Acoustic Waves for Gas and Liquid Phase Sensing

Glen McHale

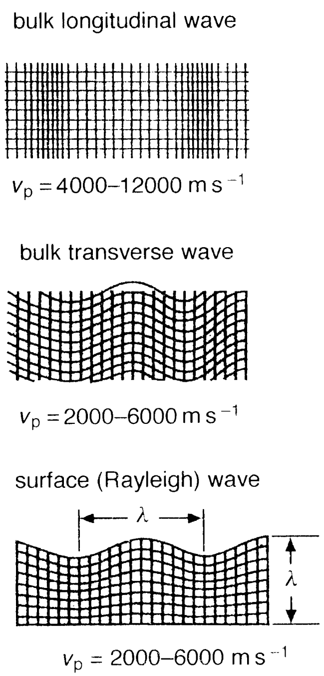
School of Science
The Nottingham Trent University
Nottingham NG11 8NS, UK

Overview

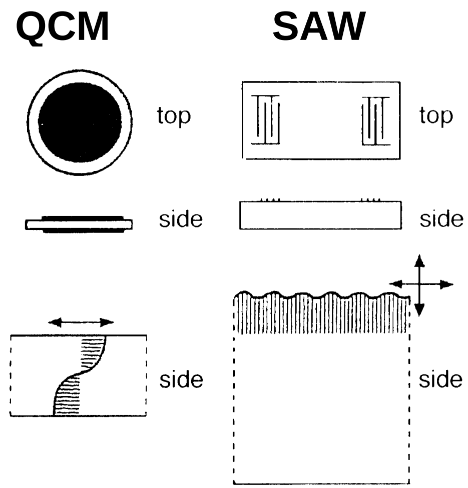
1. Acoustic Waves
    - Acoustic wave modes
    - Principles of sensing (QCM/SAW)
2. Literature Examples
    - SAW for dew/frost point sensing
    - QCM for monolayer phase transitions
3. Our Recent Work
    - Steroid and particulate detection
    - Combined optical-SAW
    - Love waves and biosensing: Theory & Experiment
    - Super-hydrophobicity and acoustic waves

Acoustic Wave Modes

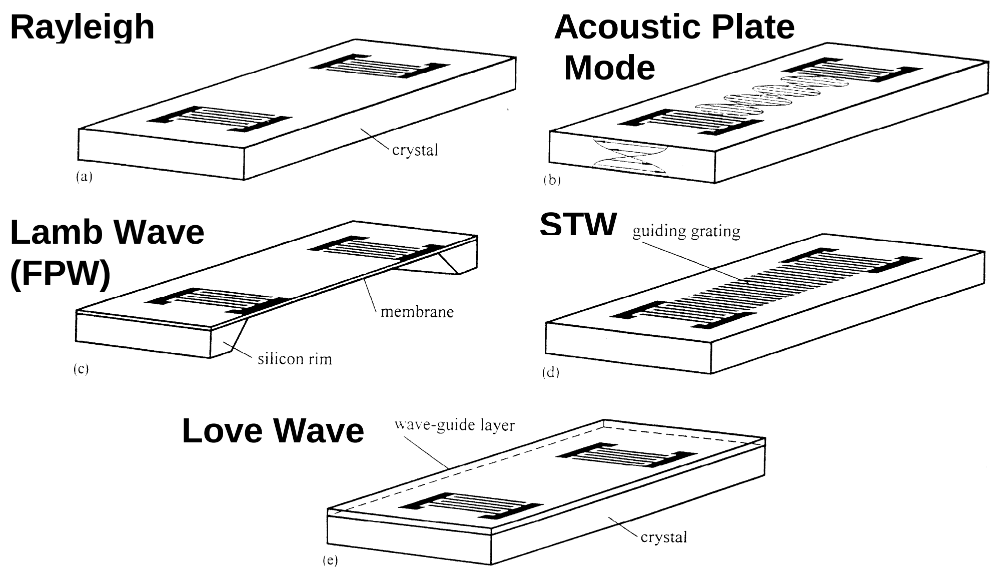
Acoustic Waves



Basic Sensor Devices

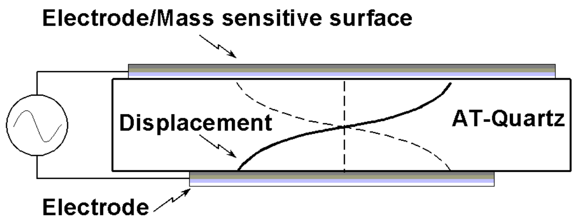


Delay Line Config's ⇒

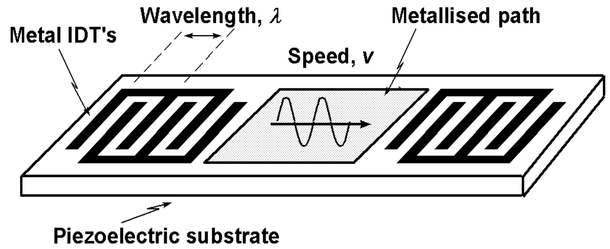


Sensing Principles

- Quartz Crystal Microbalance (QCM)
  Thickness shear mode oscillation



- Surface Acoustic Wave (SAW)
  Mechanical wave travelling along a surface (+electric field)



- Create resonator or measure impedance/spectrum
  QCM/SAW determines oscillation freq. $v=f\lambda$

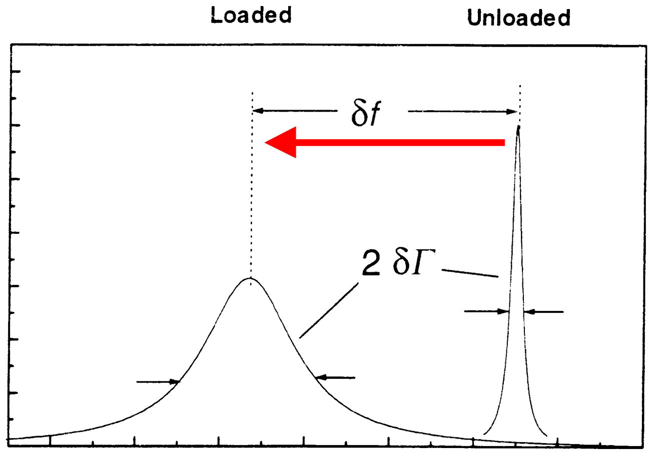
- Mass (thin film) loading
  Main effect is change in frequency
  Sauerbrey equation $\Rightarrow$ $\Delta f \propto f^2 \Delta m/A$

- Surface Loading Alters Resonance

  Mass loading reduces frequency

  Non-rigid mass (e.g. polymers) broadens resonance/creates damping

  (senses shear modulus)



- Liquid Loading & Penetration Depth

  Need shear mode devices

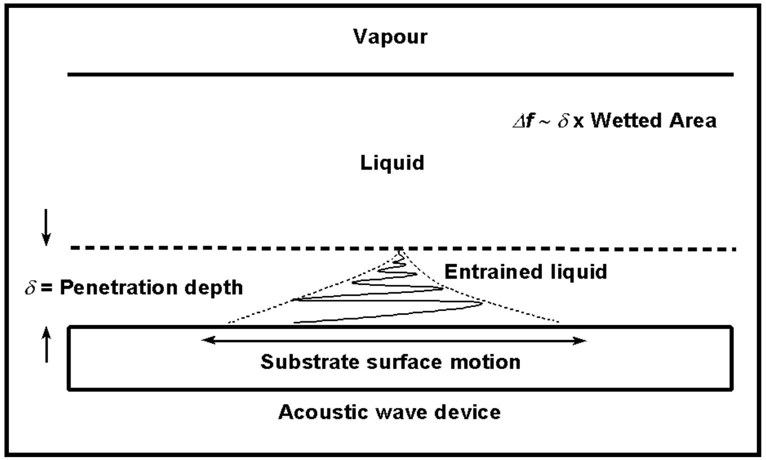
  (QCM, Shear type SAWs)

  Penetration depth $\delta = (\eta/\pi f \rho)^{1/2}$

  Sense mass in penetration depth

  Kanazawa $\Rightarrow \Delta f \propto \sqrt{(\eta\rho)}\, f^{3/2}$

  For water δ ~ 250 nm (at 5 MHz)



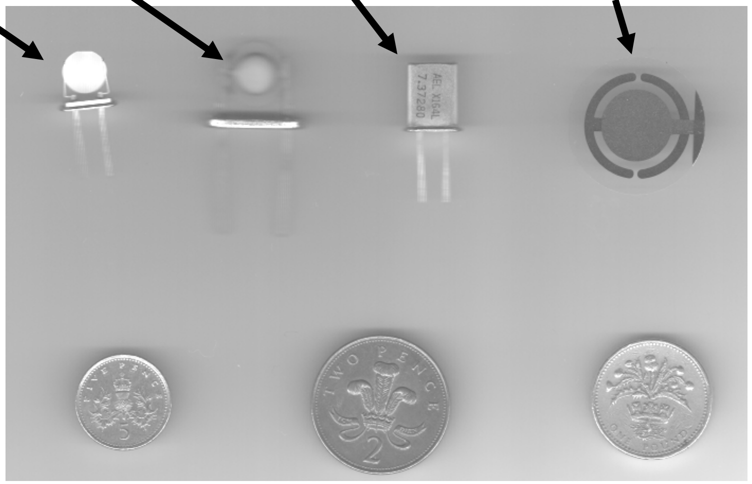
Devices

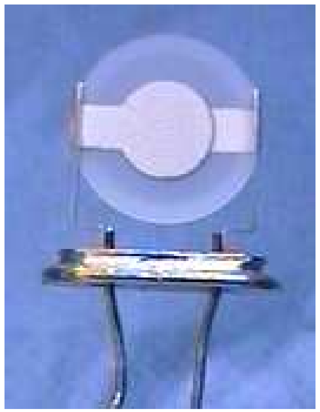
QCMs

Quartz (IQD) Blank/ with Contacts

RS 7MHz Package

Specialist Quartz Crystal/5 MHz





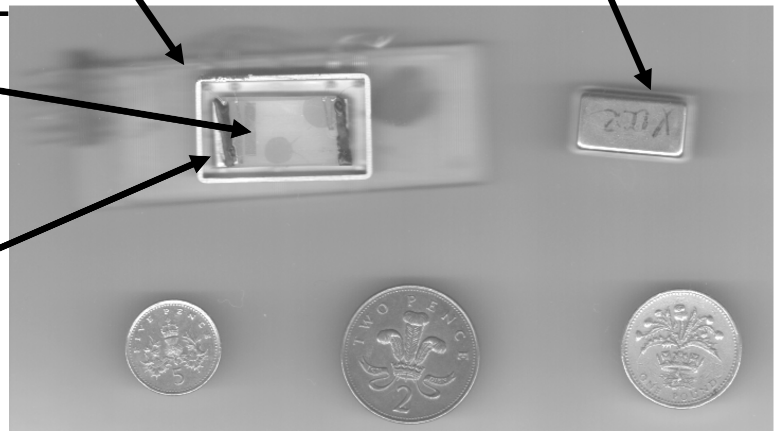
SAWs

50 MHZ RACAL MESL

SAWTEK Package

Apodized IDT
Offset IDTs
Multistrip Coupler

Acoustic Absorber



Dual delay line with one side coated

35 MHz Resonator

Central IDT

Reflectors to create cavity

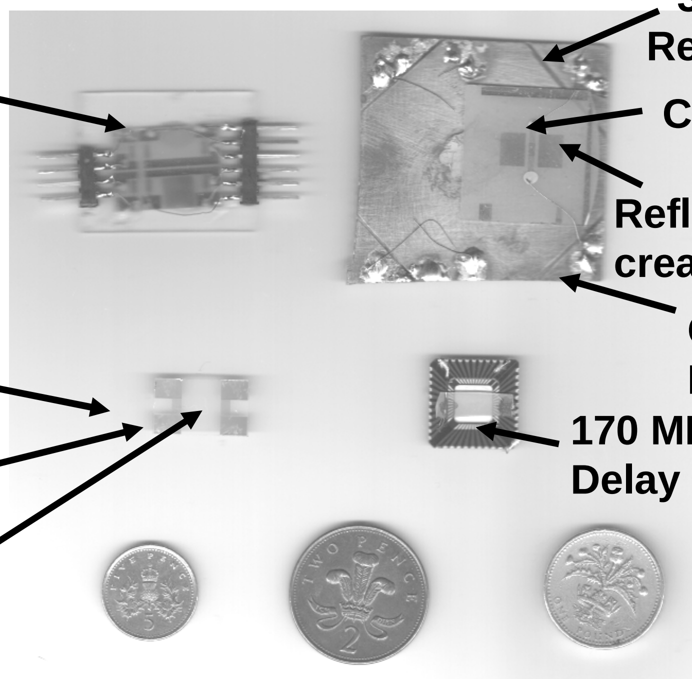
Copper Board

110 MHz SAW

Contact Pads

Sensing Area

170 MHz SAW Delay line



Two Example Applications from the Literature

Atmospheric Data

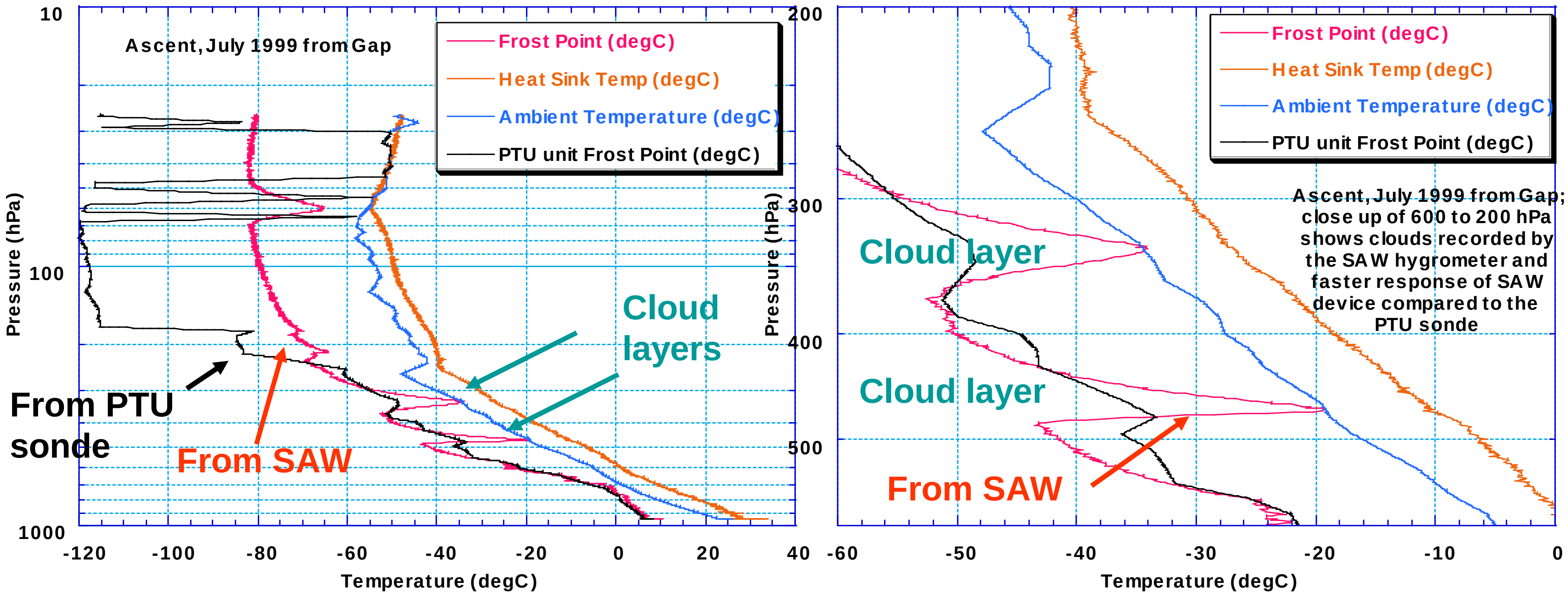
- 400 MHz Saw Based Frost Point Hygrometer

  Dr Rod Jones – Cambridge, UK

  Cycle temperature of substrate using a Peltier

  – loss of SAW resonance gives frost/dew point

  Deployed in a weather balloon



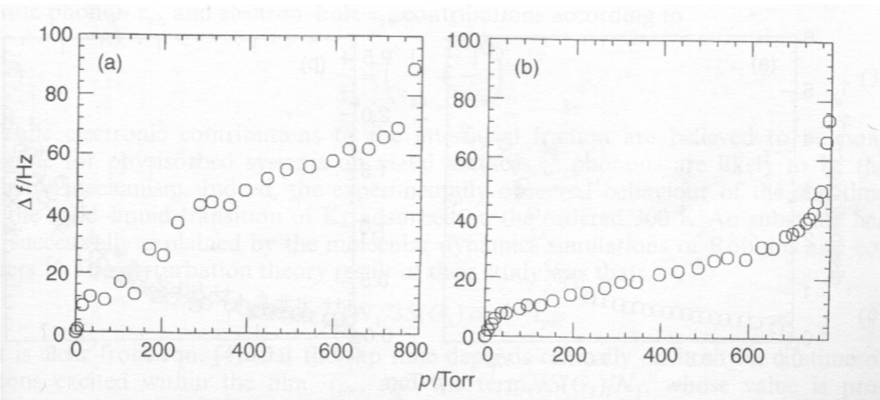
Monolayer Phase Transitions

- 8 MHz QCM
  Prof. J Krim
  Sliding friction on gold surfaces via monolayer adsorption in UHV

Nitrogen adsorption (77.4 K)

Au film deposited at

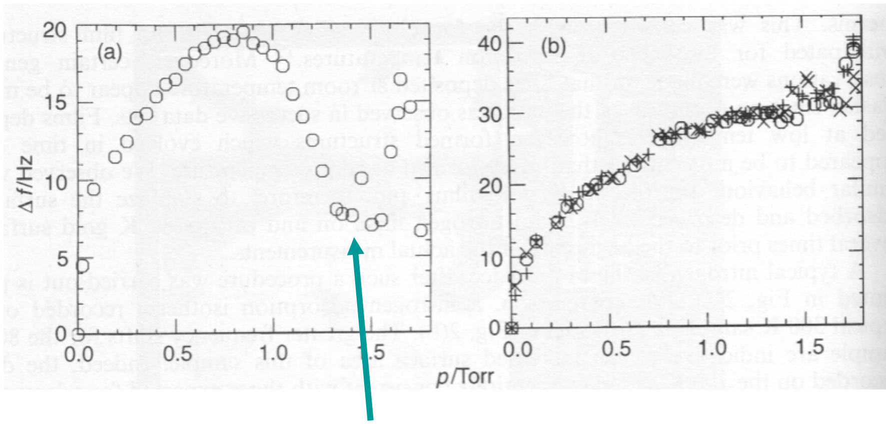
(a) 80 K (b) 300 K



Krypton adsorption (77.4 K)

Au film deposited at

(a) 80 K (b) 300 K



Larger surface area for 80 K deposited Au gives larger frequency shift

Liquid to solid monolayer transition point

NTU Based Acoustic Wave Research

Overview

- Experimental

    QCMs

    MIPs for steroids, terpenes & amino acids, SAMs for PAHs

    Selectivity

    Surface texture & hydrophobicity *Wetting*

    SAWs

    Electrostatic precipitation of atmospheric particulates

    Spreading oils and Rayleigh-SAWs *Instrumentation*

    Love waves for biosensing

    Multiple modes and layer-guided SH-APMs *Sensitivity*

- Theoretical

    Acoustic wave response to multiple viscoelastic layers

    Interfacial slip and interfacial layers of water

    Hydrophobic effects

Two of Our Applications

Molecularly Imprinted Polymers

- Target Applications (*Liquid Phase*)

  Applications: monoterpenes, amino acids, *topical steroids*

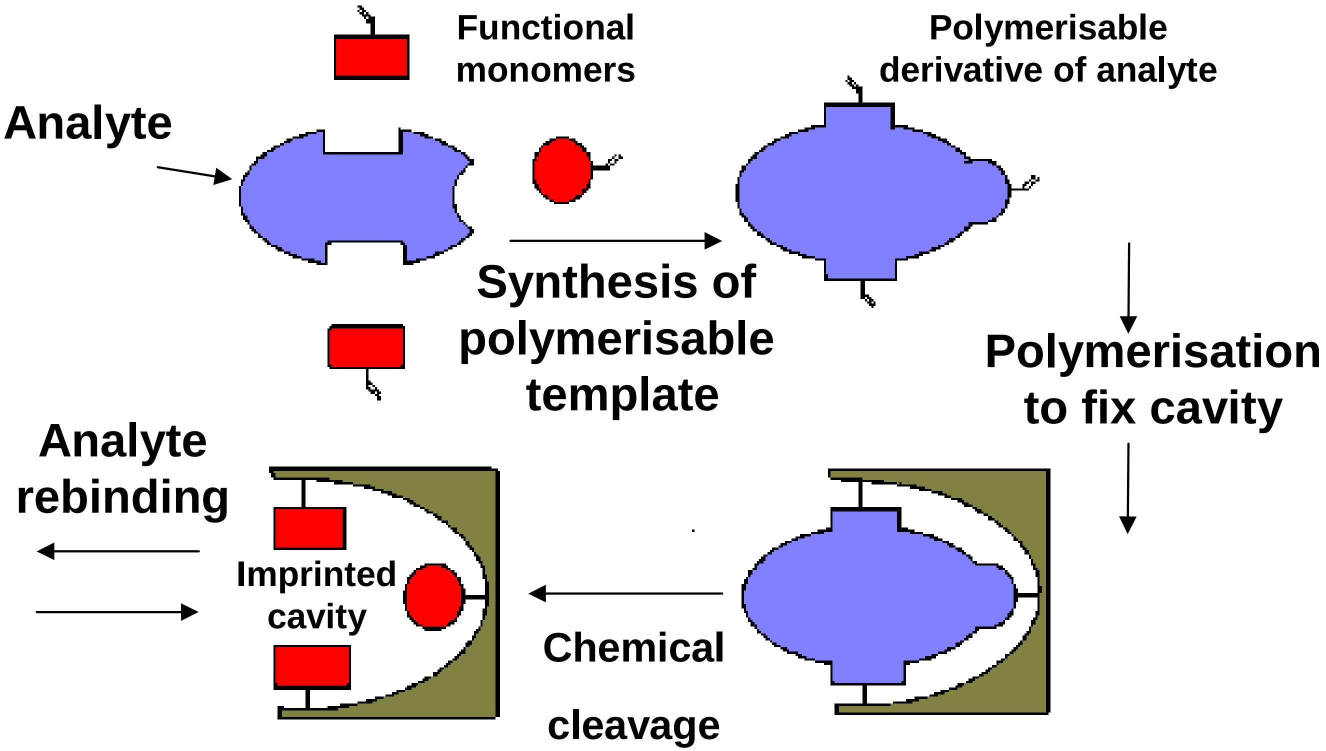
  Tailor made enantioseparation materials

- MIP - Polymer Type Artificial Receptor

  Emil Fisher's 'Lock and Key'
  (enzyme analogy)

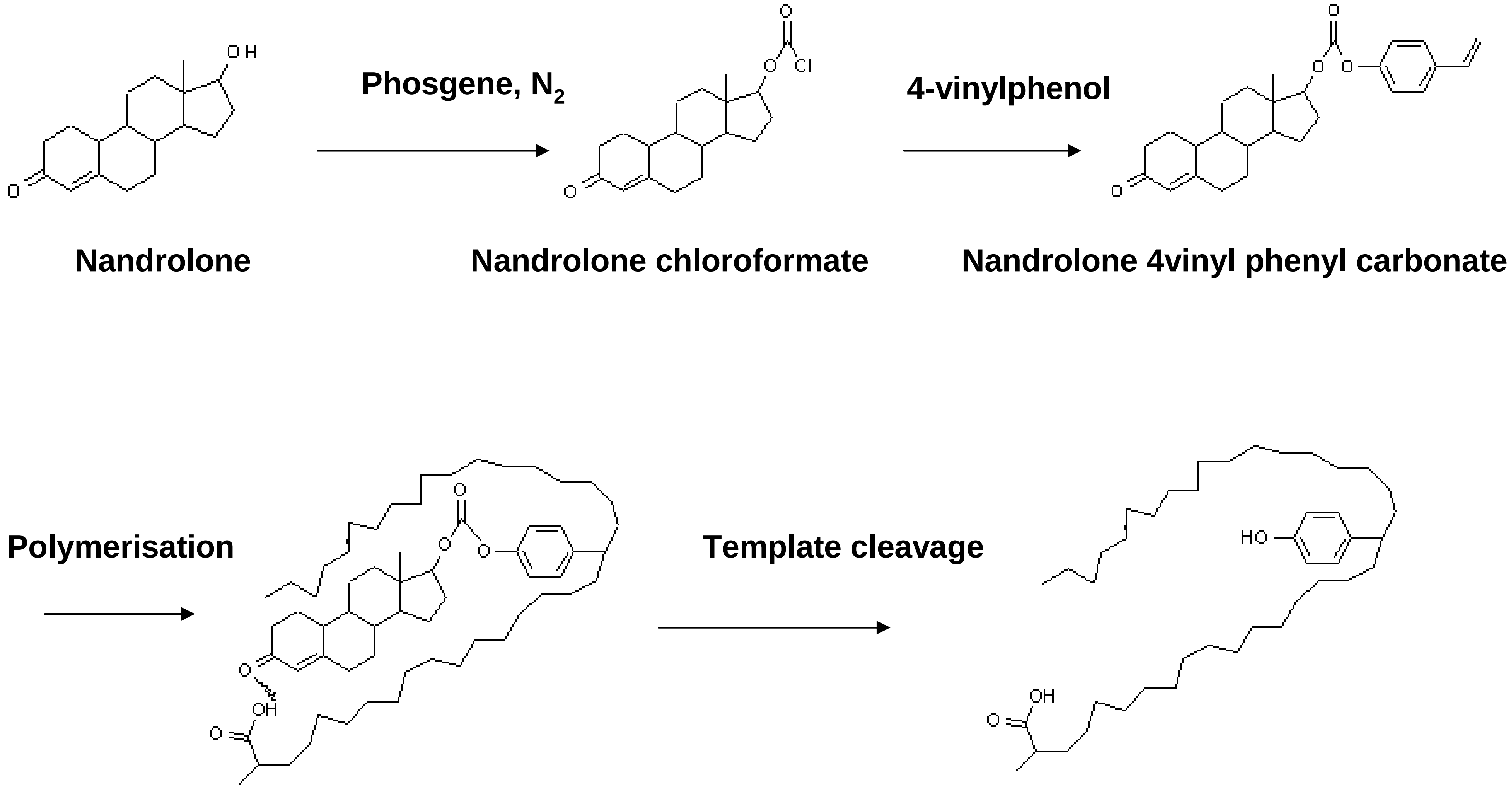
  Specific to target analyte in terms of their spatial and electronic environment

  Diagram shows a covalent approach



Synthesis of Nandrolone MIP

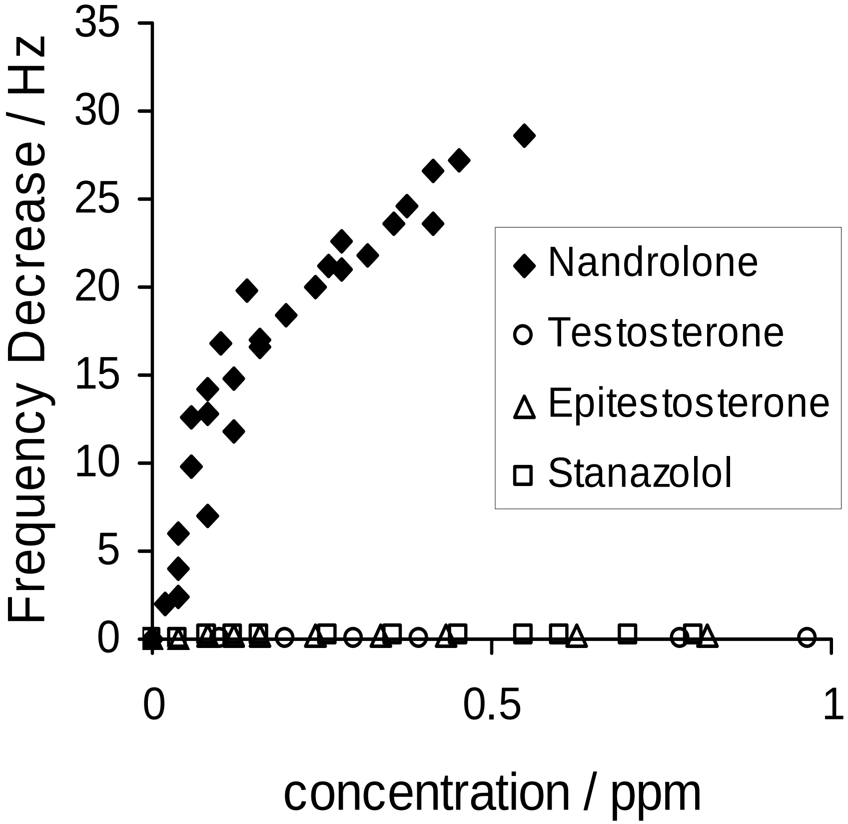
- Covalent Approach (Scheme 1)



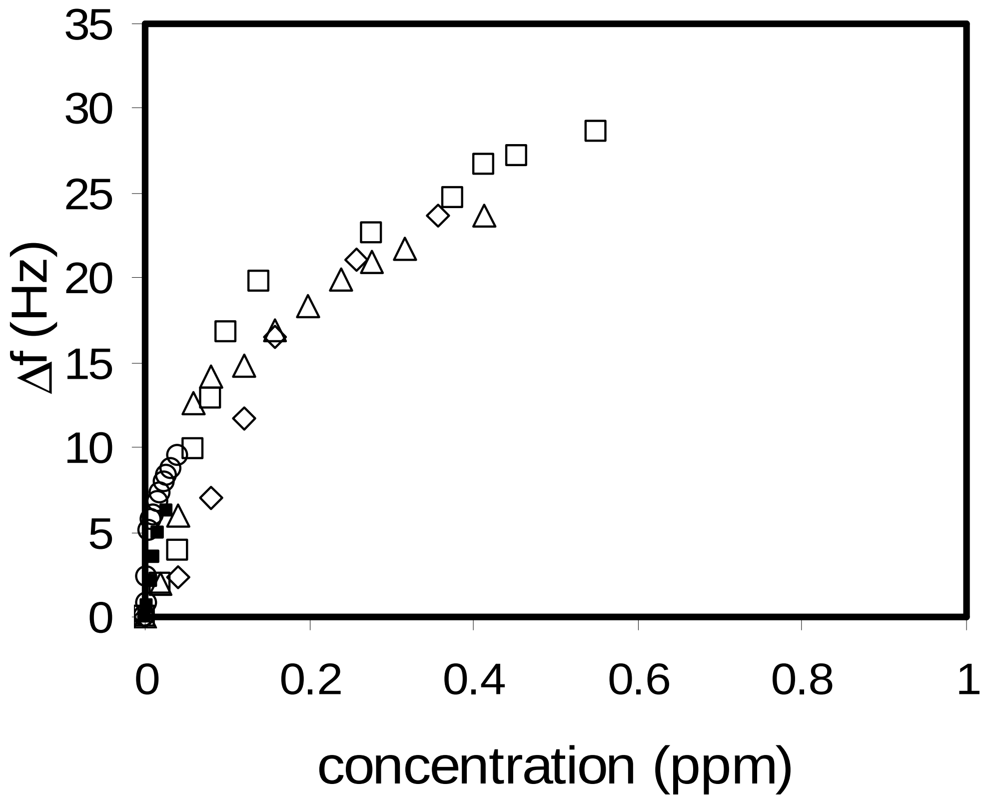
Gives non-covalent recognition sites

Selectivity to Nandrolone

- QCM Coating
  - Spin coated/cast layer
  - Covalent imprinting strategy
    - Polymer 1 - Imprinted
    - Polymer 2 - Non-Imprinted

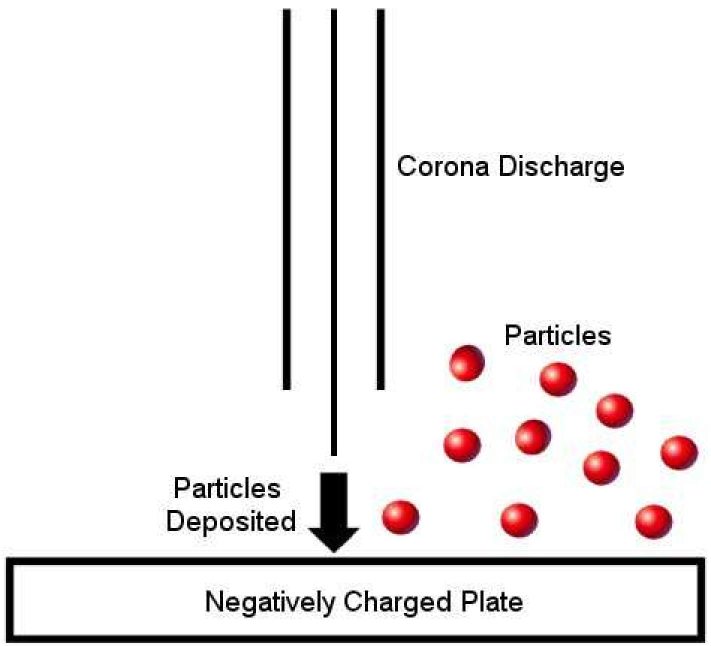


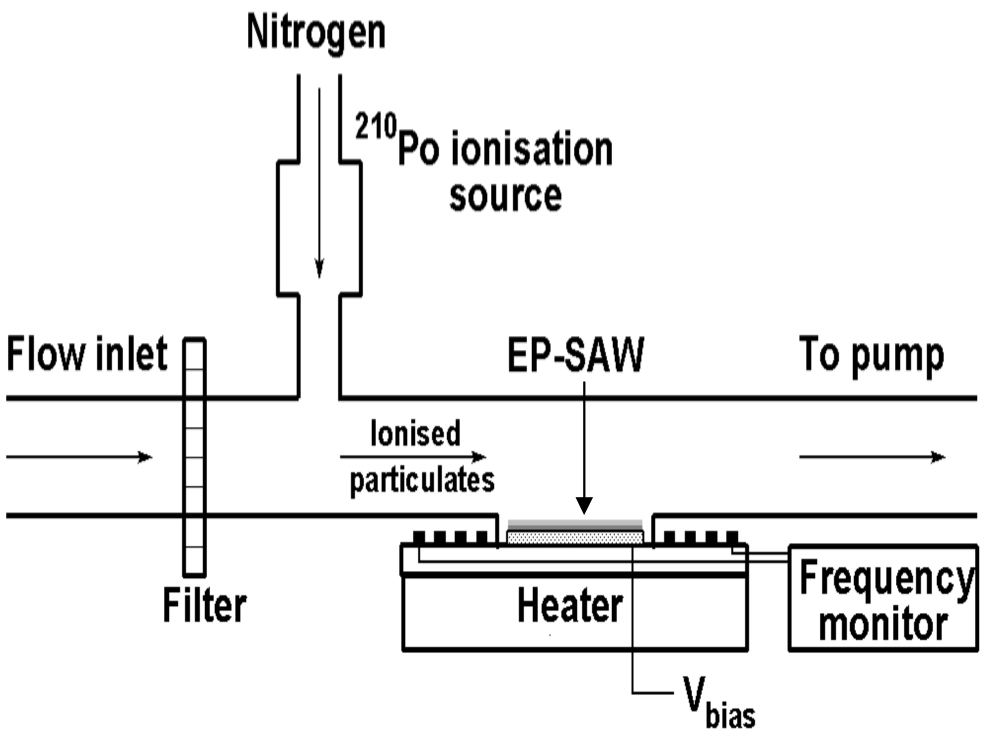
- Response to Replicates
  - One-shot screening
  - Test data for 5 crystals



EP-SAW for Atmospheric Particulates

- Electrostatic Precipitation
  - Charged particles deposited on a collector plate
  - Established principle for atmospherically borne microorganisms
  - High (99-100%) efficiency
- System Design
  - Air sampled via filter
  - Particles ionised by N_2^+
  - Particles collected onto path of biased metallised SAW
  - i.e. Electrostatic precipitation





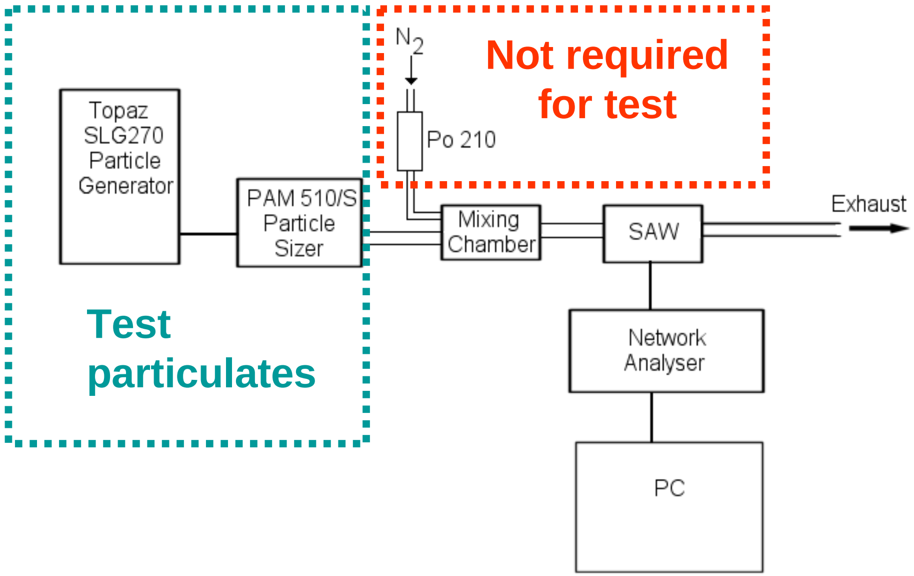
Particulate Response with Bias

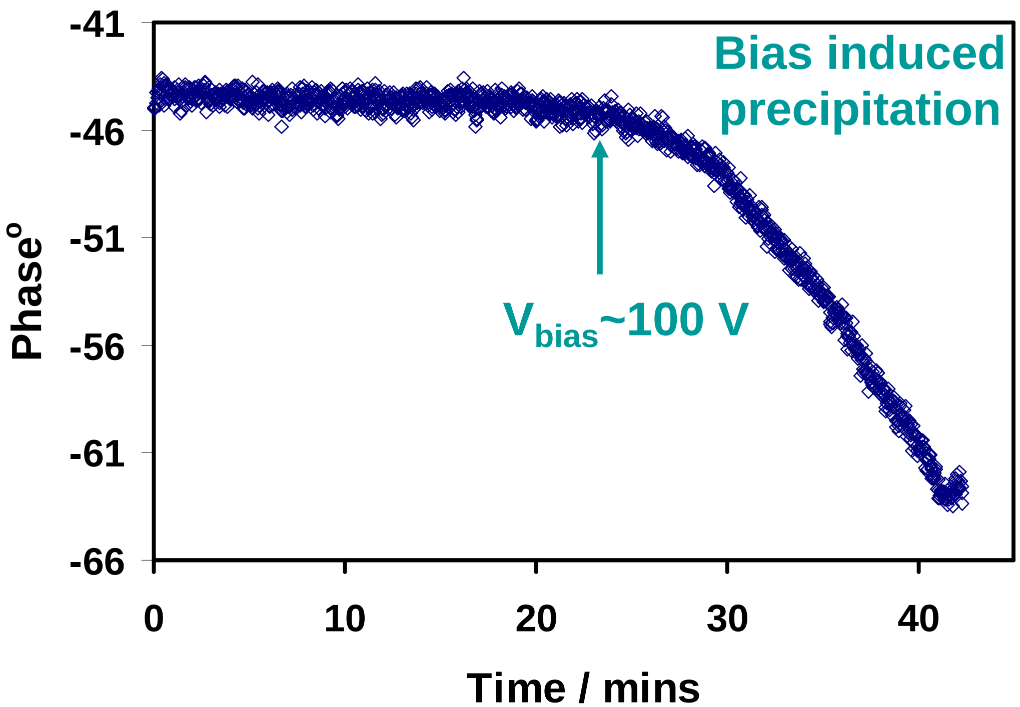
- Test Device Configuration

  $LiNbO_3$ - Rayleigh-SAW, $\lambda \sim 45$ µm
  86 MHz & 253 MHz
  Test particulates via a mono-disperse ~ (2.0±0.1) µm NaCl aerosol

- Preliminary Results

  Voltage of plate increased to > 120 V in 20 V steps
  $\Rightarrow$ Phase changes

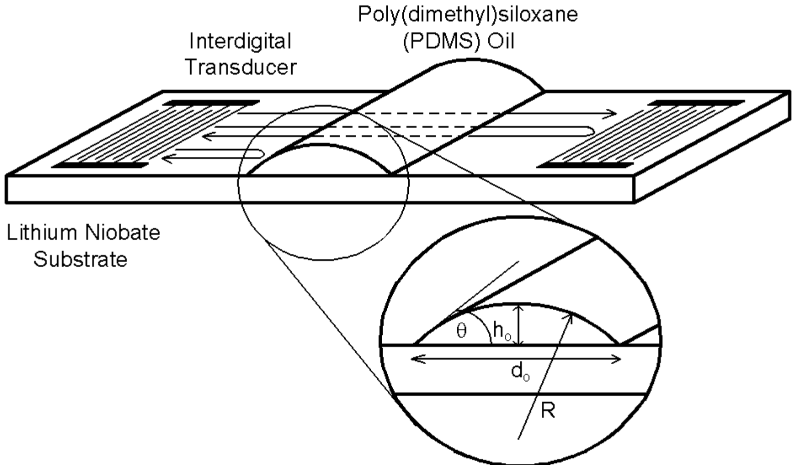




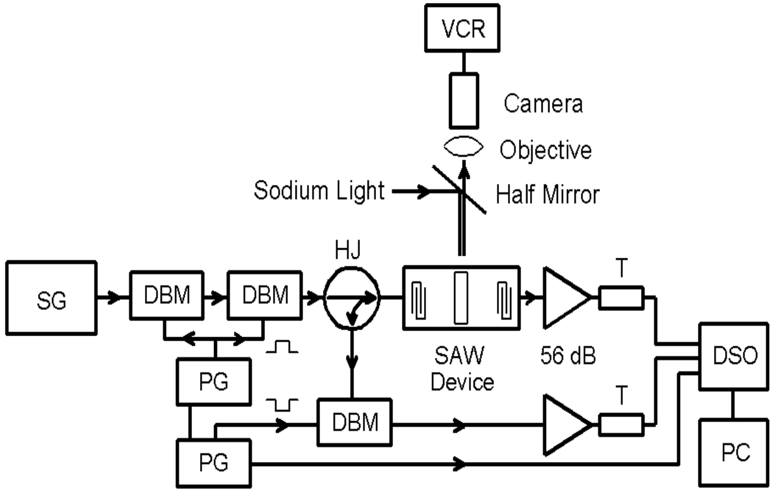
Our Historical Development

Dynamic Wetting and SAWs

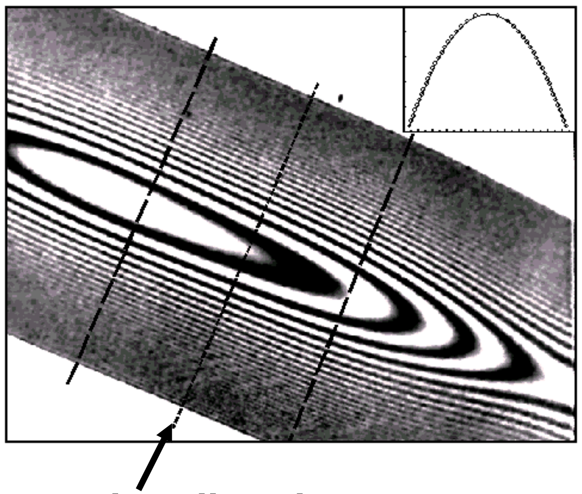
Concept of the Experiment



Schematic of Experiment

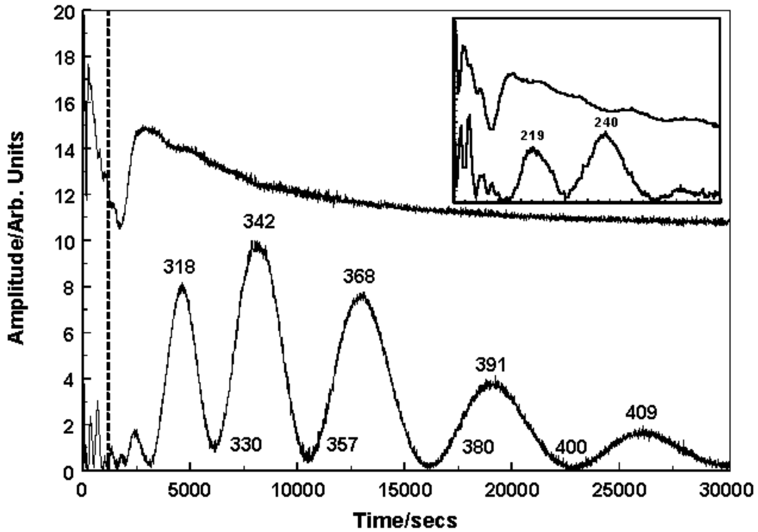


Interferometry



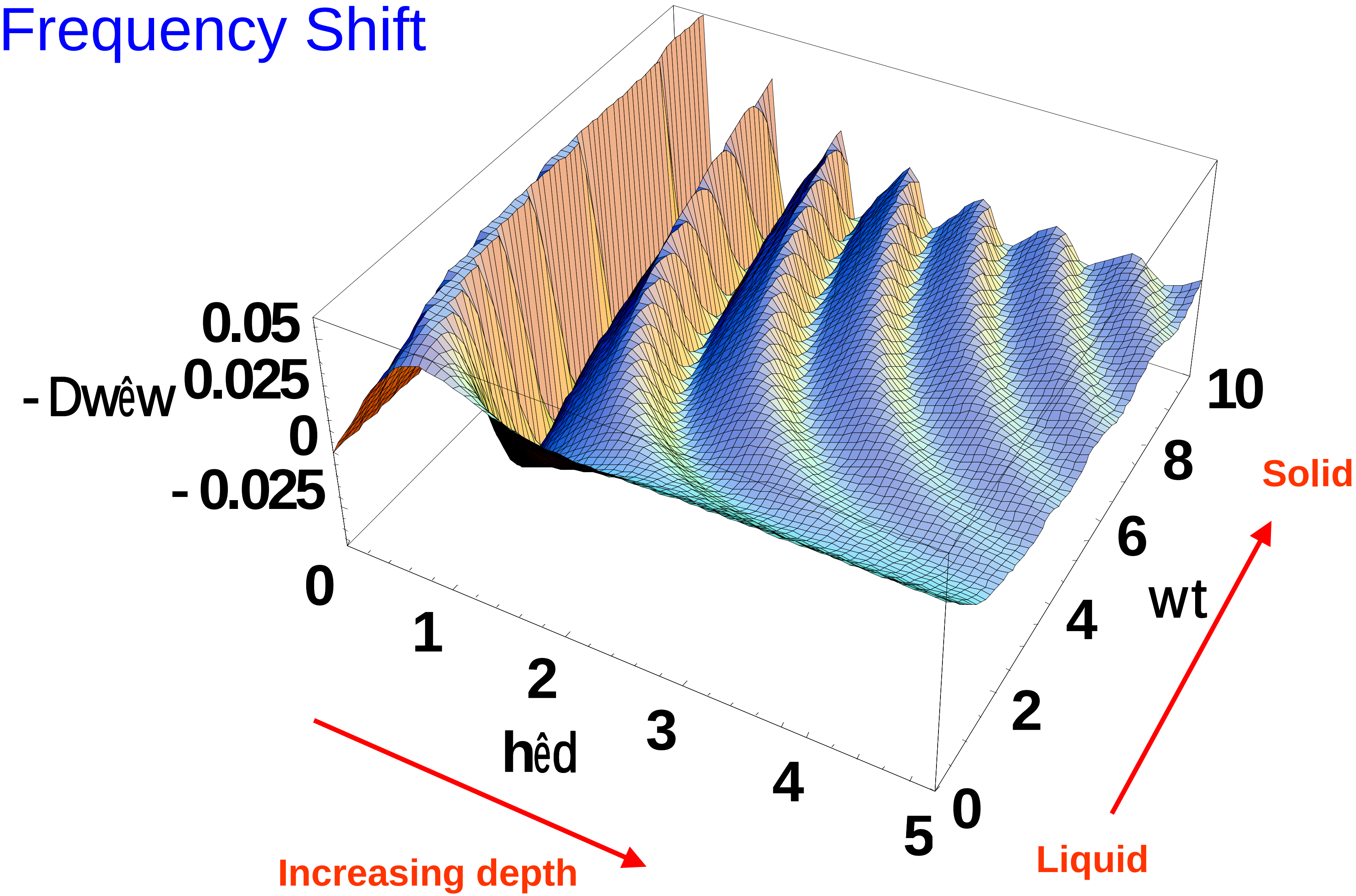
SAW propagation direction

SAW Reflection / Attenuation



Viscoelastic Layer on QCM/SAW - Theory

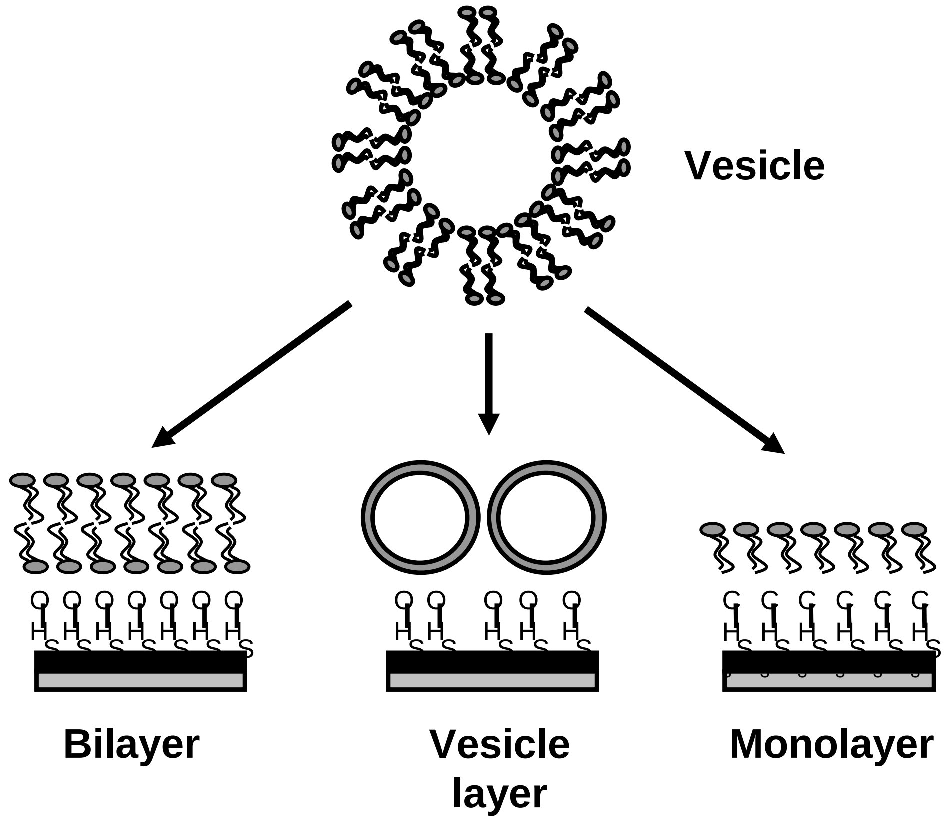
Frequency Shift



Biological Mass and Vesicle Deposition

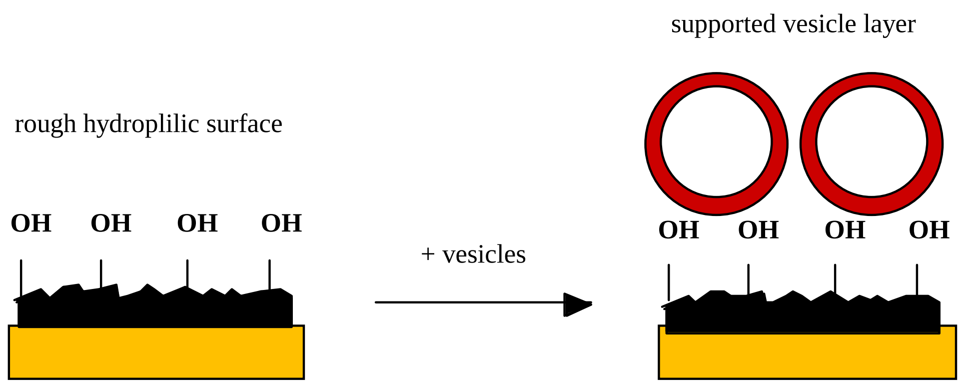
- Concept

  Vesicle deposition to give bilayers and monolayers



- Experiment

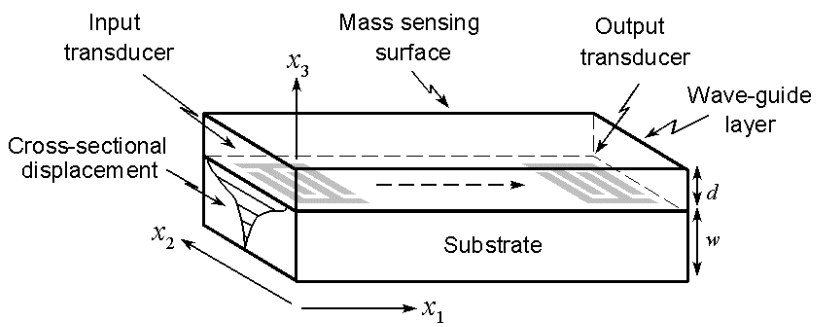
  Flow through system
  Water, buffer solution, vesicle deposition (POPC), detergent

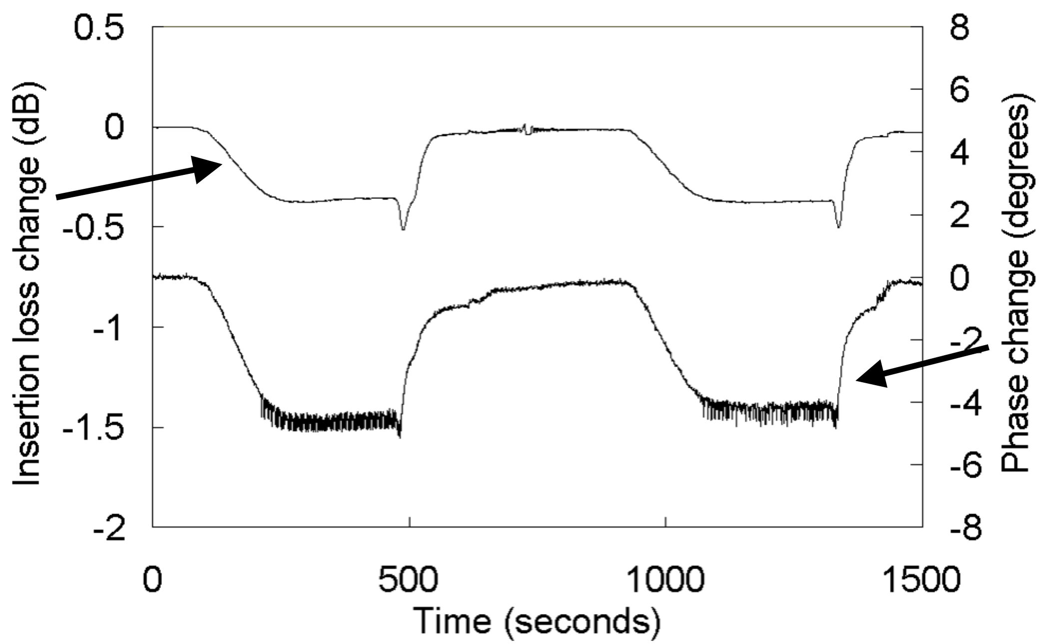


Vesicle Deposition on Love Wave Devices

- Love Wave Devices
  110 MHz (+ 330 Harmonic)
  Pulse (and CW) mode
  Flow cell used
  IL and phase measured

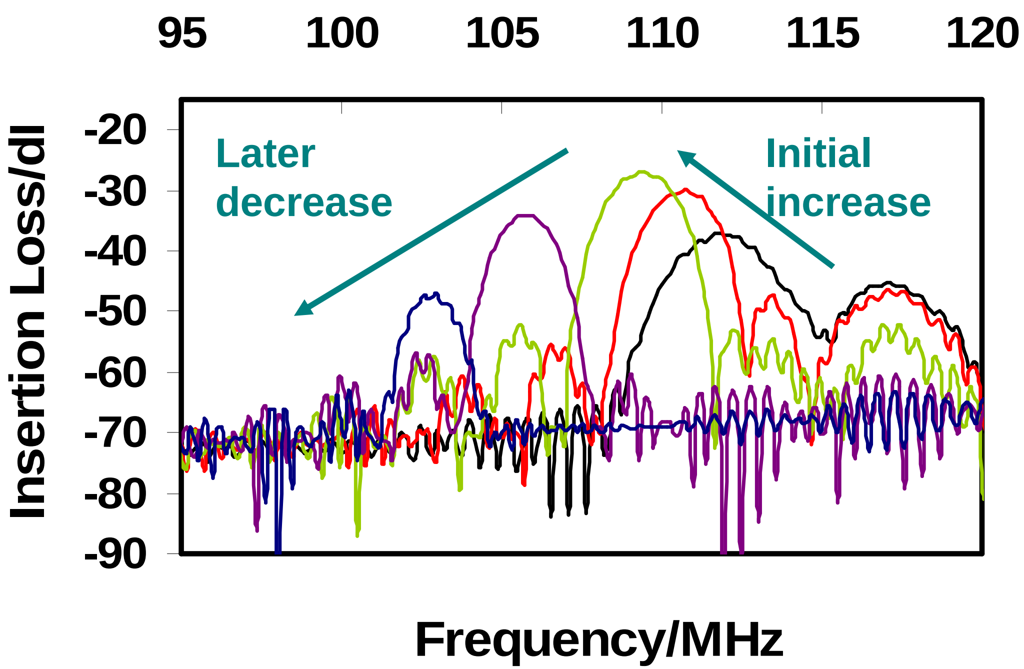
- Experimental Sequence
  Water
  Buffer solution (PBS)
  Vesicle deposition (POPC)
  Detergent
  Repeat (Buffer solution, Vesicle deposition, Detergent)

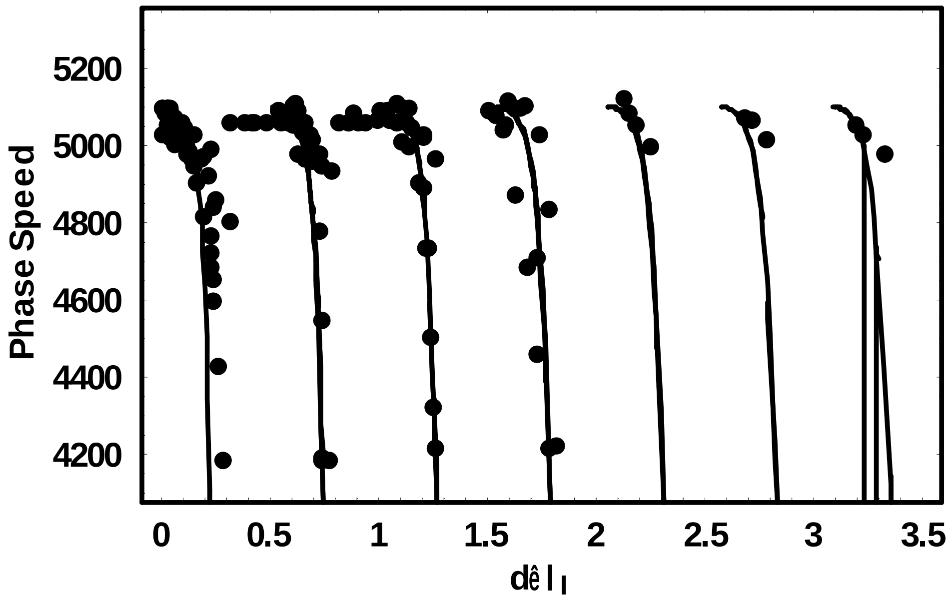




Multiple Love Wave Modes

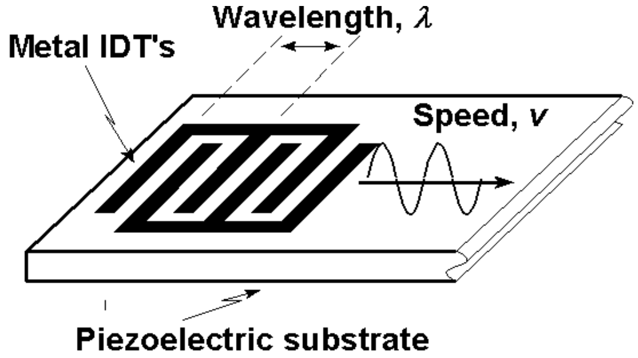
- Spectra
  - Thick guiding layers
  - Photoresist layers
  - Quartz substrate (SSBW)
- Experimental Results
  - Points = results for devices 110/330 and 309 MHz
  - Lines = theory



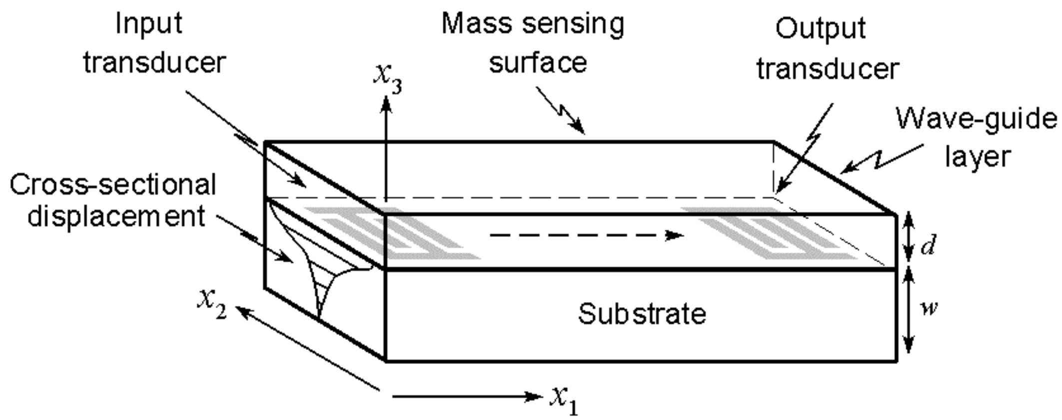


Love Waves v SH-APMs

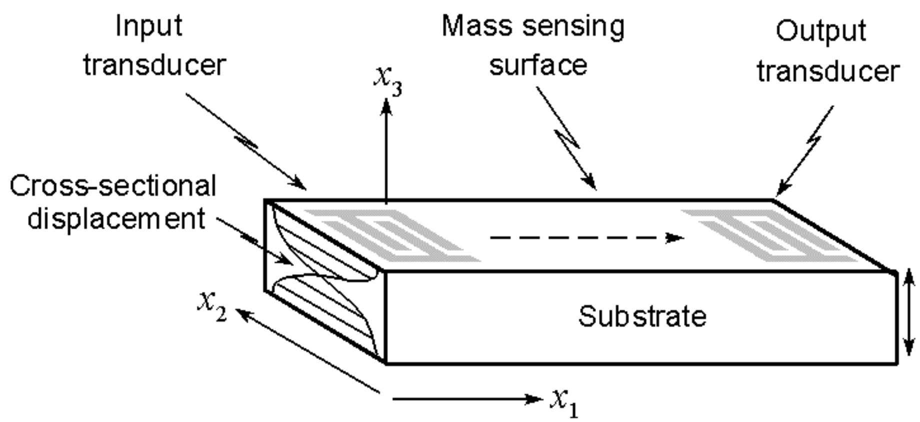
- Surface Acoustic Wave
  (SAW)



- Love Wave
  Layer guided SH-SAW
  with $v_l < v_s$

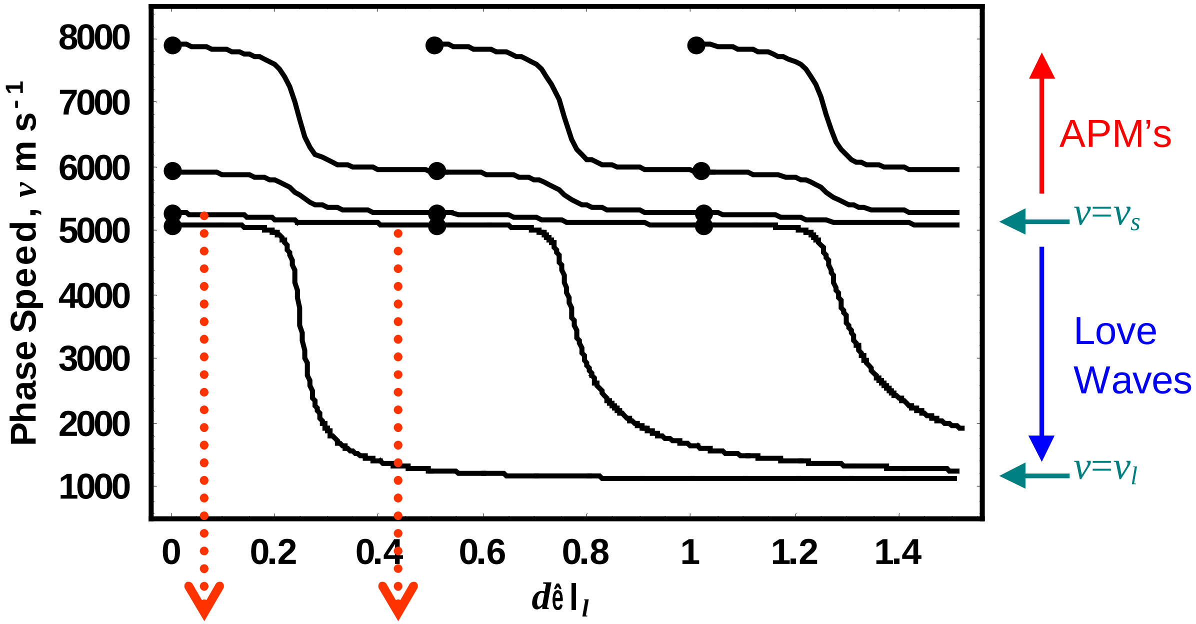


- SH-APM
  Substrate resonance



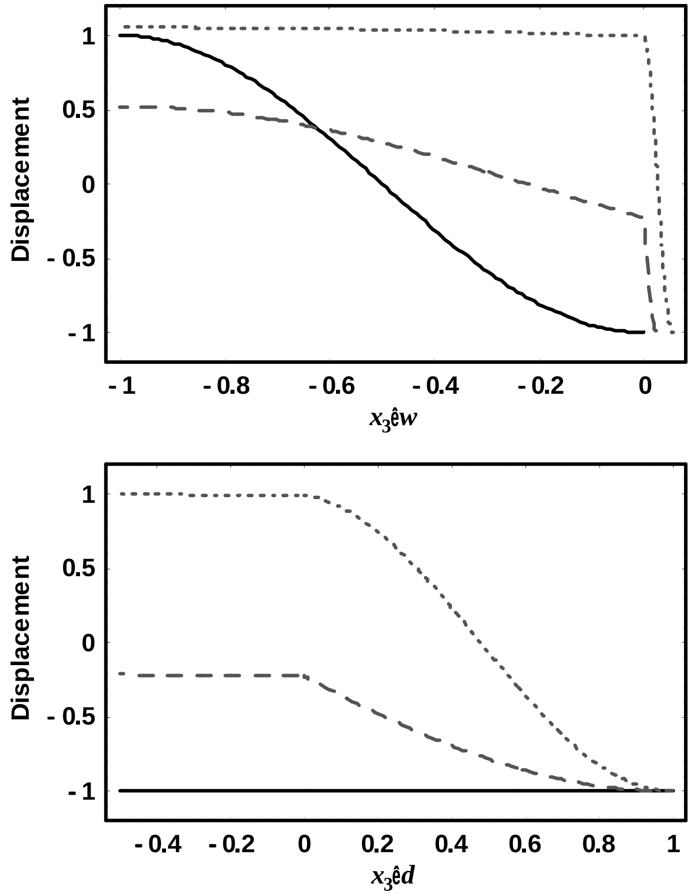
Layer-Guided SH-APMs

Dispersion Curve



Points = Anti-node moving from substrate to layer

Evolution of 1st SH-APM



Solid $\rightarrow$ dashed with increasing guiding

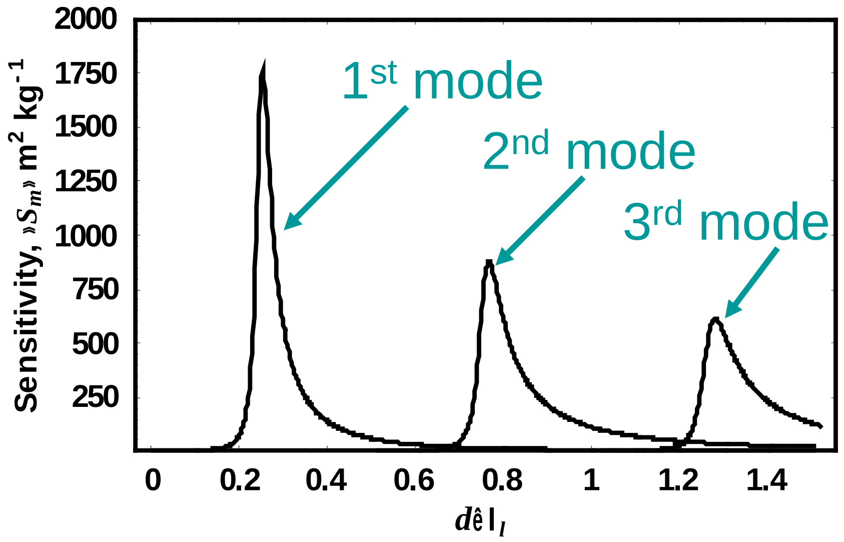
Phase Speed Mass Sensitivity

$$S_m = \lim_{\Delta m \to 0} \frac{1}{\Delta m}\left(\frac{\Delta v}{v_o}\right) \approx \frac{f_o}{\rho_l v_l}\left(\frac{d \log_e v}{dz}\right)_{z_0}$$

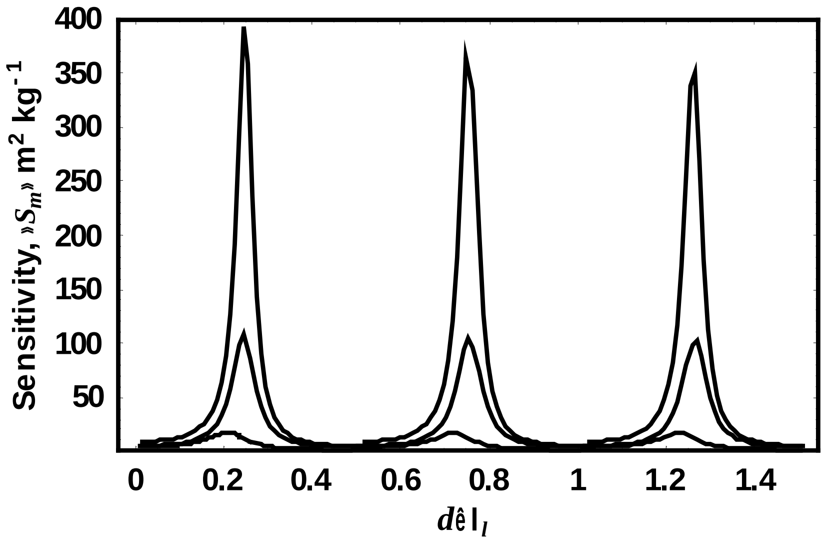
Δm is mass per unit area being sensed, $z = df/v_l$ is the normalized thickness

sensitivity is slope of dispersion curve

Love Waves



Layer-Guided SH-APMs



.

Generalized Sauerbrey-Kanazawa

Generalized Sauerbrey Equation – Love waves/SH-APMS

Complex velocity shift

$$\frac{\Delta v}{v_o} \approx \left(\frac{1-v_f^2/v_o^2}{1-v_l^2/v_o^2}\right)\left(\frac{d\log_e v}{dz}\right)_{z=z_o}\left(\frac{\tan\left(T_f^o h\right)}{T_f^o h}\right)\frac{\omega\rho_f h}{2\pi v_l^\infty \rho_l}$$

$\omega\Delta m/A$

$(\rho\eta\omega)^{1/2}$

Complex slope factor
from polymer waveguide

Care Needed

1. Slope depends on ω
2. IL response possible

tan$x$/x factor gives mass/liquid loading limits

$$\left(\frac{\tan\left(T_f^o h\right)}{T_f^o h}\right) \rightarrow \begin{cases} 1 & h \rightarrow 0 \\ \dfrac{\sqrt{-2j}}{2h\left(1-v_f^2/v_o^2\right)^{1/2}}\sqrt{\dfrac{2\eta_f}{\omega\rho_f}} & h \rightarrow \infty \quad \text{and} \quad \omega\tau \rightarrow 0 \end{cases}$$

solid limit

liquid limit

Generalized Sauerbrey-Kanazawa

Generalized Sauerbrey Equation - QCM

Complex velocity shift

$$\frac{\Delta\omega}{\omega_o} \approx \left(\frac{d\log_e\omega}{dz}\right)_{z=z_o}\left(\frac{\tan(T_f^o h)}{T_f^o h}\right)\frac{\omega\rho_f h}{2\pi v_l^\infty \rho_l}$$

Changes to Love wave/SH-APM case

tan$x$/x factor gives mass/liquid loading limits

$$\left(\frac{\tan(T_f^o h)}{T_f^o h}\right) \to \begin{cases} 1 & h \to 0 \\ \frac{\sqrt{-2j}}{2h}\sqrt{\frac{2\eta_f}{\omega\rho_f}} & h \to \infty \quad \text{and} \quad \omega\tau \to 0 \end{cases}$$

solid limit

liquid limit

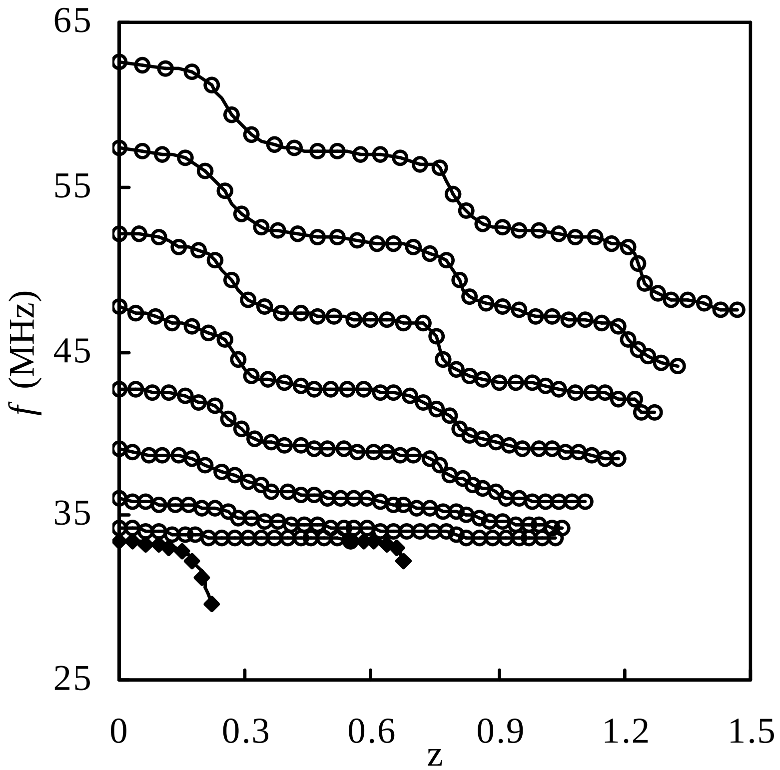
Experimental Results for SH-APMs

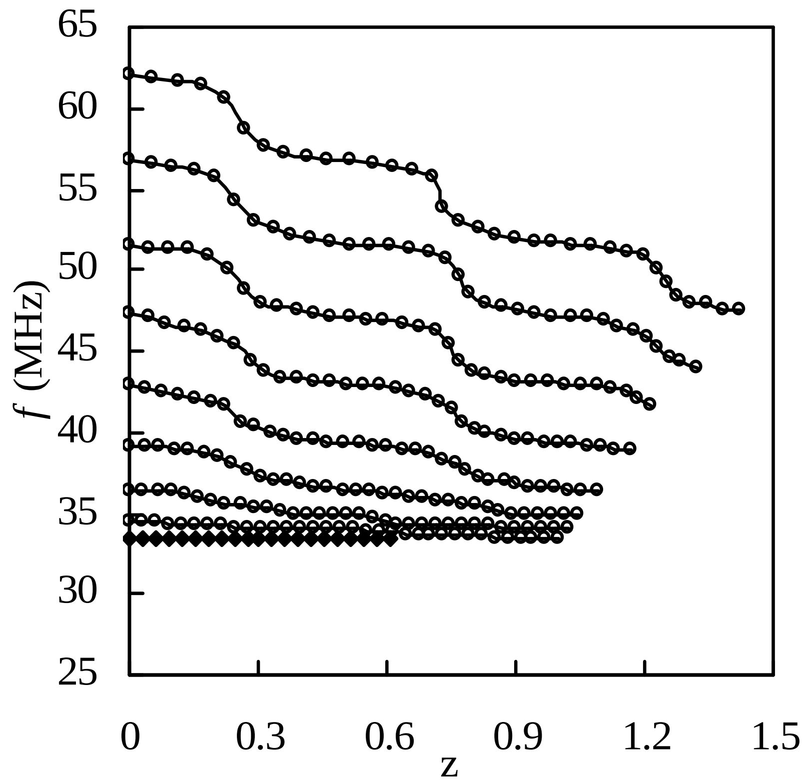
- IDT Face Coated

  Love wave and SH-APM both sensitivive

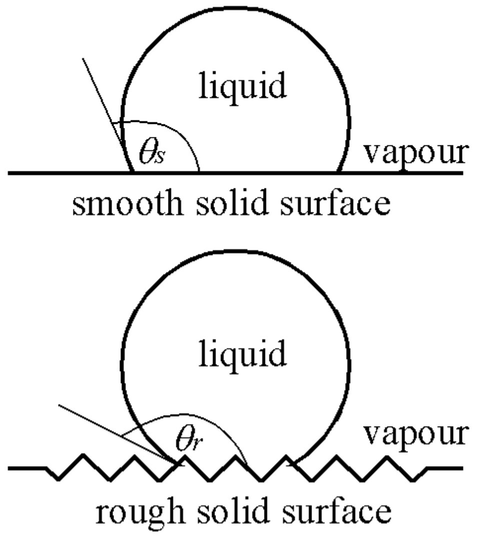
- Opposing Face to IDTs

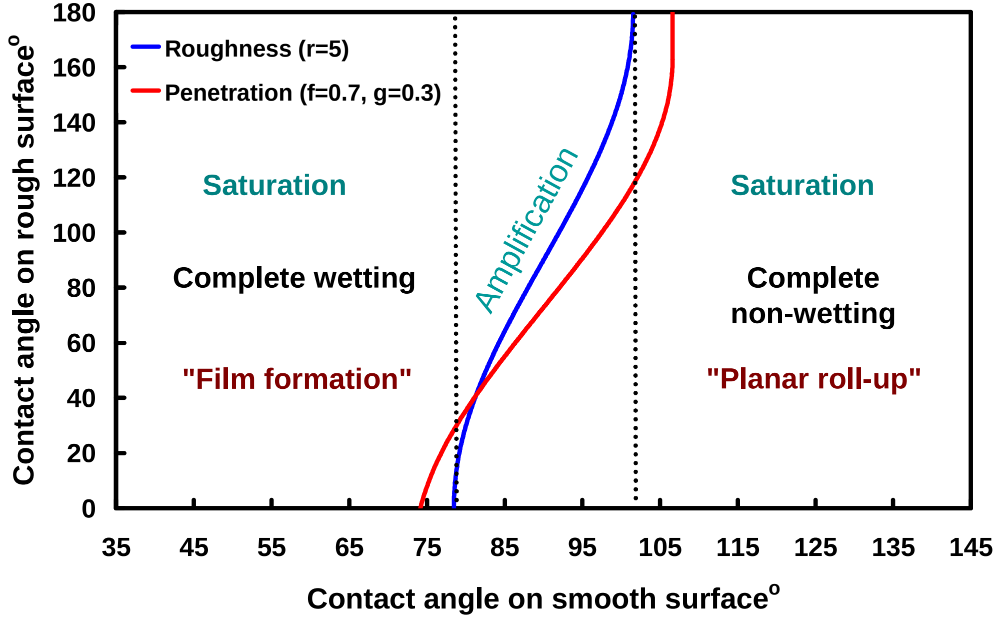
  SH-APM changes Love wave insensitive



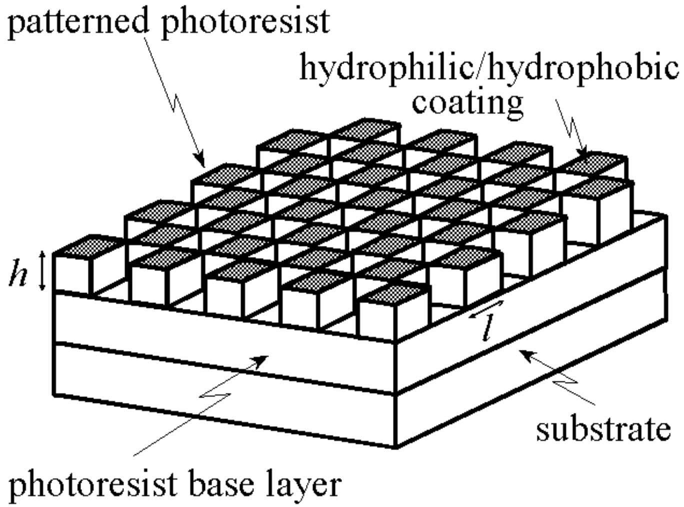


Rough/Structured Surfaces & Hydrophobicity

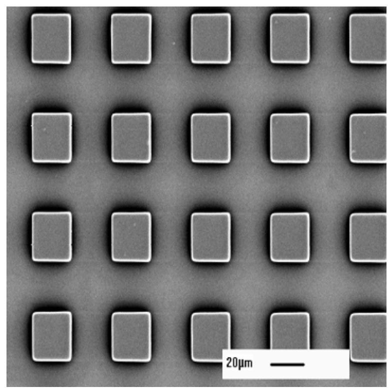


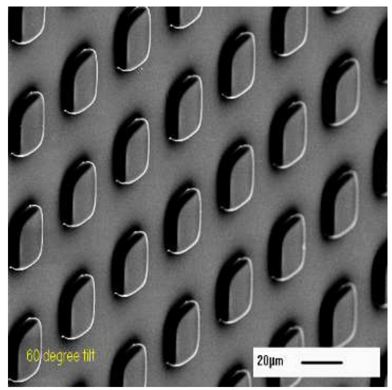


Lithographic Surface



SEM Images





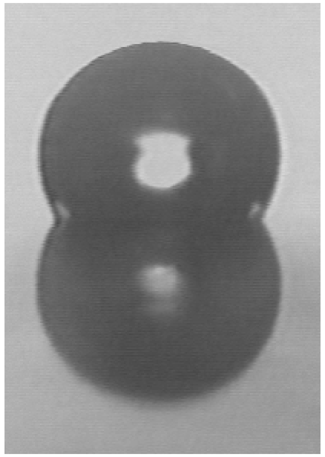
Super-Hydrophobicity

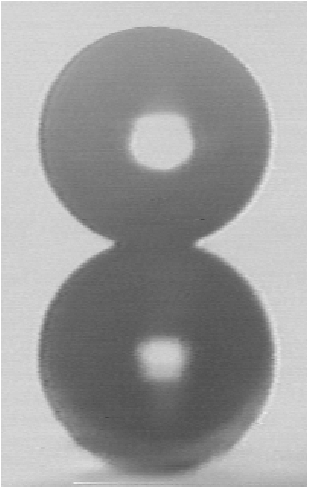
- Contact Angle

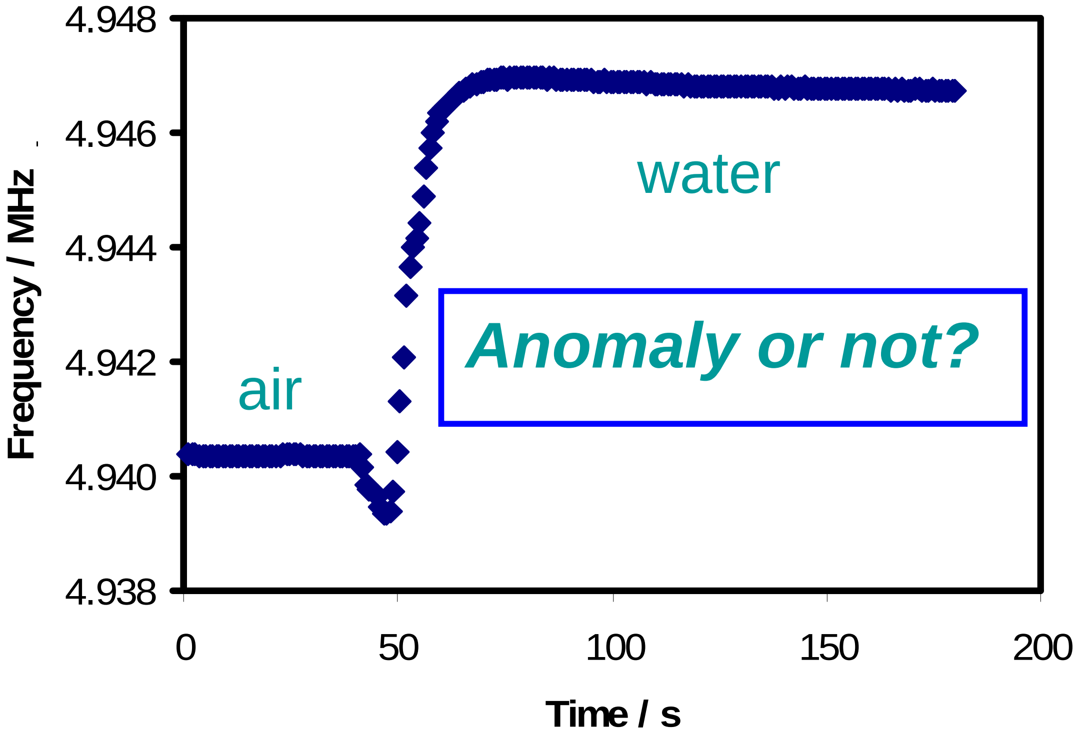
  Side view images
  Identical chemical functionality
  Different topography

- Effect on QCM?

  Response in air
  versus
  response in water







Summary

Acoustic Waves are

- Highly sensitive to interfacial properties
- Operate *in-situ* in gas/liquid phase
- Understood for

Uniform mass films
Simple liquids
Uniform viscoelastic films

Acoustic Waves are not

Intrinsically species selective
Understood for many situations

The End

Acknowledgements

Collaborators at Nottingham Trent

Academics	PDRAs/*PhDs*	
Dr Mike Newton	*Dr Fabrice Martin*	All experimental
Dr Carl Percival	Dr Simon Stanley	QCM/MIPs & SAWs for particulates
Prof. Krylov	Dr John Cowen	SAWs and wetting (Now at L'boro)
Mr Mike Rowan	*Dr Markus Banerjee*	SAWs and wetting
Dr Alan Braithwaite		MIPs
Dr Carole Perry	Dr Neil Shirtcliffe	Superhydrophobic surfaces
	Ms Sanaa Aqil + Mr Edward Harding (Student)	

External Collaborators

Dr Electra Gizeli/Dr Kathryn Melzak	Institute of Biotechnology, Cambridge University
Dr Ralf Lücklum/Prof. Peter Hauptmann	IPE, Magdeburg, Germany
Dr Wayne Hayes	Reading University, UK
Prof. Yildirim Erbil	Istanbul, Turkey
Dr Brendan Carroll	Unilever plc

Funding Bodies

EPSRC GR/L82090, GR/R36718 , GR/R01284 BBSRC 301/E11140

The Royal Society-DAAD, Nuffield Foundation, The British Council-TUBITAK/EU COST

EPSRC for funding and Dr Cernosek and Dr Casalnuovo for hosting this visit

Acoustic Waves - Comparisons

- Types of Wave
  - Thickness shear mode
    - Quartz crystal microbalance (QCM)
  - Surface Acoustic Waves (SAWs)
    - Rayleigh waves, Love waves, Surface transverse waves (STWs), Lamb waves/Flexural plate waves (FPWs)
  - Acoustic Plate Modes
    - Shear horizontally polarised SAWs (SH-SAWs)
    - Surface skimming bulk waves (SSBWs)

Mode	Rel. Sens.	Complexity	Robustness	Gas/Liquid
QCM	Low	Low/Xtal	Med	g+l
SAW	High	Med/metal on Xtal	High	g
Love	High	Med/film+metal+Xtal	High	g+l
STW	*High*	*Med/metal on Xtal*	*High*	*g+l*
Lamb	*High*	*High/membrane*	*Low*	*g+l*
APM	Med	Med/metal on Xtal	Med	g+l

Acoustic Waves Devices - Parameters

- QCM v SAW

QCM	Simple, off-the-shelf, 5 to10 MH, fragile
SAWs	Flexibility by design, MHz to GHz, robust

- Basic Characteristics

Higher frequencies	Higher sensitivity
	Smaller λ, smaller devices

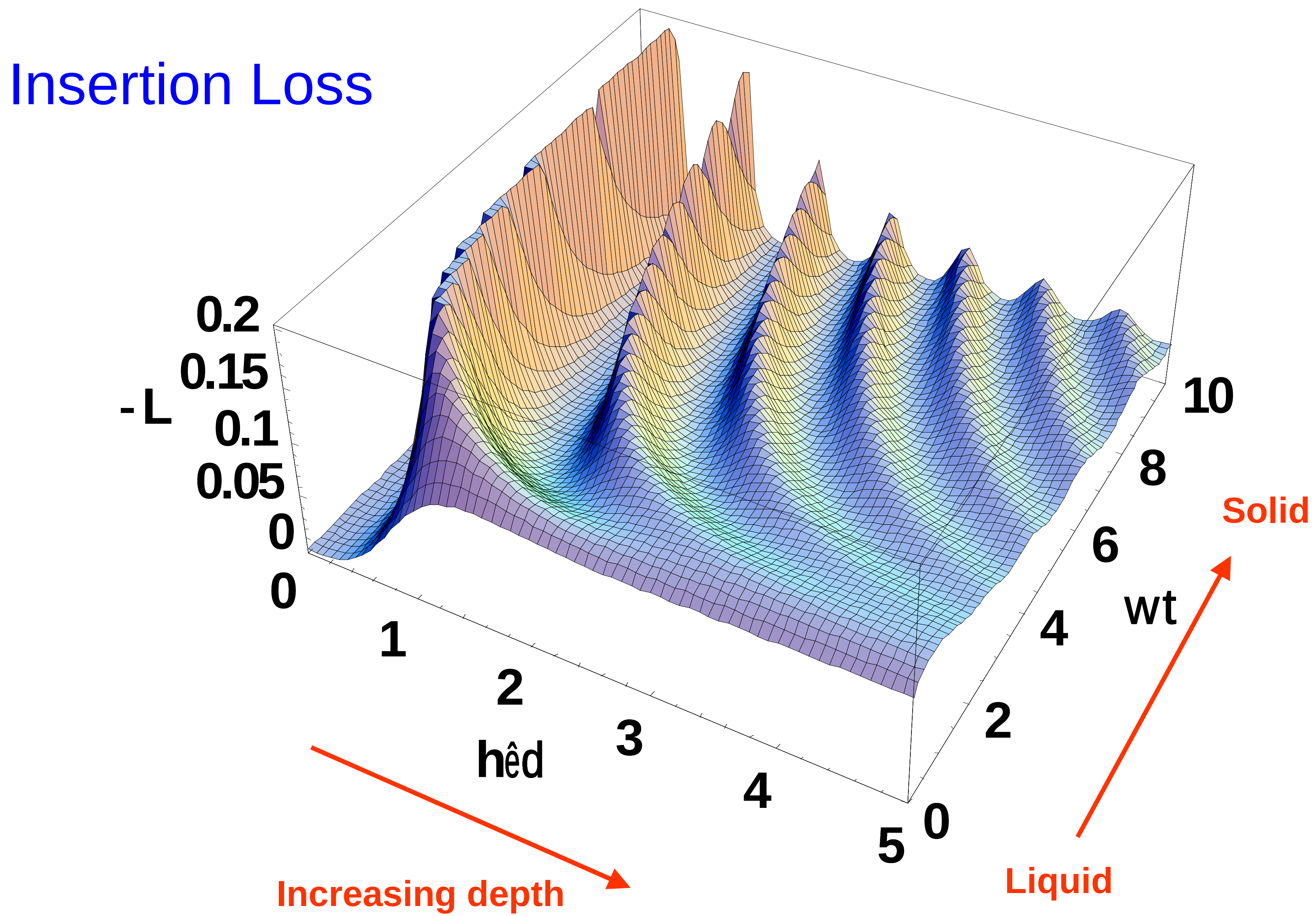
- Typical SAW Parameters

Frequency and wavelength	MHz $\rightarrow$ GHz 400 μm $\rightarrow$ 4 μm
Rapid response	in-situ and better than 10 Hz
Sensitive	13 Hz per ng cm^{-2} at 100 MHz
Size, mass and cost	mm/cm, low and < $1
Power consumption	low
Temp. stability	depends on crystal cut

- Problems?

Selectivity and reproducibility	poor and depends on coating

Viscoelastic Layer on QCM/SAW - Theory



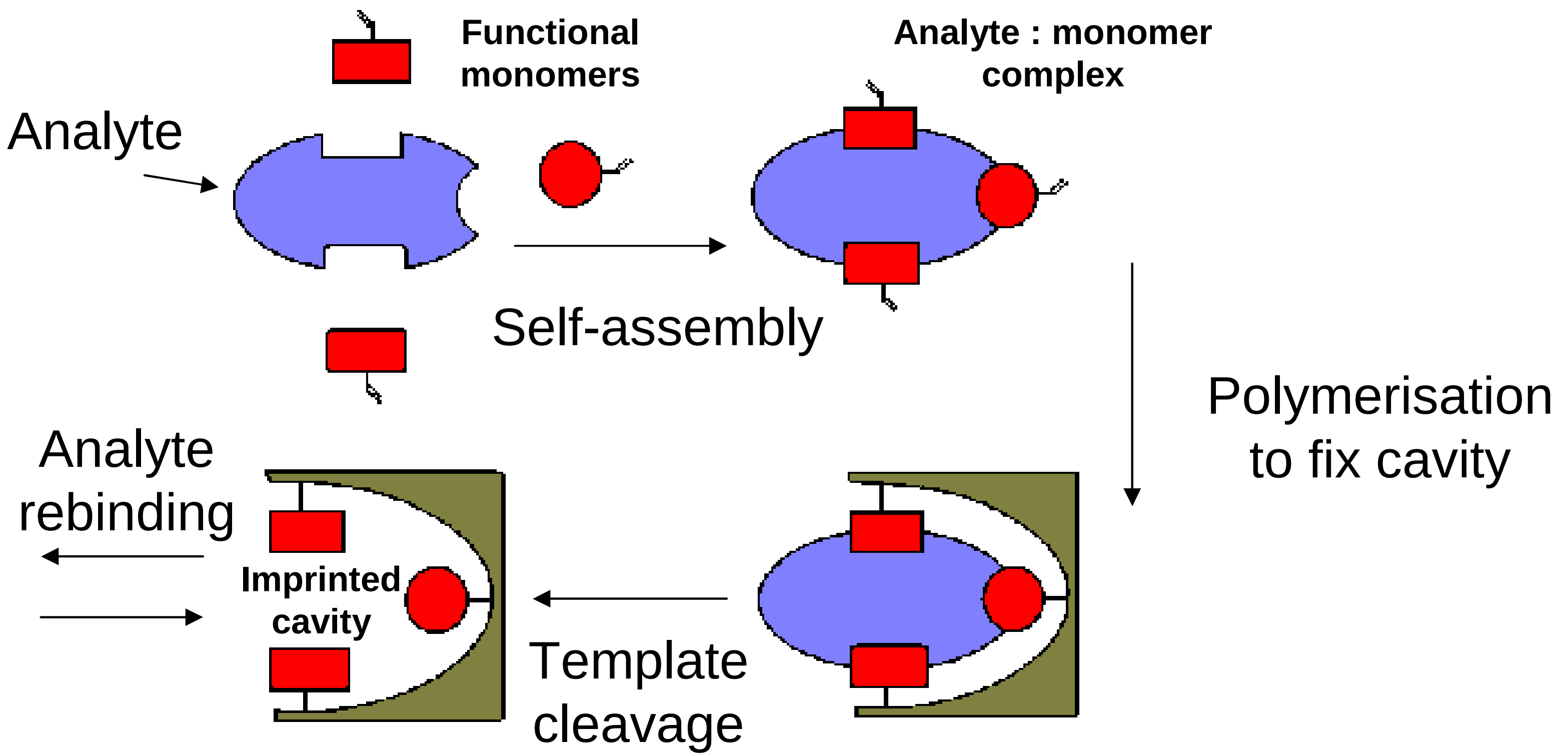
MIPs as Recognition Elements

- Non-Covalent Approach

  Self-assemble functional monomers around template molecule

  Add cross-linker and 'fix' assembly by polymerisation

  Remove non-covalently bound template via solvent



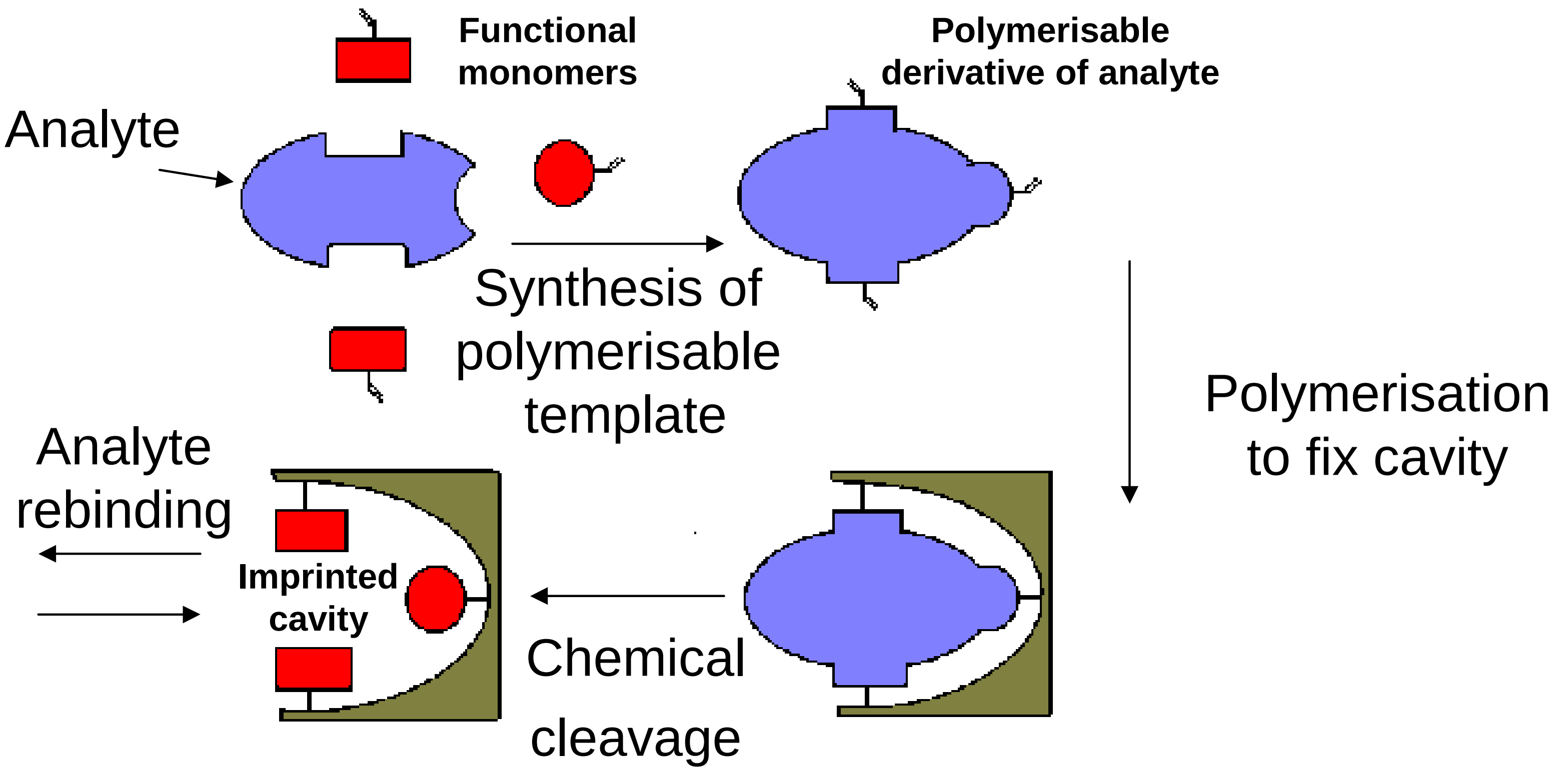
MIPs as Recognition Elements

- Covalent Approach

  Convert template into a polymerisable derivative

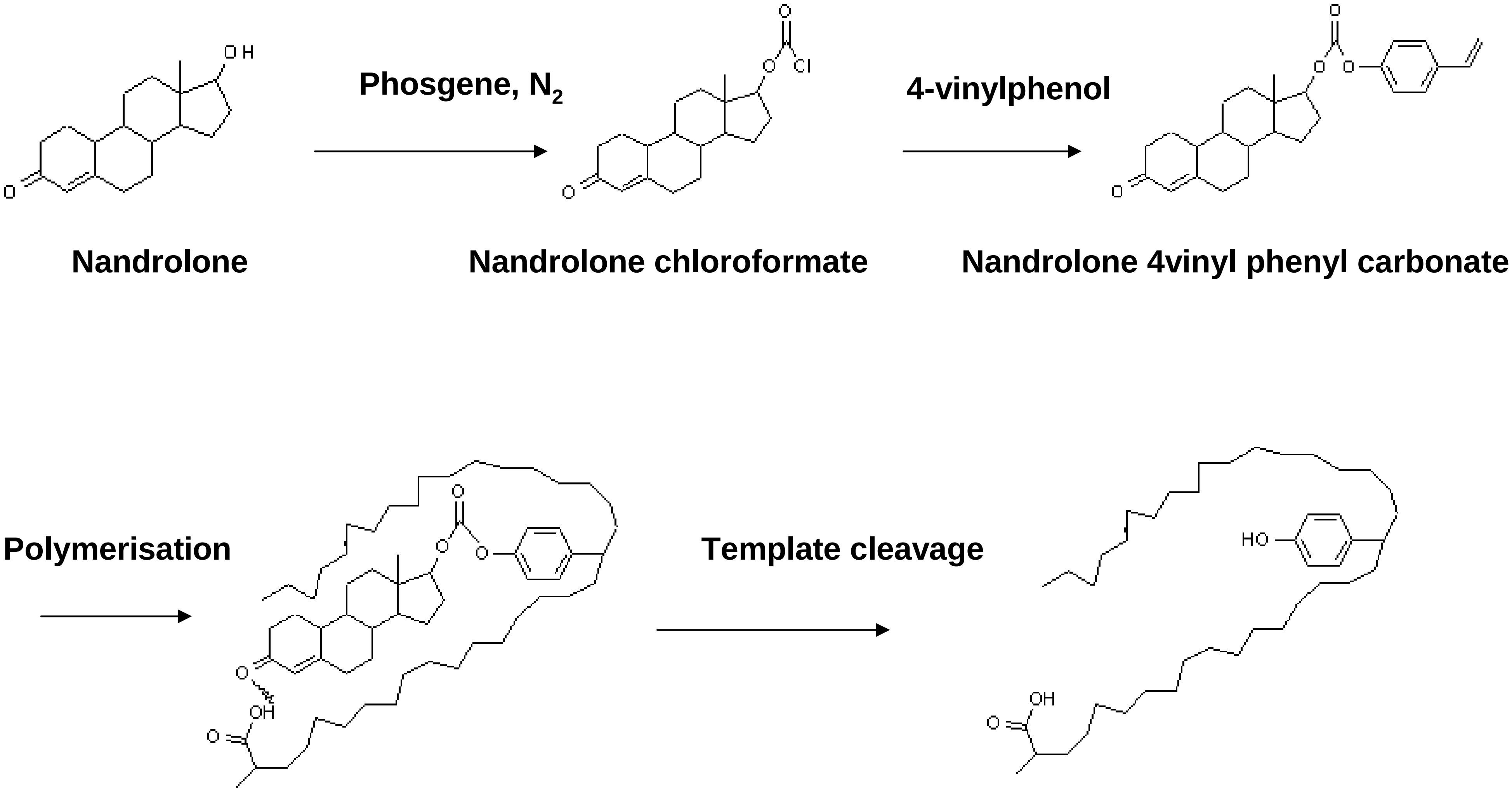
  Co-polymerise with a cross-linker

  Resin covalently incorporates the template



Synthesis of Nandrolone MIP

- Covalent Approach (Scheme 1)



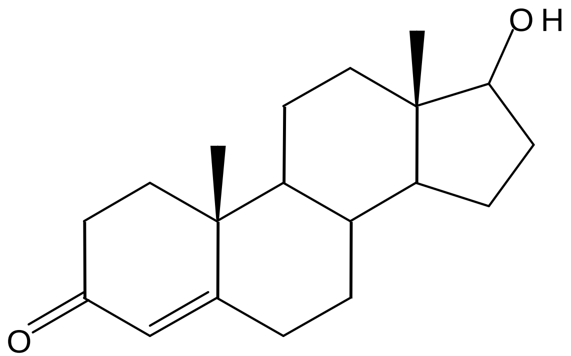
Gives non-covalent recognition sites

<u>Selectivity Between Steroids</u>

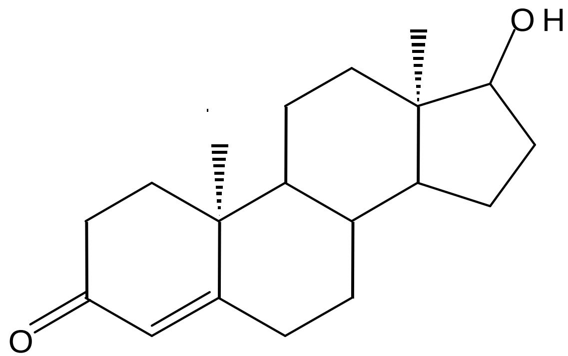
- <u>Future</u> Extension of Scheme 1

  Can be applied to any steroid containing an OH moiety

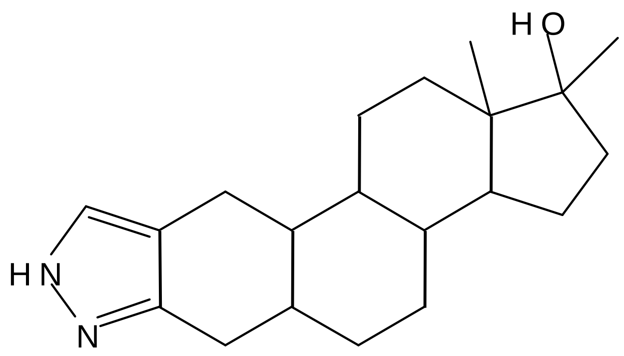
- Steroids of Interest



Testosterone



Epitestosterone



Stanazolol

- Selectivity between Stereoisomers

  Stereoisomers testosterone and epitestosterone

  preliminary work shows can distinguish them

  Natural ratio is 1.5:1 steroid abuse disturbs this ratio