Instruments

Dissipative Quartz Crystal Microbalance

Applications, Measuring Principle, Results & Modeling

Dr. Tapani Viitala

Instruments

Modular Design

Standard Cell

Basic Electronic Unit

Ellipsometer Cell

Open beaker Cell

E-QCM

Window Cell

Instruments

Liquid handling options

Peristaltic pump for controlled continuous flow measurements

Automatic 4 or 8 syringe pump for repetitive batch sampling

Instruments

Dissipative QCM - Features

- Based on true impedance analysis
- Can perform gas and liquid phase measurements
  - Continuous flow
  - At air/water interfaces
- Flexible choice of surfaces
- Frequency range: 0.1 – 55 MHz, Resolution: 0.01 Hz
  - 5 overtones for 5 MHz crystal
  - Sensitivity up to 0.9 ng/cm^2
  - Measuring speed up to 8 datapoints/second
- Visco-elastic properties of adsorbed layers
- Test mode for verifying crystal OK
- Working temperature: 10 – 60 ^{o}C

Instruments

Available coatings

- Metals (in stock): Au, Stainless steel (AISI316)
- Metals (by request): Ag, Al, Cu, Cr, Sn, Pt, Ca, Li, Mg, Ni,
- Inorganic (in stock): SiO/SiO_2, SiO_2, TiO/TiO_2, ITO
- Polymers(by request) : PANi, Teflon AF, PMMA, PS, PC, PE, PP, AKD

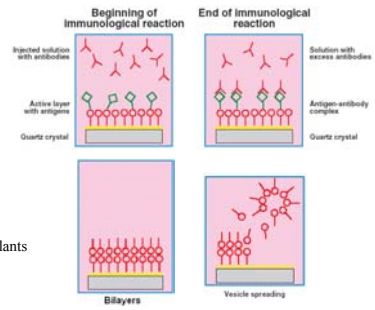
Interested in another coating? → Please ask!

Instruments

Applications

Biology/Medicine

- Affinity interactions, e.g. antibody-antigen
- Binding of proteins at surfaces (specific or non-specific)
- Cell attachment / detachment
- Cell-membrane specific proteins
- Deposited lipid bilayers
- Vesicle attachment
- Biocompatibility of surfaces/implants
- Biofilm formation/prevention
- Drug release



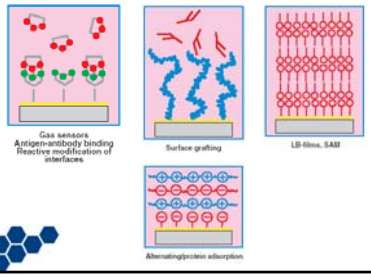
Applications

Chemistry

- Gas/liquid phase measurement/reactions
- Surfactant adsorption
- Polymer adsorption
- Nanoparticle adsorption
- Corrosion
- Self-assembly
- Polymeric surface coatings
- Surface gels

Industry

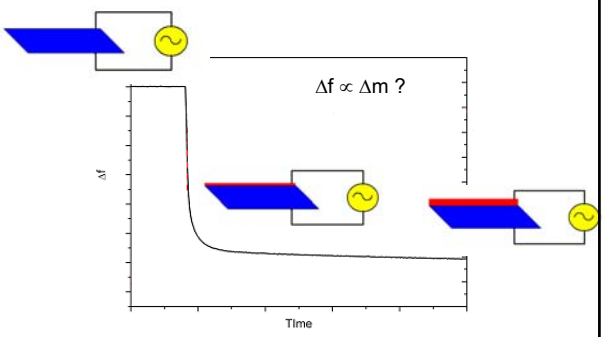
- Fouling/cleaning
- In-line sensing
- Non-ideal surfaces, e.g. polymers



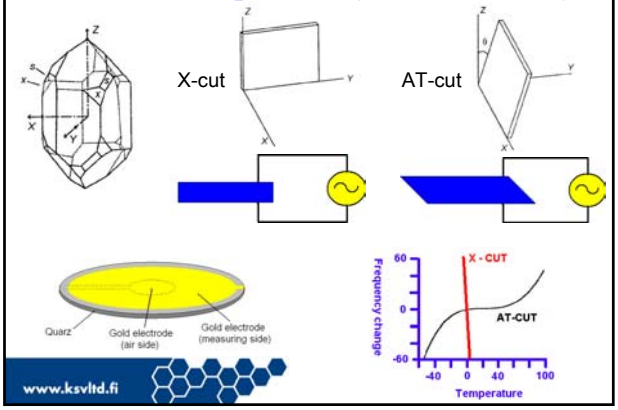
Examples of QCM customers

- Unilever, Bebington, UK ---------- Detergents, cleaning
- Geological Survey of Finland, Outokumpu ---------- Mineral processing
- Department of Phys. Chem., Turku, Finland ---------- Biofilm growth, implants
- DSM R&D, Geelen, The Netherlands ---------- Bio-fouling, protein adsorption
- Department of Physics, Brussels, Belgium ---------- Surface physics
- Indian Institute of Technology, Mumbai ---------- Polymer surfaces, swelling
- Toyota Central R&D, Aichi, Japan ---------- Biosensors, biomaterials
- Universite Paris Marie Curie, Paris, France ---------- Functional surfaces, biosensors
- Department of Chem., Florida, USA ---------- Polymers, biomembranes
- Deptartment of Pharmacy, Montreal, Can ---------- PE multilayers, biofilms
- Kyushi University, Japan ---------- Funcitional surfaces, biosensors
- Department of Chem., Houston, USA ---------- Polymers, PE multilayers
- Institute for Surface Chemistry, Stockholm, Swe ------ Miscellaneous
- Ugelstad Lab, Trondheim, Norway ---------- Corrosion inhibition, bio-fouling
- ANU, Canberra, Australia ---------- Colloid & Surface Sci.

Basic idea - Simple ?

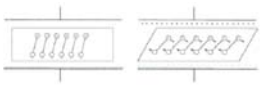


The quartz crystal is the key



What happens in the crystal ?

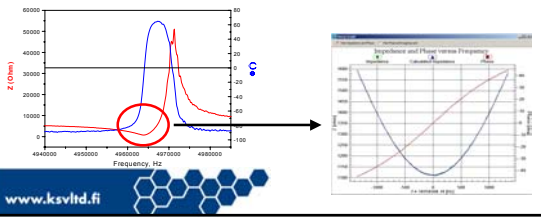
U reorients dipoles in acentric material ⇒ lattice strain and shear deformation



Vibrational motion establishes transverse acoustic wave ⇒ standing wave at $\lambda = 2\ t_q$

Impedance measurement principle

- I measured as f(U(ω))
- Impedance: Z = U/I
- Impedance curve holds all necessary info on quartz crystal and deposited layers



Rigid films

$$f = \frac{n\nu_q}{2t_q} = nf_0 \qquad df = -\frac{f}{m_q} dm_q$$

Sauerbrey equation: $\Delta f = -\frac{f}{t_q \rho_q} \Delta m = -\frac{n 2 f_0^2}{\nu_q \rho_q} \Delta m = -k \Delta m$

Sauerbrey equation holds only if:

- the added mass is small compared to weight of the crystal
- the added mass is rigid
- the added mass couples perfectly to the the quartz surface
- evenly distributed over the active area of the crystal

Newtonian liquids

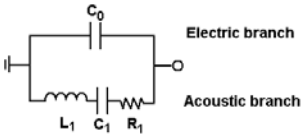
Kanazawa equation: $\Delta f = -\frac{f^{3/2}}{2\pi^{1/2} t_q \rho_q} (\rho_l \eta_l)^{1/2}$

Sauerbrey equation: $\Delta f = -\frac{f}{t_q \rho_q} \Delta m = -\frac{n 2 f_0^2}{\nu_q \rho_q} \Delta m = -k \Delta m$

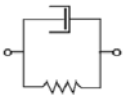
The unloaded crystal

Lumped element model

Electrical



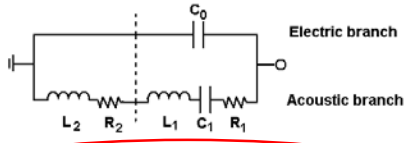
Mechanical



$$Z_m^{\,0} \approx R_1 + j\omega L_1 + \frac{1}{j\omega C_1}$$

The loaded crystal

Lumped element model



$$Z_m = (R_1 + R_2) + j\omega(L_1 + L_2) + (1/j\omega C_1)$$

Rigid film

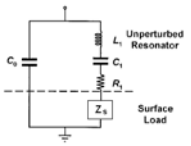
$$R_2 = 0 \qquad \omega L_2 = \frac{N\pi}{4K^2\omega_s C_0} \frac{\omega\rho_s}{Z_q}$$

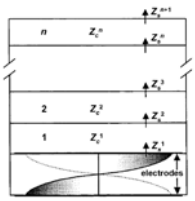
Newtonian liquid

$$R_2 \equiv \omega L_2 = \frac{N\pi}{4K^2\omega_s C_0 Z_q} \left(\frac{\omega\rho_l\eta_l}{2}\right)^{1/2}$$

Modeling multiple visco-elastic layers

Transmission line model





$$Z_s^{(n)} = Z_c^{(n)} \left[\frac{Z_c^{(n+1)} \cosh(\gamma^{(n)} h_l^{(n)}) + Z_c^{(n)} \sinh(\gamma^{(n)} h_l^{(n)})}{Z_c^{(n)} \cosh(\gamma^{(n)} h_l^{(n)}) + Z_c^{(n+1)} \sinh(\gamma^{(n)} h_l^{(n)})}\right]$$

$Z_c^{(n)} = (\rho^{(n)} G^{(n)})^{1/2}$ = impedance for n^{th} viscoelastic layer

$\gamma = j\omega(\rho_l/G)^{1/2}$ = complex wave propogation constant

G = G' + jG"
= μ + jωη

Modeling visco-elastic layers

Transmission line model

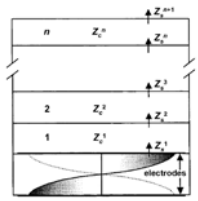
Viscoelastic layer in air:

$Z_s = j(\rho_l G)^{1/2} \tan(\omega(\rho_l/G)^{1/2} h_l)$

G → G´ : Sauerbrey equation
G → G´´ : Kanazawa equation

Viscoelastic layer in Newtonian liquid:

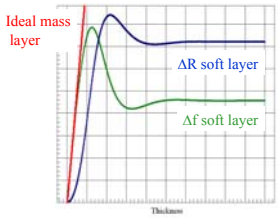
$$Z_s = Z_s^{film}\left[\frac{Z_s^{fluid}\cosh(\gamma h_l) + Z_s^{film}\sinh(\gamma h_l)}{Z_s^{film}\cosh(\gamma h_l) + Z_s^{fluid}\sinh(\gamma h_l)}\right]$$



G = G' + jG"
= μ + jωη

Soft films

- Frequency shift will be less than predicted by Sauerbrey eq
- Energy will be dissipated through frictional losses



Soft film:

Elastic modulus: 0.1 MPa

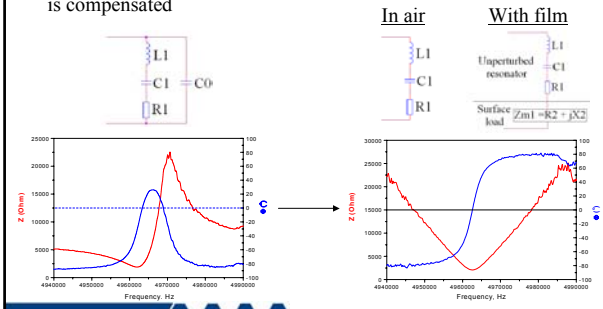
Viscosity: 10 mPas

What is the Goal of Impedance Analysis?

- To extract the mechanical properties of the load on the quartz crystal from electrical measurements
  - Harmonics (Overtones) easily measured
  - Very well established technique, theories and treatment of obtained data are well accepted

Measurement principle

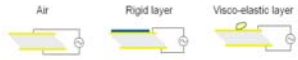
- During measurement the parasitic capacitance (electrical branch) is compensated

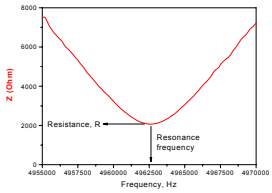


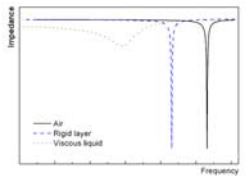
Measurement principle (cont.)

$$f = \frac{1}{2 \cdot \pi \cdot \sqrt{LC}}$$

$$Q = \frac{1}{D} = \frac{2 \cdot \pi \cdot f \cdot L}{R}$$







Why f and R at several overtones?

- Higher overtones have better sensitivity

- When adsorbed film soft and the upper region is far away from the crystal surface i.e. film do not couple to crystal oscillation
  ⇒ Normalised f and R at different overtones do not superimpose
  ⇒ Sauerbrey relation overestimates the mass

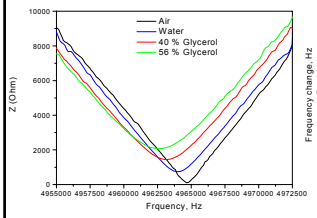
- Frequency signal reflects the total mass of the adsorbed film, while the R-value reflects the softness of the film.
  ⇒ A soft and a rigid film may give close to the same frequency change, while they induces completely differences changes in the R-value.

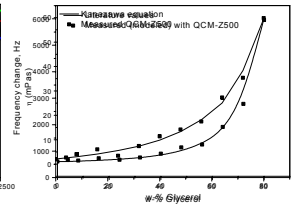
- Several overtones enables the determination of visco-elastic properties, film thickness, film density in the case of soft films

Example Measurements

- Newtonian liquid
- Rigid film in air
- Rigid film in liquid
- Visco-elastic finite layer in air
- Visco-elastic layer in liquid
- Liposome adsorption
- A few other very recently obtaines results

Newtonian liquid

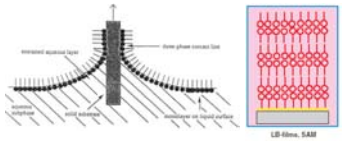


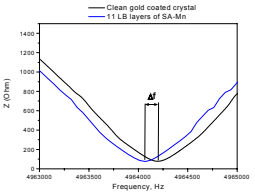


• Need only to use 1 frequency because of only one unknown parameter i.e. √ρη

Rigid Film Deposition (Air)

Stearic acid + $MnCl_2$, pH = 5.6, π = 30 mN/m

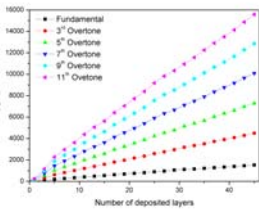


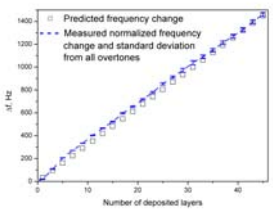


• Can use the Sauerbrey equation to predict mass increase during deposition

Rigid Film Deposition (Air)

Stearic acid + $MnCl_2$, pH = 5.6, π = 30 mN/m

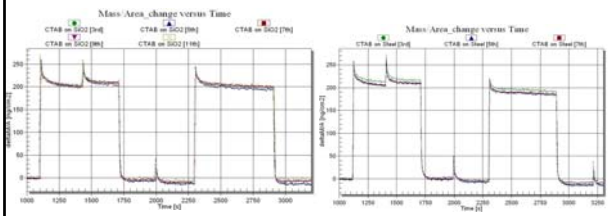




Prediction based on:
Molecular area: 20 Å^2/molecule
Dissociation degree: 50 %
1:1 complex SA:Mn(OH)

Rigid Film Deposition (liquid)

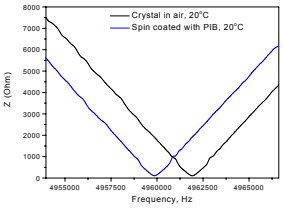
CTAB on silica and Stainless Steel (AISI316)

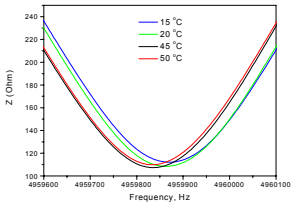


Surface	Δf , Hz	ΔMi/Ai , ng/cm^2
SiO_2	11.8 ± 0.1	208 ± 2
Stainless Steel (AISI316)	11.5 ± 0.6	202 ± 11

Visco-elastic layer (Air)

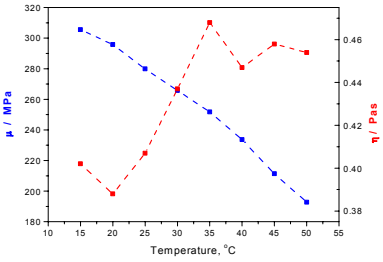
Polyisobutylene: MW 380 000 g/mole, T_g = - 68 °C, ρ = 0.92 g/ml
Spin coated at 2000 rpm from Chloroform containing 3 w-% PIB





3 unknowns: h, G´(μ) and G´´(η) ⇒ Use of overtones when modeling

Visco-elastic layer (Air)

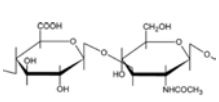


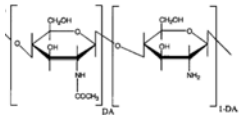
Thickness from modeling: 0.42 μm

Results in good agreement with
R. Lucklum et. al.
J. Phys. D. Appl. Phys. 1997, vol. 30, p. 346

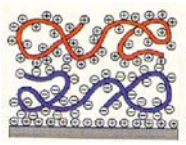
Visco-elastic multilayer (in liquid)

- Hyaluronic acid (HA) and Chitosan (CHI), 0.15 NaCl, pH = 4



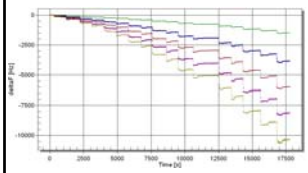


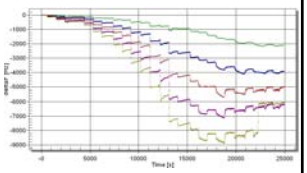
- 2 different molecular weights:
  - HA: 31k and 360k
  - CHI: 30k and 160k



Visco-elastic multilayer (in liquid)

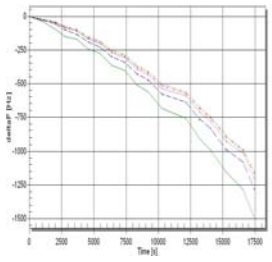
Low molecular weight compound High molecular weight compound

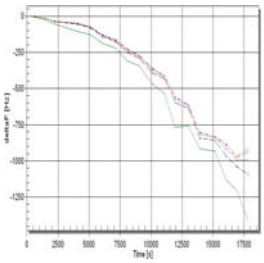




Visco-elastic multilayer (in liquid)

LWM HMW

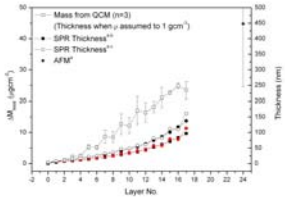


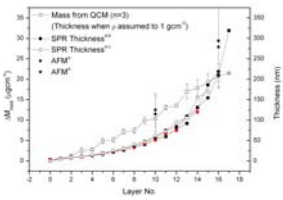


Visco-elastic multilayer (in liquid)

- Thickness

LMW HMW



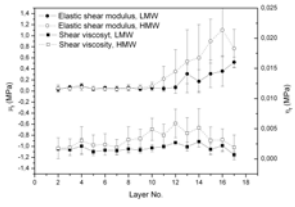


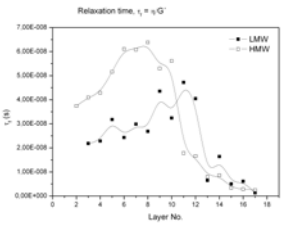
SPR & AFM data taken from
P. Kujawa et. al. JACS, 127 (2005) 9224.

Visco-elastic multilayer (in liquid)

- Visco-elastic properties

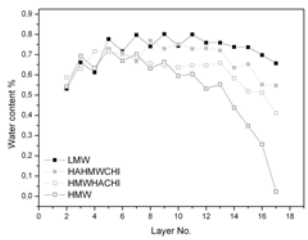
Elastic Shear Modulus & Viscosity Relaxation time

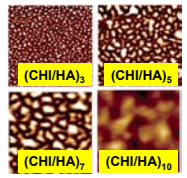




Visco-elastic multilayer (in liquid)

- Water content

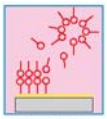


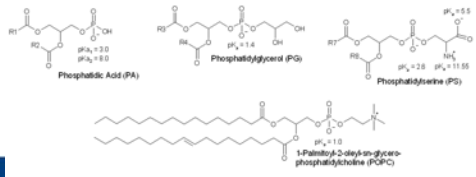


Vesicle adsorption on silica

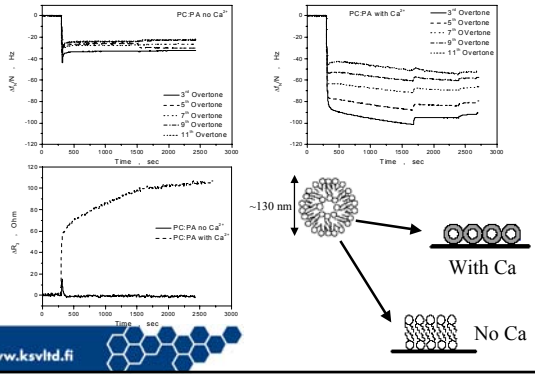
3 different compositions:
- POPC:PA (80:20)
- POPC:PS (80:20)
- POPC:PG (80:20)

- 20 mM Hepes, pH 7.4
- With or without 3 mM $CaCl_2$





Vesicle adsorption on silica

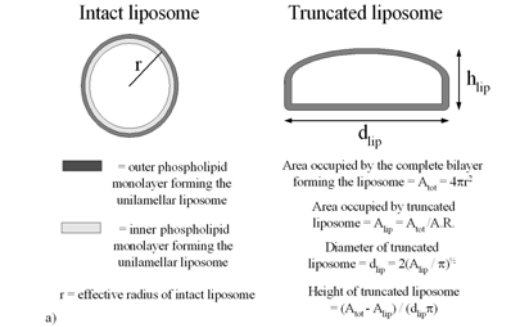


Vesicle adsorption on silica

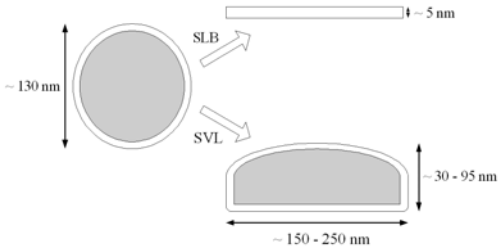
- Results from modeling

Liposome matrix	ΔR	Type of structure	Film thickness h_f (nm)	Film viscosity η_f (mPas)	Film elasticity μ_f (MPa)	Liquid bulk viscosity η_l (mPas)
POPC:PG no Ca^{2+}	Small	SLB	5.03 ± 0.66	-	-	0.88 ± 0.02
POPC:PG with Ca^{2+}	Small	SLB	4.89 ± 0.26	-	-	0.88 ± 0.01
POPC:PS no Ca^{2+}	Large	SVL	10.40 ± 2.16	4.91 ± 0.52	0.54 ± 0.02	0.89 ± 0.01
POPC:PS with Ca^{2+}	Large	SVL	9.83 ± 0.39	3.05 ± 0.57	0.34 ± 0.13	0.92 ± 0.04
POPC:PA no Ca^{2+}	Small	SLB	4.97 ± 0.23	-	-	0.84 ± 0.03
POPC:PA with Ca^{2+}	Large	SVL	11.10 ± 2.12	3.27 ± 1.19	0.39 ± 0.09	0.93 ± 0.03

Vesicle adsorption on silica



Vesicle adsorption on silica

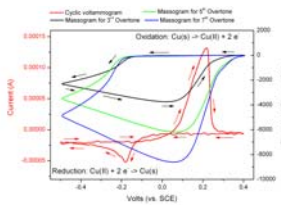


Width-to-Height ratio for SVL: ~ 4. In good agreement with width-to-height ratio of ~5.2 for diluted eggPC vesicles determined by Schönherr et.al., Langmuir, 20 (2004) 11600.

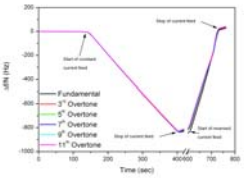
Electrochemical QCM

- Deposition of copper metal from a solution of 10 mM $CuSO_4$ in 0.1 M H_2SO_4

Potential sweep

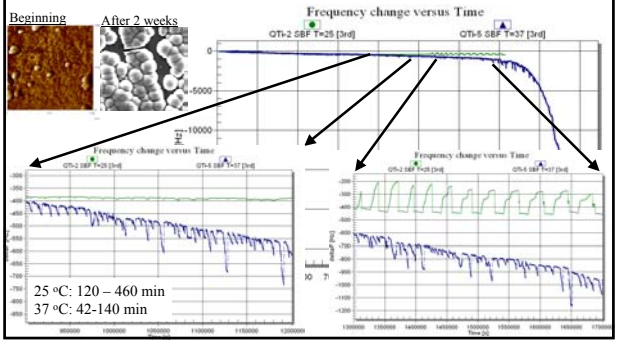


Constant current



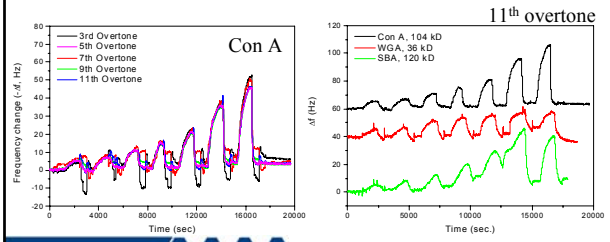
Porous sol-gel TiO_2 coating

- Calcium phosphate growth from a SBF solutions – bioactive material
- Important in order to integrate implants with bone



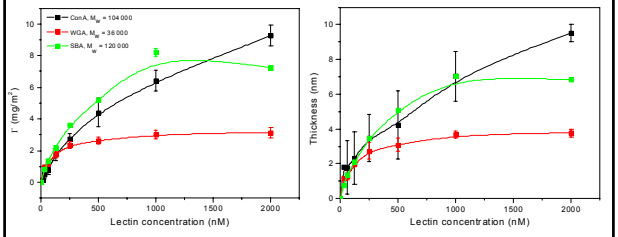
Protein interaction

- Specific Lectin interaction with oligosaccharide coatings
  - Mannose-α6-Mannose-Mono vs. Concanavalin A
  - Glucose NAc-β4-Glucose NAc-Mono vs. Wheat Germ Agglutinin
  - Galactose NAc-α6-Glucose-mono vs. Soybean Agglutinin



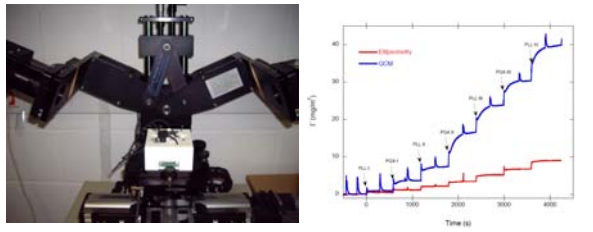
Protein interaction

- All normalized overtone frequencies behaves the same ⇒ Use the Sauerbrey equation to calculate Mass areal density and Thickness



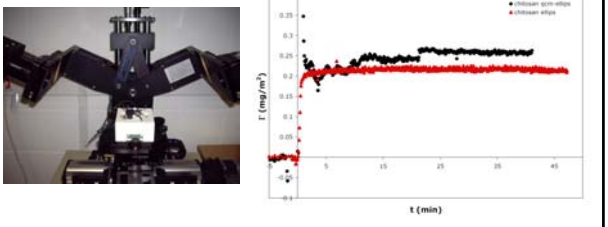
QCM and Ellipsometry combined

- Polypeptide multilayers on Ti
- PLL = Poly-l-lysine, PGA = Poly-l-glutamic acid



QCM and Ellipsometry combined

- 20 ppm Chitosan injected at time = 0



Main references for modeling theory

D.A. Buttry and M.D. Ward, **1992**, vol 92, p. 1355
S.J. Martin et. al. Anal. Chem. **1991**, vol. 63, p. 2272
R.W. Cernosek et. al. IEEE Transactions, **1998**, vol. 45, p. 1399
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