

Theory of QCM and SAW Devices in Sensors and Biosensors Applications

M. Voinova^{1,2}, *A. Vikström*¹

¹*Chalmers University of Technology, Göteborg, Sweden*

²*National Technical University, Kharkiv, Ukraine*

marina.voinova@chalmers.se

Abstract

The surface acoustic waves-based (SAW) sensors and the quartz crystal microbalance (QCM) are widely employed for the ultrasensitive surface mass detection in volatile organic compounds and air quality control measurements. In ‘wet’ conditions, the linear relation (Sauerbrey) between the rigidly attached small amount of deposited mass (the principle of a quartz microbalance) can be violated in case of adsorption of liquid on the top of the film. The correction function for the mass sensitivity should include the losses due to the viscosity of the liquid. This so-called “missing mass” has been studied previously for the QCM sensors operated in a liquid phase. In the present work the “missing mass” effect is analyzed within the theoretical model for the surface shear waves with horizontal polarization (SH SSW-type) acoustical sensors.

Key words: acoustic sensors, QCM, SAW, gas and liquid applications, ‘missing mass’ effect.

Introduction

The surface acoustic waves (SAW) - and bulk acoustic waves (BAW) - based sensors have been intensively used for the precise mass measurements in the air, gases and vapors [1, 2, 5-25]. Since the 1980s, the sensing in liquids with SAW devices, such as SH SSW, Love mode resonators [5,6,7,10,11,16,17,20,21] and BAW resonators (among others, the QCM as the most often employed in liquids [2,4]), many theoretical and experimental efforts (see for review a new book of Johannsmann [2]) were aimed to improve the sensitivity of the acoustic devices. In ‘dry conditions’, the linear response of the QCM resonance frequency to the small amount of mass adsorbed from air or gas serves for *in situ* monitoring of mass deposition. In ‘wet conditions’, the response may deviate from this linear (Sauerbrey, [3]) relation. Knowledge of reasons causing the deviation from linear relation between the shift in the resonance Δf and the surface mass is essential for the correct interpretation of gravimetric results of acoustic sensor measurements, specifically in vapors and liquid environments. One of the possible reasons could be the softness of the sensitive layer. Other factors contributing to observed nonlinear behavior of the resonance frequency changes and the dissipation are viscous losses in the testing

material due to its fluidity or viscoelasticity. This so-called “missing mass” has been described for the QCM sensors operated in a liquid phase. In the present work a similar effect is analyzed within the theoretical model for the acoustical surface shear waves with horizontal polarization (SH SSW-type) sensors.

The model

We study characteristics of acoustic surface shear waves with horizontal polarization (SH-SWW waves) propagating in the two-layer system on the oscillating substrate (considered as an elastic half-space) (Fig.1).

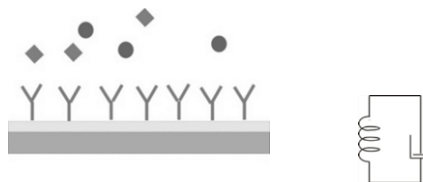


Fig. 1. Left: The geometry of the system consisting of the elastic substrate (index ‘s’) coated with two layers of different viscoelastic materials (indices ‘1, 2’) of the thickness h and Δh , respectively. The viscoelasticity of layers is introduced within the Voight model of elastic and viscous elements in parallel (to the right).

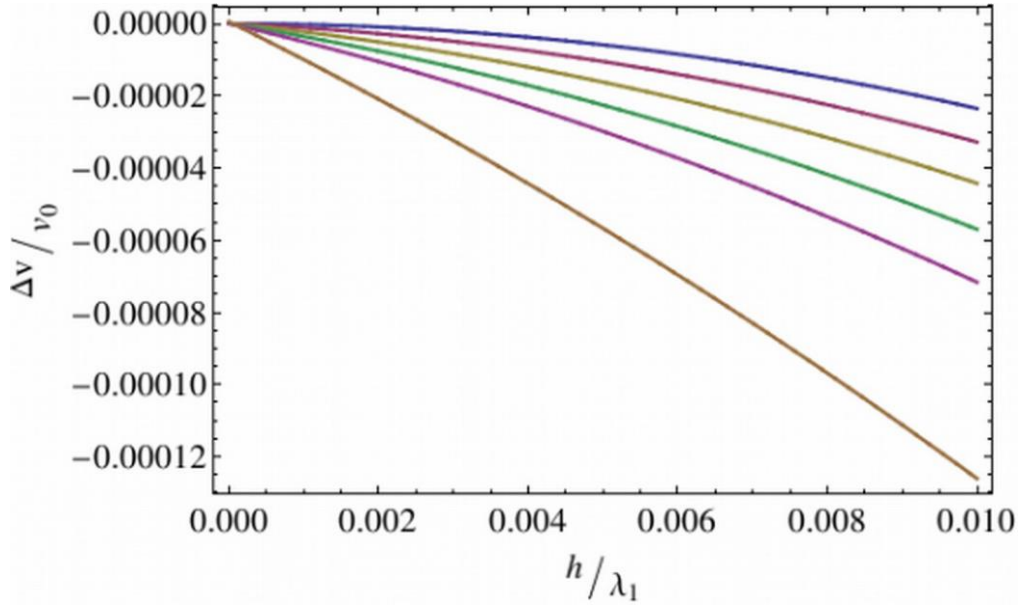


Fig. 2. Calculated relative shift in SAW phase velocity versus a film thickness scaled to the wavelength in the guiding layer (PMMA) deposited onto the substrate (the ST-cut quartz crystal); $f = 100$ MHz. The system is submerged in different viscous fluids (the plots in the figure, top-to-bottom, correspond to the Table (1) entries, top-to-bottom, respectively).

The material parameters of the layers usually introduced in the linear viscoelasticity theory as a combination of storage and loss shear moduli. For the Voight model, these parameters are the elastic modulus μ (corresponding to the elastic spring element) and the dynamic shear viscosity coefficient η (the dashpot element) in parallel.

Theory and results of numerical calculations

The dispersion equation for the SH-SSWs propagating in the two-layer system is given by the following expression:

$$\kappa_t = \frac{\mu_1^* \xi_1}{\mu_s} \cdot \frac{g_1 - \exp(2h\xi_1)g_2}{g_1 + \exp(2h\xi_1)g_2} \quad (1)$$

Here

$$g_1 = \mu_1^* \xi_1 - \mu_2^* \xi_2 \cdot \tanh(\Delta h \xi_2);$$

$$g_2 = \mu_1^* \xi_1 + \mu_2^* \xi_2 \cdot \tanh(\Delta h \xi_2)$$

with notations

$$\kappa_t \equiv \sqrt{q - \frac{\omega^2}{v_s^2}}; v_s \equiv \sqrt{\mu_s / \rho_s}$$

$$\mu_{1,2}^* \equiv \mu_{1,2} + i\eta_{1,2}\omega$$

$$\xi_{1,2} \equiv \sqrt{q_{1,2}^2 - \frac{\omega^2 \rho_{1,2}}{\mu_{1,2}^*}}$$

The phase velocity changes can be found from

$$\Delta v / v_s \approx -\frac{1}{2} \operatorname{Re}(\kappa_t^2 v_s^2 / \omega^2)$$

From eq. (1) for the limit cases of a bulk fluidic layer on the top of an acoustically thin soft film we get for the phase velocity shift:

$$\Delta v / v_s \approx \frac{\omega^{3/2} m_1 v_s^2}{2\mu_s^2} \sqrt{2\eta_2 \rho_2} \cdot \left[1 - \frac{\eta_2 \omega \rho_2}{\rho_1} (J_1' + J_1'') \right] \quad (2)$$

$$m_1 \equiv \rho_1 \cdot h_1$$

$$v_s \gg v_1$$

In eq. (2) the following notations are used:

$$J_1' = \frac{\mu_1}{\mu_1^2 + (\eta_1 \omega)^2}; J_1'' = \frac{\eta_1 \omega}{\mu_1^2 + (\eta_1 \omega)^2}$$

For the QCM operating in liquid phase and coated with a thin viscoelastic film, the resonance frequency shift of the resonator is given by the formula [8,9]:

$$\Delta f \approx -\frac{\eta_2}{2\pi m_s \sqrt{2\eta_2 / \rho_2 \omega}} - \frac{m_1 \omega}{2\pi m_s} \left\{ 1 - 2\omega \frac{\rho_2}{\rho_1} J_1'' \right\} \quad (3)$$

For the ‘dry conditions’, for the quartz covered with the acoustically thin film (viscous, viscoelastic or rigid), and for non-slip boundary conditions, the Sauerbrey [3] relation is valid:

$$\Delta f / f_0 \propto -m_1 / m_s \quad (4)$$

When the environment is changed to the liquid phase, for example, for the humid air or vapors

near the water condensation point, the viscosity (or viscoelasticity) of the film is revealed and, thus, the surface mass value includes the liquid viscosity and a viscoelasticity of the guiding layer:

$$\Delta f / f_0 \propto -m_1(1-\alpha) / m_s \quad (5)$$

where α is a function of layers material parameters, namely, the density, storage and/or loss shear moduli [2,8,9]. For the SAWs, the relative shift in the phase velocity for the acoustically thin film (in the linear approximation on small h) is proportional to the surface mass (see eq. (2)) while the contribution of the top viscous fluid (e.g. water) for reasonable SAWs working frequencies (~ 100 MHz) is very small

$$\Delta v / v_s \approx \frac{\omega^2 \eta_2^2}{2\mu_s^2} \sim 10^{-10}.$$

Comparing with the QCM resonance frequency shift, one can find that the bulk liquid term

$$\Delta f \approx -\frac{\eta_2}{2\pi m_s \sqrt{2\eta_2 / \rho_2 \omega}} \quad (6)$$

is not infinitesimally small. The eq. (6) is a well-known result of Kanazawa and Gordon [4] which opened a way for the quantitative analysis of the QCM immersed in a bulk Newtonian liquid.

In Fig. 2 we present the results of numerically calculated SH-SSWs phase velocity shift for the PMMA guiding layer loaded with liquids of different viscosities on the top (Tab.1).

Tab.1: Dynamic viscosity range for the top liquids

Top bulk liquid	Mass density (kg/m ³)	Dynamic viscosity (Pa s)
Air	1.2	1.8*10 ⁻⁵
Water	10 ³	10 ⁻³
Blood	1.1*10 ³	4*10 ⁻³
60% glycerol in water	1.2*10 ³	9.6*10 ⁻³
70% glycerol in water	1.2*10 ³	2.0*10 ⁻²
85% glycerol in water	1.2*10 ³	8*10 ⁻²

Theoretical modeling shows [12] that, for the rigid elastic thin film for the ‘dry conditions’, the relative phase velocity shift is proportional to the squared surface deposited mass value

$$\Delta v / v_0 \approx \frac{\omega^2 m_1^2 v_s^2}{2\mu_s^2} \left(1 - \frac{\rho_1}{\rho_s} \cdot \frac{\mu_s}{\mu_1}\right)^2 \quad (7)$$

which is in the agreement with the results of McHale and co-authors [10,11]. By comparing the eq. (7) and eq. (2) one can find that for the ‘wet conditions’ when a soft surface-attached film is in contact with a liquid on the top, the phase velocity shift is directly proportional to the film mass. The solution of the dispersion eq. (1) for two viscoelastic layers with varied elasticity modulus and dynamic shear viscosity provides the general expression for the phase velocity as a function of material parameters of the layers. Fig. 3 represents the numerically calculated phase velocity shift for the system of thin rigid (PMMA) guiding film coated with the bulk viscoelastic material. This is a model of the experimental conditions typical for the sensing with SAW-based devices in biological fluids. Our calculations show that the dominant contribution comes from viscous losses in the bulk coating layer.

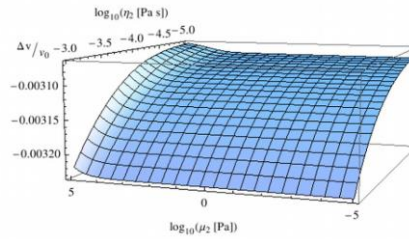


Fig. 3. Calculated relative shift in SH-SSWs phase velocity for the two-layer system of rigid (PMMA) guiding film coated with different viscoelastic top layers. The plot shows the waves phase velocity shift versus the elastic modulus μ and the dynamic viscosity coefficient η in a given range of material parameters; the frequency $f = 100$ MHz, $h = 0.1\lambda_1$.

The general analysis of the eq. (1) is reported elsewhere [25].

Conclusions

Theoretical analysis and modeling show that in both SH SSW-based resonators and in the QCM case the viscosity of the top layer essentially contributes to the mass sensitivity of resonators. This effect reveals the necessity of correction of measurable characteristics for both types of sensors when operating in liquid environments.

Acknowledgements

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