5)	
(6)	 (branched)
(7)	

The positive secondary ion mass spectrum

- The most intense peak in the spectrum corresponds to (28 D)
- Sillicon substrate is not completely covered
- The thickness of multilayer assembly is not sufficient to mask the substrate ion emission
- 2 main series of ions:
  - Main chain (MC)- peaks of N (58 D, 84 D, 98 D, 104 D, 120 D, 132 D)
  - Pedant group (PG) – phenyl (carbohydrate) (41 D, 55 D, 77 D)

The negative secondary ion mass spectrum

- (2 isotopes – 79 D, 80 D) polyelectrolyte *(1)*
- (64 D, 80 D, 97 D) from PG polyelectrolyte *(7)*

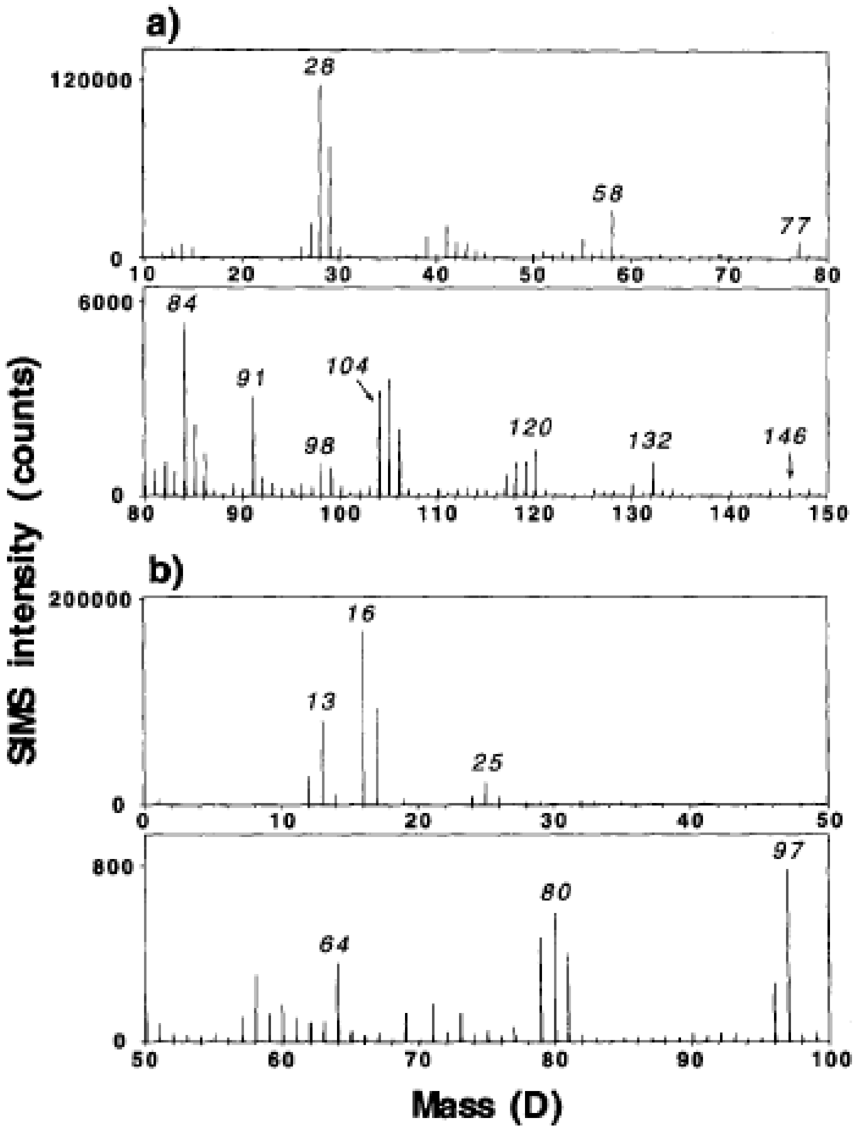
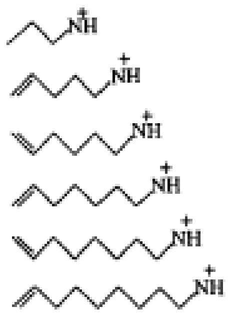
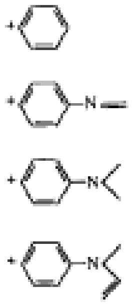


Fig. 1. Positive (a) and negative (b) SI mass spectra of the assembly *(6)/(7)/(1)*.

Table 3
Formulae of the main characteristic ions observed in the positive SI mass spectrum of polyelectrolyte (*1*). The ion mass is indicated in daltons (D)





Main Chain (MC)		Pendant Group (PG)	
	M = 58 D		M = 77 D
	M = 84 D		M = 104 D
	M = 98 D		M = 120 D
	M = 112 D		M = 132 D
	M = 126 D		
	M = 140 D		

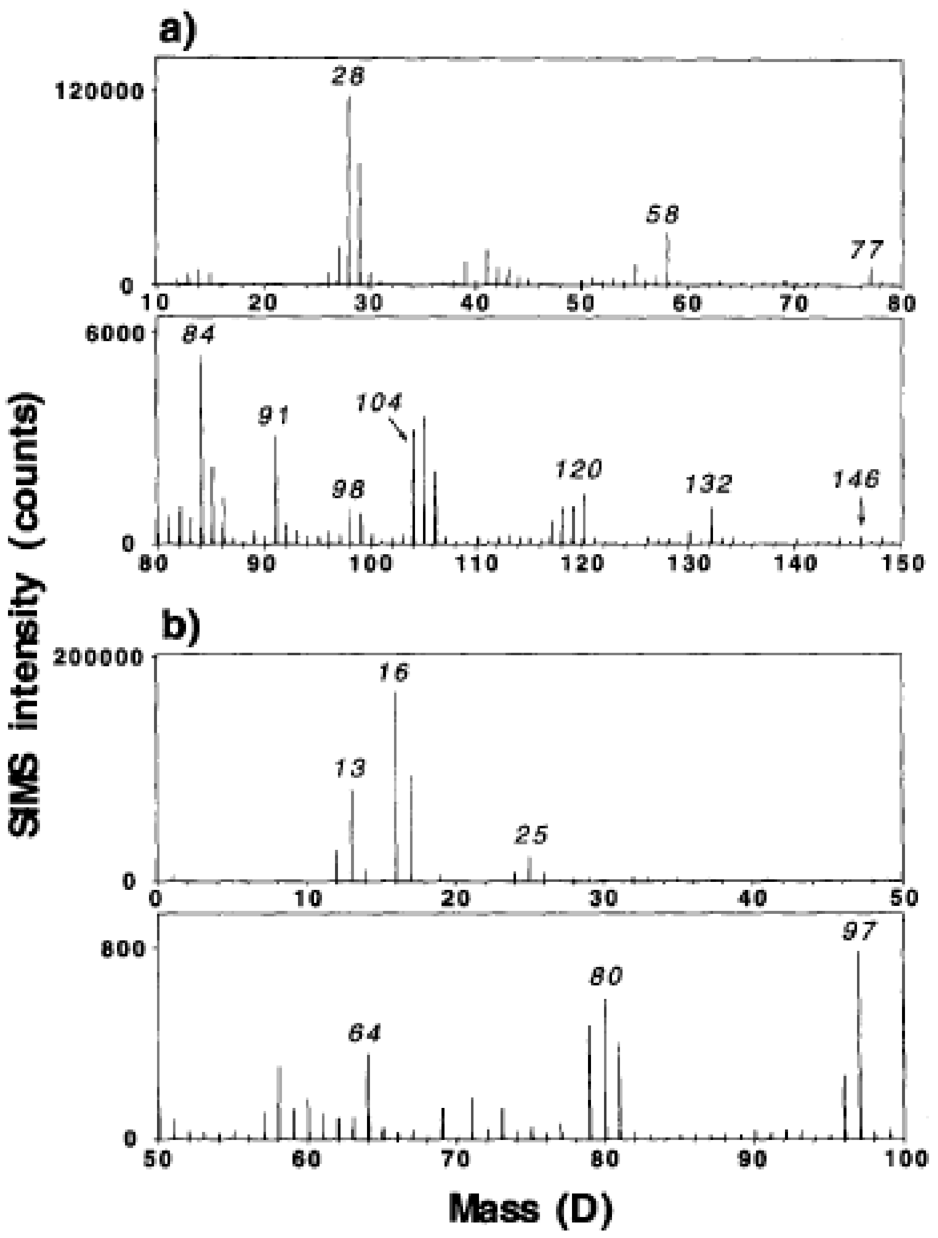
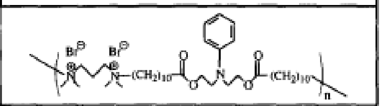
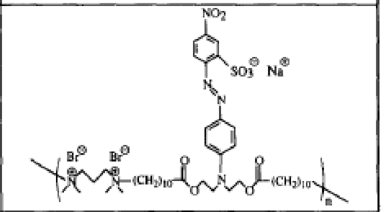
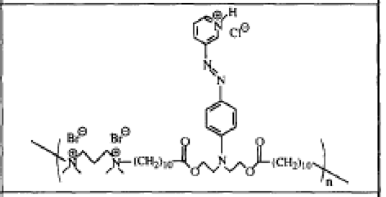


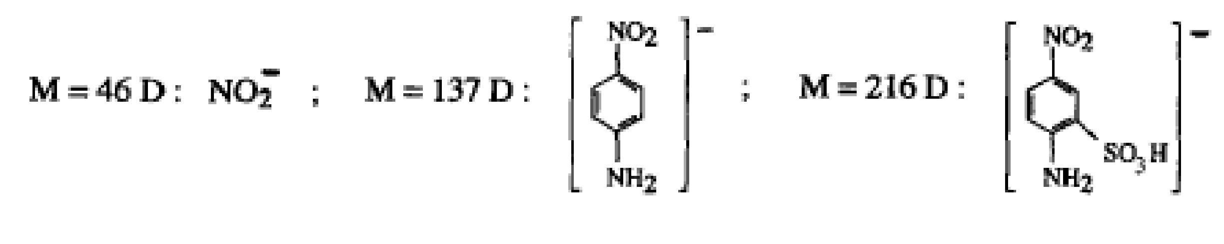
Fig. 1. Positive (a) and negative (b) SI mass spectra of the assembly (*6*)/(*7*)/(*1*).

The sensitivity of ToF-SIMS

- Sensitivity to the PG (pendant group)
- $\sum PG$ decreasing from(1)*to* (3) - Lower abillity to produce ions from polyelectrolytes (*2,3*)
- Difference of the polyelectrolytes only in PG groups – but not constant MC peaks
  - Main chain is mask by the pendant group
- Activation of polyelectrolytes
  - Characteristic fragments of functional group (46,137, 216 D)

	(6)/(7)/(1)	(6)/(7)/(2)	(6)/(7)/(3)
Positive ions			
$\sum$MC	2.0	1.24	1.39
$\sum$PG	79×10^{-2}	28×10^{-2}	7.9×10^{-2}
$\sum$PG/$\sum$MC	40×10^{-2}	23×10^{-2}	5.7×10^{-2}
peak 78 D/peak 77 D	0.20	0.21	1.27
Negative ions			
peak 46 D (NO_2^-)	3.0×10^{-3}	29×10^{-3}	9.6×10^{-3}
peak 137 D	1.4×10^{-4}	10×10^{-4}	1.4×10^{-4}
peak 216 D	2.0×10^{-5}	83×10^{-5}	15×10^{-5}
peak 80 D (SO_3^-)	9.1×10^{-3}	15×10^{-3}	12×10^{-3}
peak 97 D (SO_4H^-)	16×10^{-3}	6.1×10^{-3}	7.4×10^{-3}

Polyelectrolyte	Chemical Formula
(1)	
(2)	
(3)	



Sensitivity to the length of the alkyl chain contained in the polymer backbone

- Compare (1) and (4) – very similar from ther chemical viewpoint – different MC peak intesities
- Difference :

(1) - produce ($C_xH_yN^+$) with 14 carbon atoms

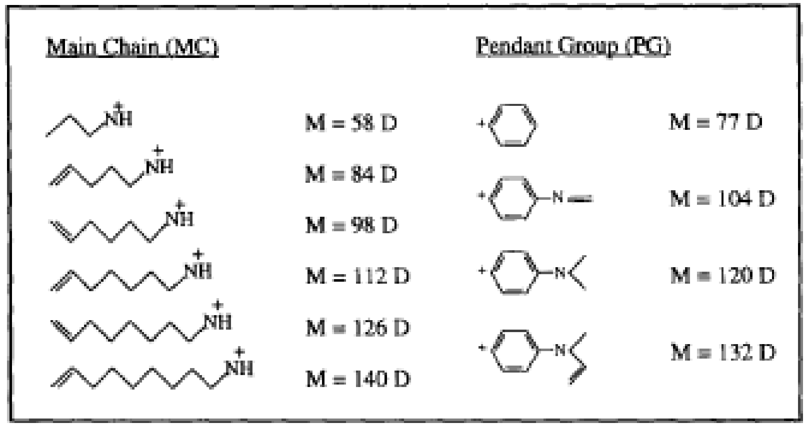
(4) – produce ($C_xH_yN^+$) with 7 carbon atoms

- Small changes in the chain structure

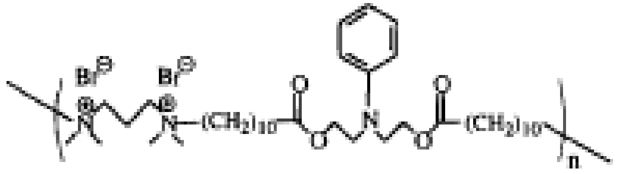
of the polyelectrolytes give rise marked

effect in their organization within coating

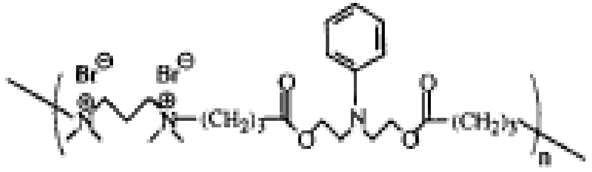
Table 3
Formulae of the main characteristic ions observed in the positive SI mass spectrum of polyelectrolyte (1). The ion mass is indicated in daltons (D)



(1)



(4)



MC peaks	A:(6)/(7)/(1)	B:(6)/(7)/(4)	A/B
peak 58 D	1.0	1.0	1.0
peak 84 D	1.7×10^{-1}	1.7×10^{-1}	1.05
peak 98 D	3.1×10^{-2}	1.7×10^{-2}	0.56
peak 112 D	1.0×10^{-2}	0.56×10^{-2}	0.53
peak 126 D	0.69×10^{-2}	0.29×10^{-2}	0.43
peak 140 D	0.61×10^{-2}	0.20×10^{-2}	0.33

Chemical mapping of the surface

- – looks homogeneous
- ( ) (substrate ion) – strongly inhomogeneous
- Inhomogenities – ( )

  - counterions of (3)

  - counterion of substrate

Contrast is weak – different emission depth

Conclusion:

(3) covers the whole area but thickness of layer varies from place to place

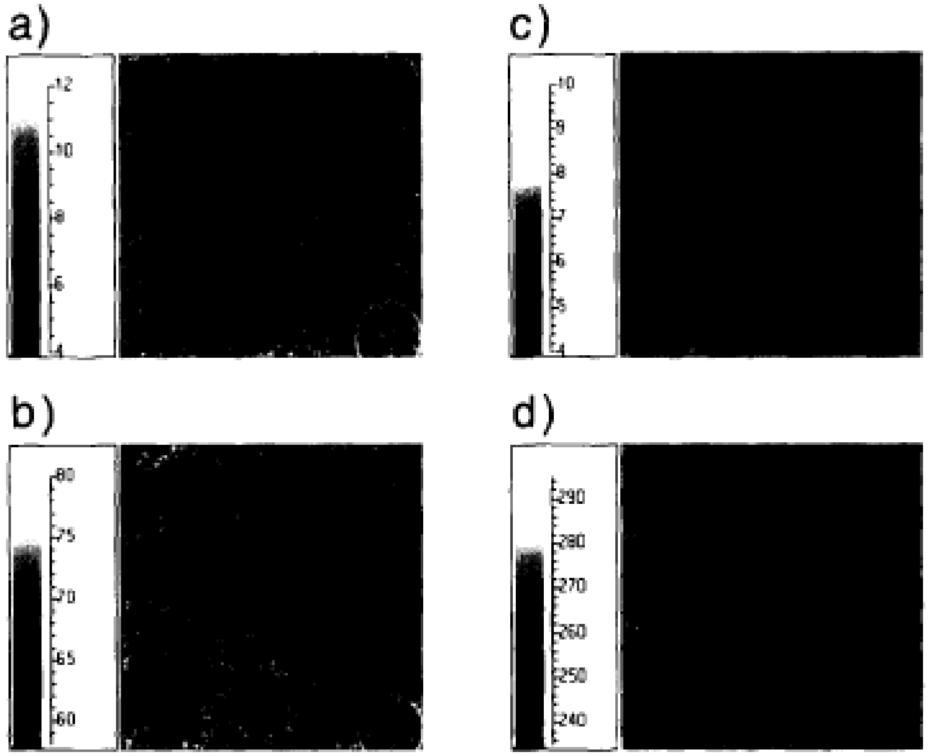


Fig. 2. Chemical imaging of an imperfect assembly (6)/(7)/(3). Images (a) to (d) show respectively the distribution of the $C_3H_8N^+$, Si^+, Cl^- and O^- ions on the surface. The field of view is approximately 50 × 50 μm². The bright circle indicates the same defect in the four images.

Effect of the multilayer build-up

b

(6)(7)(2) – thickness 30 Å
(6)(7)(3) – thickness 20 Å

Conclusion:

layers (2) are either less complete or

that the arrangement is such that the

pendant groups are not perpendicular

to the surface – slower decay of the

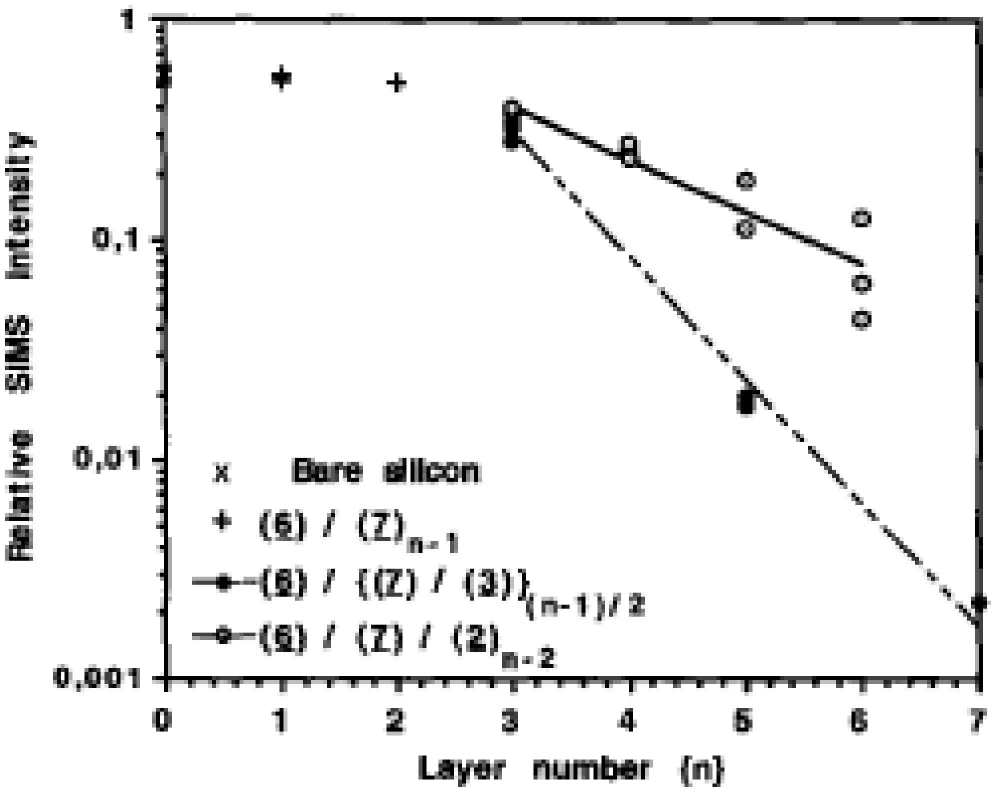


Fig. 3. Relative intensity of the Si^+ substrate ion as a function of the layer number (n) for two types of assembly, $(6)/((7)/(3))_n$ and $(6)/(7)/(2)_n$.

Information depth in SIMS

- Emission depth in static SIMS – 1nm – organic materials ?
- Knowledge of the emission depth of the substrate ions seemed of great interest for the evaluation of the layer quality
- If depth was similar for atomic (Si^{+}, Si^{-}) and molecular ions (SiO_3H^{-}, SO_3^{-})
- For deeper understanding of results
- Two methods have been used
  - SIMS – XRR correlation between SI intensities and the thickness of the multilayer assamblies
  - SIMS – XPS correlation

⟐ SIMS – XRR correlation

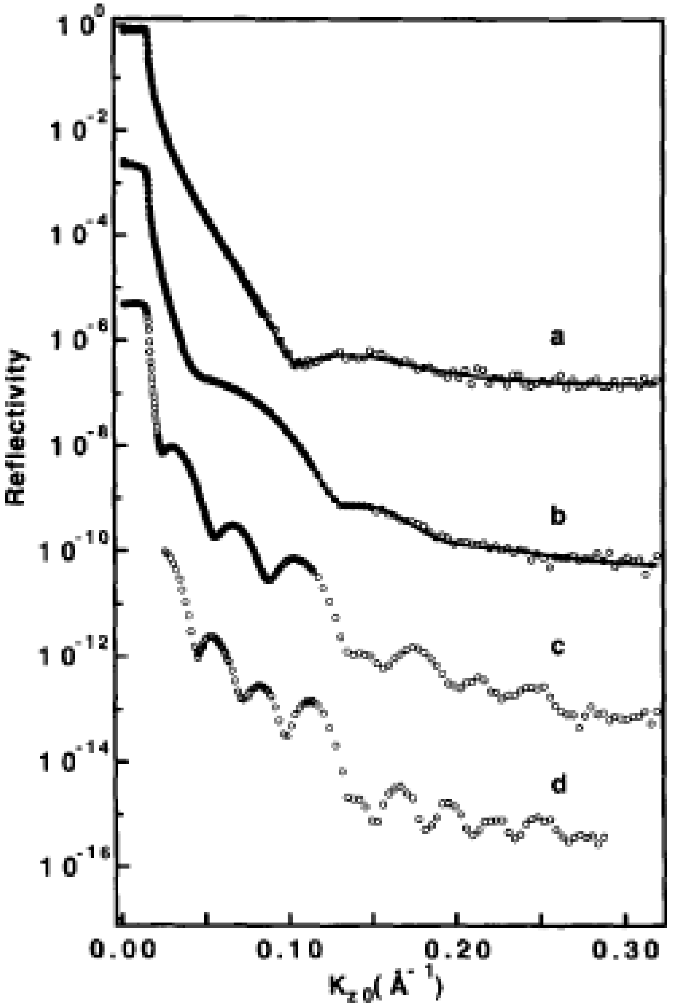


Fig. 4. X-ray reflectivity versus the component of the photon wavevector perpendicular to the interfaces (K_{z0}), and best fits to the data. The points are shifted vertically for clarity. The formulations of the assemblies analyzed are (a): $(6)/(7)/(2)_1$, (b): $(6)/(7)/(2)_2$, (c): $(6)/(7)/(3)_2$, and (d): $(6)/(7)/(3)_3$.

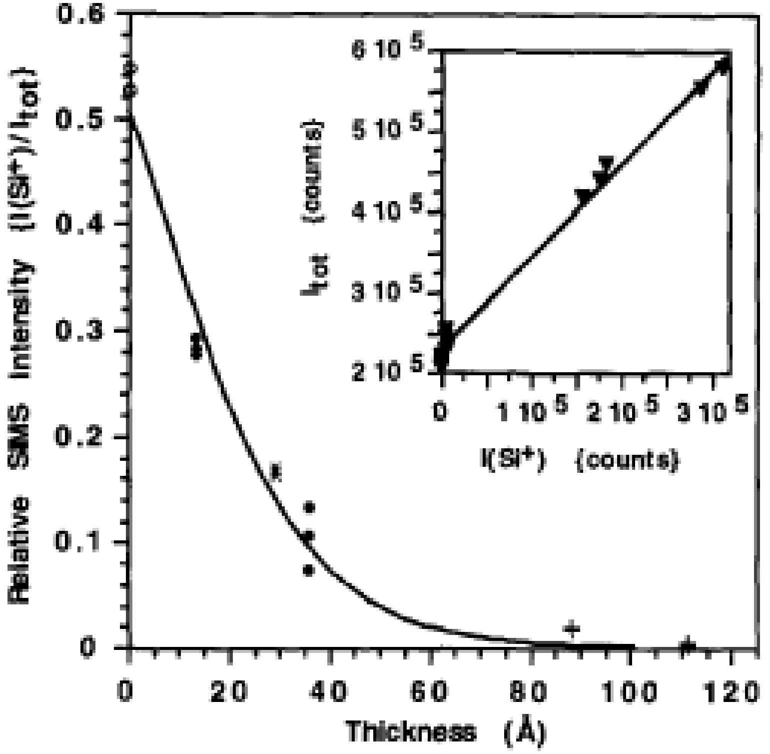


Fig. 6. Relative intensity of the Si^+ substrate ion as a function of the film thickness for three types of assemblies and for a cleaned silicon wafer. The open circle (○) refers to the clean silicon wafer, the full circle (●) to the assemblies $(6)/(7)/(2)_x$ ($x=1,2$), the cross (x) to the assembly $(6)/(7)/(5)_2$ and the plus (+) to the assemblies $(6)/((7)/(3))_x$ ($x=2,3$). The thickness is measured by XRR, except in the case of the assembly $(6)/(7)/(5)_2$, where it is measured by AFM. The inset shows the linear relation between the Si^+ signal and the total intensity.

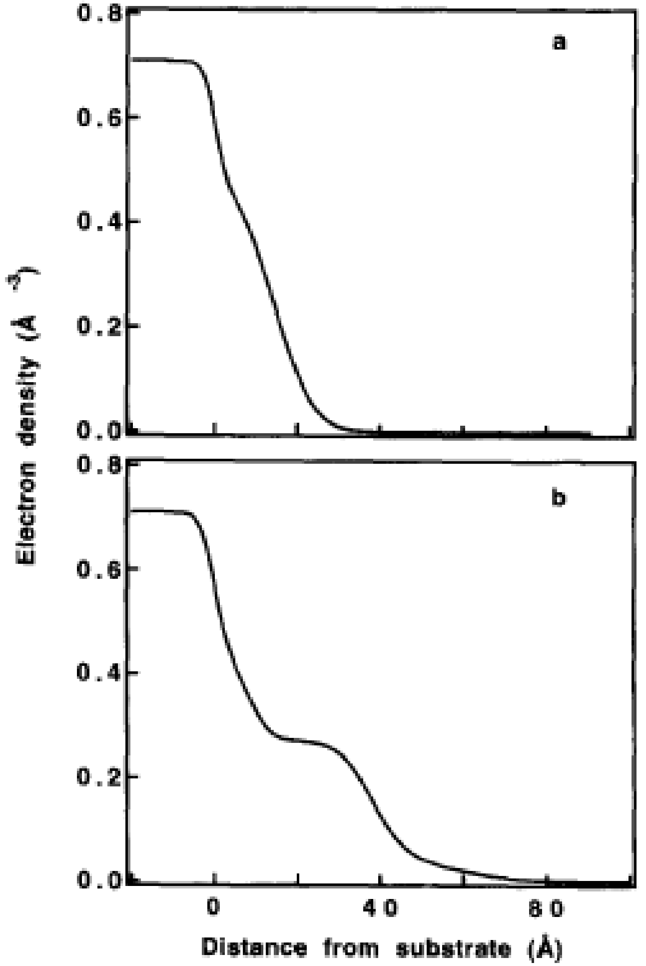


Fig. 5. Electron density profiles computed from the data of Fig. 4 for the assemblies (a): $(6)/(7)/(2)_1$ and (b): $(6)/(7)/(2)_2$.

⟐ SIMS – XPS correlation

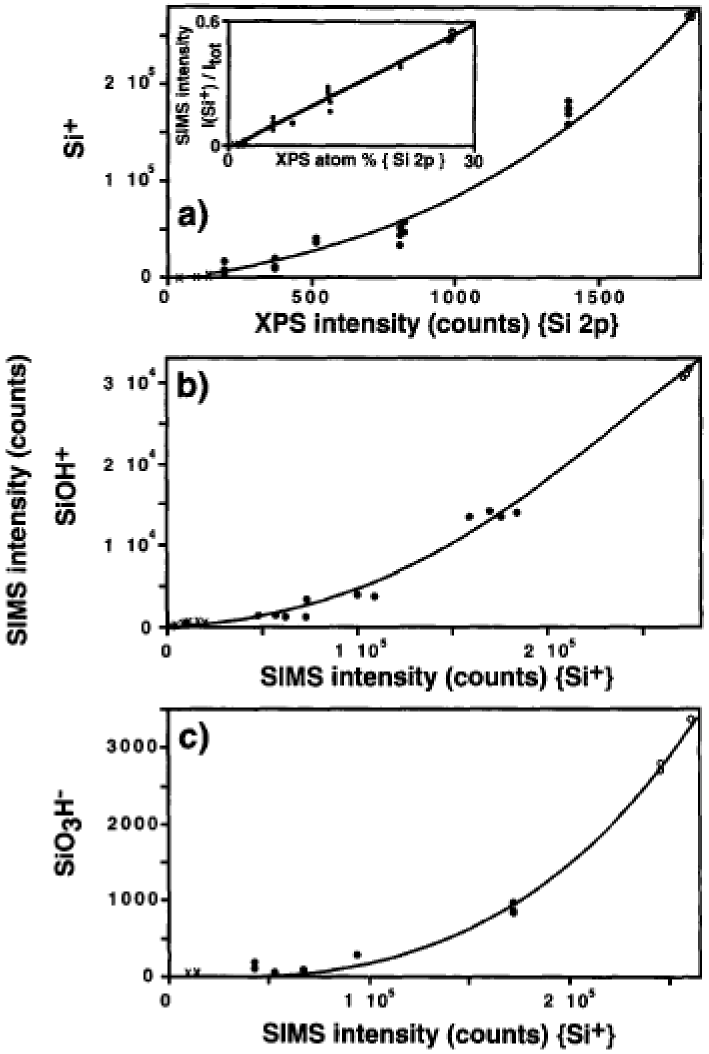


Fig. 7. (a) Correlation between the *absolute* Si^+ SI intensity and XPS Si 2*p* intensity (Si–Si). The open circle (○) refers to the assemblies *(6)* and *(6)/(7)*, the full circle (●) to the assemblies *(6)/(7)/(1)* and *(6)/(7)/(2)*$_x$ ($x=1,2$), and the cross (x) to the assemblies *(6)/((7)/(3))*$_x$ ($x=2$–4). The inset shows the linear correlation between the *relative* intensity of Si^+ and the XPS atom percentage of Si. (b) Correlation between the absolute $SiOH^+$ and Si^+ SI intensities. (c) Correlation between the absolute SiO_3H^- and Si^+ SI intensities.

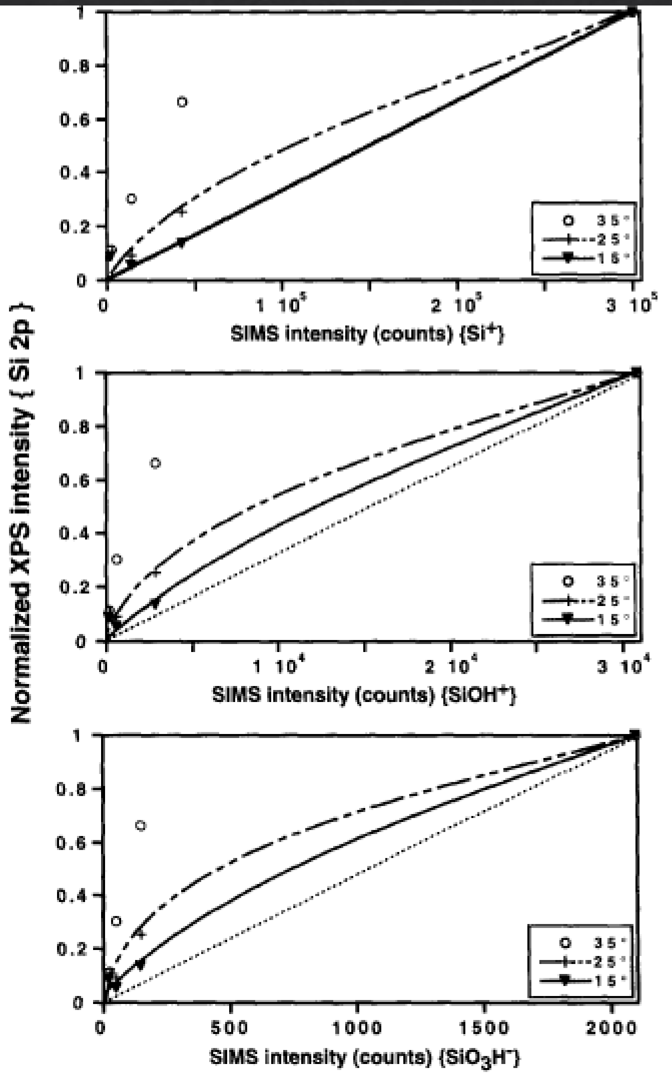


Fig. 8. (a) Correlation between the XPS Si 2p absolute intensity at different angles (15°, 25°, 35°) and the Si^+ SI absolute intensity for 4 samples {cleaned silicon, assembly *(6)/(7)/(2)*$_x$ ($x=2,3$), assembly *(6)/((7)/(3))*$_2$}. The SI intensities are mean values (3 values at least). (b) Correlation between the XPS Si 2p absolute intensity at different angles and the $SiOH^+$ SI absolute intensity. (c) Correlation between the XPS Si 2p absolute intensity at different angles and the SiO_3H^- SI absolute intensity.

Conclusion

- ToF SIMS offers valuable information about polyelectrolyte multilayeres assemblies
- The sensitivity to the sample thickness in the case of very thin films – another tool to evaluate the sample quality
- From correlation SIMS – XRR, XPS – atomic or small molecular ions are less surface sensitive than large molecular ions
- Combination of several complementary techniques leading to a more fundamental understanding

THE END

Thank you for your attention