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The role of shear modulus and viscosity of thin organic films on the adsorption response of QCM sensors

Z.I. Kazantseva[1], I.A. Koshets[1,*], Yu.M. Shirshov[1], V.I. Kalchenko[2]

[1]*Institute of Semiconductor Physics, NAS of Ukraine, 41, prospect Nauky, 03680 Kyiv, Ukraine*

[2]*Institute of Organic Chemistry, NAS of Ukraine, 5, Murmanska str., 02660 Kyiv, Ukraine*

[*]*E-mail: koshets@isp.kiev.ua*

Abstract. This work reports on the results of numerical calculations of quartz microbalance (QCM) sensors response under adsorption of analyte molecules. The influence of share modulus and viscosity has been studied. It was shown that even in the case of sufficiently thin films (hundreds of nanometers), the viscosity effects can significantly affect the sensor response during adsorption. In the case of sufficiently thick layers, the viscosity effects can turn out to radically change the response of QCM to the adsorption of volatile molecules. Thus, utilizing QCM-based sensors in viscous medium it is necessary to take into account not only mass loaded (adsorbed) onto quartz surface but also effect of viscosity on sensor response.

Keywords: QCM sensor, polymer coating, viscosity, adsorption.

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1. Introduction

It is usually believed that the change in the frequency of oscillation of a quartz crystal with a change in the parameters of the sensitive layer is due solely to an increase in its mass. Therefore, such devices are called quartz crystal microbalance (QCM). The adequacy of this approach for thermally deposited metal films has been repeatedly confirmed [1, 2]. However, the response of QCM to changes in the composition of the environment is related not only to changes in the mass of the film, but also to its mechanical parameters, shear modulus μ_f and viscosity η. The resonance frequency oscillation of quartz with the deposited film depends on the thickness of the quartz plate h_q, as well as the thickness h_f, density μ_f and complex shear modulus of the sensitive layer $G_f^* = G_f' + G_f''$. Usually G_f' is associated with shear modulus $G_f' = \mu_f$ and G_f'' is associated with viscous loss in the material, which is product of viscosity and frequency, F, $G_f'' = \omega\eta_f = 2\pi F\eta_f$. For the numerical calculation of the frequency of quartz with a sensitive layer applied, the following approaches are used: direct solution of the problem of free oscillations of a layered system within the framework of continuum mechanics [3, 4], the electrotechnical approach (Butterworth–Van Dyke equivalent circuit (BVD) [5] as well as the passage of an electromagnetic wave in a system of lines with distributed parameters (feeders) [6-8]. In the latter case, the piezoelectric crystal, electrodes, sensitive layers or other load elements are considered as segments of waveguides. In the article [9], the question of the results identity of the indicated examinations was specially analyzed and their correspondence was shown numerically.

However, quantitative calculations of the effect of volatile molecules adsorption on G_f^* have not been considered sufficiently. Indeed, when molecules are adsorbed in a porous sensitive film, four parameters may change: density (due to embedding the molecules into pores), thickness (expansion or contraction of the film), shear modulus and viscosity. Virtually, almost all publications on the effect of adsorption on the QCM frequency are interpreted solely as an increase in the mass δm, understood as the product $\delta\rho_f h_f$. G_f'' variation during adsorption is almost not taken into account. There is only limited information on the mechanical parameters of polymer films deposited in various ways on the surface of quartz and widely used in engineering. Adduced below is Table 1 of known data on the mechanical parameters of polymer films obtained from measurements of frequency and *Q*-factor.

As can be seen from Table 1, the shear modulus of polymer films G' are located in the range $2\ldots8\cdot10^8$ Pa in the *glassy state* and 10^6 Pa in the *elastic state*. For metal films, amorphous metal alloys, and reinforced polymers,

Table 1. Experimental data on the mechanical parameters of thin films.

	Material	Characteristics of the film and deposition method	Parameters	Source
1	Isobutylene	280 nm spin coating	$G' \sim 2{\cdot}10^8$ Pa	[10]
2	Polyacrylate (methyalbutyl)	Bulk material	K (elasticity) = $1.6…1.8{\cdot}10^8$ Pa	[11]
3	Polyglutamate	LB films 68 and 136 nm	$G' \sim 4{\cdot}10^7$Pa	[12]
4	Polyisobutylene	Rolled films	$G' = 10^8$ Pa (glass form, 50 °C) $G' = 10^6$; $G'' = 3{\cdot}10^6$ Pa (rubbery 150 °C)	[9]
5	Polydityophene	Electropolymerization, thin and thick films	$G' = 0.3{\cdot}10^6$ Pa and $4.85{\cdot}10^5$ Pa $G'' = 2.4{\cdot}10^6$ and $4.46{\cdot}10^5$ Pa	[13]
6	Polyethylamine + glucoseoxidase	Layered films ~1 μm	$G' = 2{\cdot}10^6$ Pa $G'' = 4{\cdot}10^6$ Pa	[14]
7	Human srun albumine on gold film	Adsorbed film 2.7 nm	$G' = 1{\cdot}10^5$ Pa $G'' = 3.7{\cdot}10^5$ Pa	[15]
8	Stitched polyuretane	Films 5…10 μm	$G' = 10^8…10^9$ Pa	[16]
9	Polyethylene-dioxythiophene (PEDOT)	Electropolymerized films $h = 0.47$ and 0.31 μm	$G' = 8.9{\cdot}10^7$ and $9{\cdot}10^7$ Pa $G'' = 5{\cdot}10^6$ and $1.1{\cdot}10^7$ Pa	[17]
10	Glutamate	Glutamate-reinforced LB films LB films	$G' = 2{\cdot}10^8$ Pa $G'' = 1…3{\cdot}10^9$ Pa	[6]
11	Polydimethylsiloxane	Reinforced by clay nanoparticles	Yung modulus = $1.1…1.3{\cdot}10^6$ Pa	[18]
12	Zinc oxide	Sputtered films	Yung modulus = $1.0…1.6{\cdot}10^{11}$ Pa	[19]
12	Polyether	Thick films 40…100 μm	$G' = 3.5{\cdot}10^7$ Pa	[20]
14	Zr+Cu, Co, Ni	Amorphous metal films	$G' = 24…56{\cdot}10^9$ Pa	[21]
15	Polystyrole	Spin coated multilayer films 10 and 93 nm PS loaded with Al	$G' = 2.0…2.5{\cdot}10^9$ Pa	[22]
16	Wormlike micelles in water	Surfactant solution	Bulk viscosity = 0.001…0.1 Pa·s at frequency 10…100 Hz	[23]
17	Polypeptides and proteins	Connected to surface using couple avidine-biotine	These films demonstrate presence of elasticity	[24]
18	Polyacrylic acid photopolymerization	Grown on gold surface using precusor	Thin (<50 nm) $G' = 1.25{\cdot}10^4$ Pa Thick (>50 nm) $G' = 1.8…3.6{\cdot}10^5$ Pa	[25]

the value of G' is $10^9…10^{11}$ Pa. For photo-polymerized thin polyacrylene films $G' = 10^4…10^5$ Pa. Data on the value of G'' for thin films are negligible. It is known only that for polyisobutylene in the elastic state $G'' = 3{\cdot}10^6$ Pa, for PEDOT $G'' = 5…11{\cdot}10^6$ Pa, for polyethyleneamine with glucose oxidase $G'' = 4{\cdot}10^6$ Pa, and for reinforced glutamate $G'' = 1…3{\cdot}10^9$ Pa (close to metal films). Information on the mechanical parameters of organic films obtained by thermal deposition, spraying, sedimentation with subsequent drying, centrifugation, electrospinning, *etc*., we didn't find in literature.

In all cases, deposition of the film on QCM properly led to a decrease in the frequency of vibration. Adsorption of molecules in the deposited film also almost always leads to a decrease in the frequency. The response of this type is called as the Sauerbrey-like one. However, there are a significant number of anomalies.

In the paper [5], 14 types of polymer films were studied with respect to alcohols, aromatic and chlorine-containing molecules, and it was found that the response of 13 polymer films to adsorption of molecules was of the Sauebrey-like type (the frequency decreased with adsorption), but triethanolamine-tribenzoate films showed a positive responses. With the concentration of volatile molecules close to 400 ppm, the positive response was up to 140 Hz and was reversible. The nature of this response was supposedly associated with a change in the viscosity of the polymer film. Note that the thickness of the film was small (the reduction of frequency by deposition of the film itself was about 3 kHz, which corresponds to a thickness of approximately 150 nm).

Similar positive responses were described in [26]. Here, the sensitive material was layers of an ionic liquid with cations based on methylimidazole derivatives and anions based on sulfonylamide and tetrafluoroborate. Positive responses to saturated vapors of volatile molecules were up to 3 kHz (with a basic negative response of the film itself, about 6 kHz).

Later similar responses with the use of ionic liquids were also described [27, 28]. The authors of [29] used chromatographic phases as the sensitive layer. The authors [30] described a positive response to CO_2 adsorption by ferrocene-terbutyl C4A films, and [31] described an array of seven QCM coated with various ionic liquids, where anti-Sauerbrey responses were used to characterize molecules in the gas phase.

An opposite feature of some organic QCM coatings is the giant increase in the amplitude of the adsorption response, when using the so-called block materials (polymers). Thus, the authors [32] noted that the use of a material consisting of a mixture of styrene blocks with ethylene-cobutylene gaps allows to significantly improve the sensor properties of devices. And in article [33] was demonstrated an unprecedented increase in sensitivity to chlorine-containing molecules (up to ppb concentrations) using polyimide copolymers with silicon blocks. This effect is difficult to explain solely by an increase in the mass of the adsorbate, since the distribution coefficient *K* calculated for this case 100-times overcome the usual values.

On the other hand, the authors of [34], using dioxim (porphyrins with branched peripheral substituents) as sensitive layers, demonstrated the important role of hydrogen intermolecular bonds in increasing the sensitivity of QCM to molecules with unshared electron pairs. These interactions give not only a higher response, but also exhibit a memory effect, which cannot be explained only in the context of a change in the film mass during adsorption.

All the foregoing leads to the conclusion that the response of a quartz crystal with an organic sensitive layer to adsorption of volatile molecules in certain situations is determined not so much by the actual increase in mass but by the change in the mechanical parameters *G′* and *G″* of the sensitive material. This circumstance makes it possible to shed light on the nature of the described anomalous effects and to formulate some ideas for controlling the sensitivity and specificity of gas analyzers based on quartz crystals. The existence of such effects was indicated in [8].

2. Simulation of *G*' and *G*'' influence on the resonant frequency

Below, we will give the results of calculating the response of QCM with thin sensitive layer to the adsorption of volatile molecules due to two effects: an increase in the mass of the sensitive layer and a change in the complex shear modulus. For the calculation, the formula was adopted from [4], where the case of a two-layer sensitive material on the surface of a quartz plate in a medium with an arbitrary viscosity was considered. As already mentioned above, the results of this examination are completely adequate to other approaches [9].

The authors of these studies suggest that two layers are applied to the quartz; the outer layer is in contact with a liquid or gaseous medium. In our calculation, only one layer is used in contact with the gas phase, which is described by four parameters – thickness h_1, shear modulus μ_1, viscosity η_1 and density ρ. The parameter to set is also the frequency ω; output data are frequency change ΔF and *Q*-factor change ΔD.

Adduced below are the results of calculations for sufficiently thin films of the material within the range of 100…500 nm, since these film thicknesses are obtained using the most common deposition methods.

Figs 1a and 1b shows the change in the quartz oscillation frequency with increasing the mass of sensitive layer under the conditions when *G*' = 5000 Pa and *G*'' is assumed to have values from $6\cdot10^4$ up to 10^6 Pa. The film thickness is 200 nm (a) and 500 nm (b). It is quite expected that the dependence of the resonance frequency on the mass shows a linear form, but the slope of the line obviously depends on the film thickness and the loss factor *G″*.

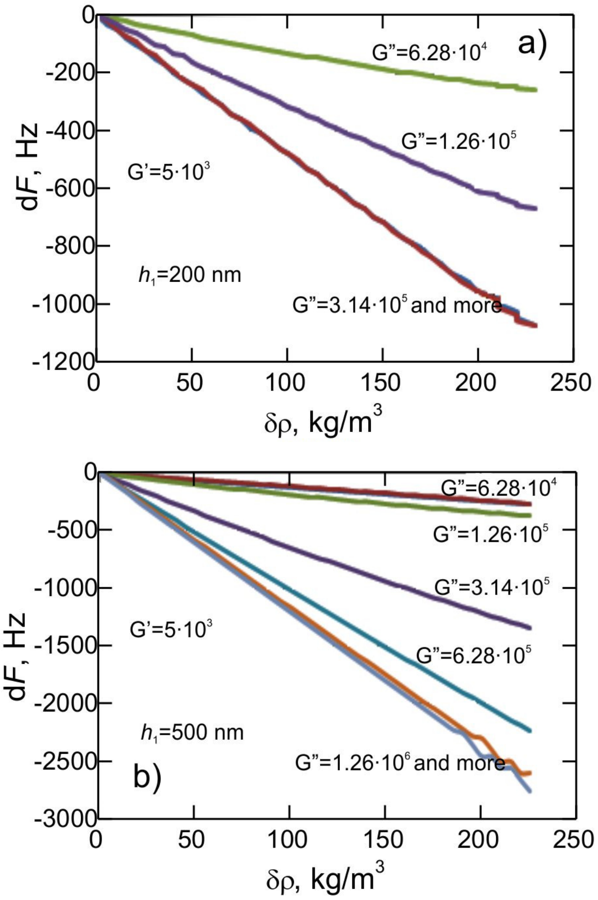

Fig. 1. QCM sensor response with respect to film density. The parameter *G′* equals to 5000 Pa, film thicknesses are 200 nm (a) and 500 nm (b), the parameter *G*'' is varied. Calculated sensitivities (*dF*/*d*ρ) are approximately 0.3, 0.4, and 1 Hz·cm^2/ng (a) and 0.4, 0.5, 1.5, 2 and 3 Hz·cm^2/ng (b) for the indicated values of *G*''.

The registration sensitivity calculated from the slope is 0.3 to 3 Hz·cm^2/ng as the film thickness and parameter *G*'' increase. We note a disproportional increase in sensitivity with an increase in *G*''. Thus, when *G*'' reaches $3\cdot10^5$ Pa (Fig. 1a) and $1\cdot10^6$ Pa (Fig. 1b), this parameter ceases to affect the slope $\delta F/\delta\rho$. It follows that the value of *G*'' in certain limits significantly affects the ability of quartz microbalances to register the increment of the mass inherent to the sensitive film (for example, due to adsorption). In more detail, the influence of *G*' and *G*'' is given below (at a constant material density).

Figs 2a and 2b show the dependence of the frequency shift *dF*(*G″*) in the region $10^5…3\cdot10^6$ Pa, where *G*' varies as a parameter in the region $10^4…4\cdot10^5$ Pa. It is seen that for films of 100 and 200 nm at low *G*''-values, the oscillation frequency is significantly reduced, especially for high values of the shear modulus *G*' (the numbers in the plot are arranged in descending order of *G*'). The increase in *G*'' leads to a rapid decay of the curve to a certain stationary value, which does not depend on *G*''. The frequency decline is ~2400 Hz for 100 nm and ~4800 Hz for 200 nm. A qualitatively similar behavior is demonstrated by thicker films of 300 and 500 nm (Fig. 2b). However, the

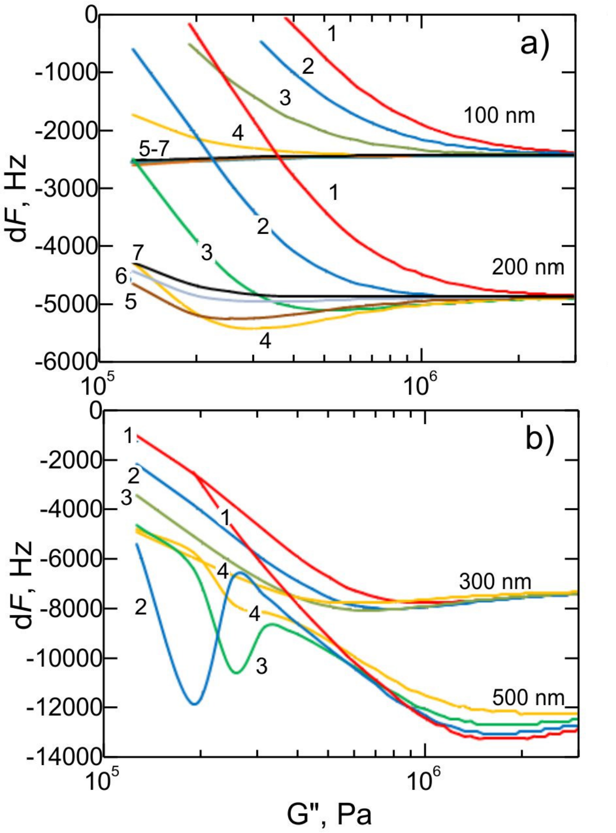

Fig. 2. Effect of the parameter *G''* on the sensor response (*dF*) for films with the thickness 100 and 200 nm (a) as well as 300 and 500 nm (b) and different values of the real part of the shear modulus *G'*: $14\cdot10^5$ (*1*), $3\cdot10^5$ (*2*), $2\cdot10^5$ (*3*), 10^5 (*4*), $5\cdot10^4$ (*5*), $2\cdot10^4$ (*6*), 10^4 Pa (*7*).

stationary state is reached at higher values of *G*'' ~10^7 Pa (not shown here) and is about 7500 and 13000 Hz for 100- and 200-nm films, respectively. Thus, even in the absence of a change in the film density, a change in the parameter *G*'' can cause a multiple increase or decrease of *dF*.

Figs 3a, 3b shows the effect of the shear modulus *G*' for fixed values of *G*''. Attention is drawn to the presence of a horizontal section in the region of low *G*'-values (up to 10^4 Pa). It means that the frequency is practically independent of *G*' in this region. The derivative *dF*/*dG'* is close to zero in this region, but, like to Fig. 2, the value of *G*'' strongly influences the value of *dF*. Curves *1* to *3* in Fig. 3A show reduction in the frequency from 3900 to 2600 Hz with increasing *G*''. The same behavior is also observed for thicker films up to 500 nm (Fig. 3b). However, here the horizontal section expands to 10^5 Pa, and the frequency modulation is observed in the wider limit of *G*' variation (up to 10^5 Pa). In this case, the frequency of the resonance changes almost 5-fold – from 2000 to 10,000 Hz. And it happens without changing the density at all!

This result allows us to make a much more definite conclusion that by changing the parameter *G*' within the range $10^2…10^3$ Pa, and *G*'' within the range $10^3…10^6$ Pa, the resonant frequency of the crystal can be varied by several times with the material density unchanged! This rule can be extended to higher ranges of *G*' and *G*'', if the corresponding relationship between *G*' and *G*'' is maintained, namely: *G*' must be one or two orders of magnitude smaller than *G*''.

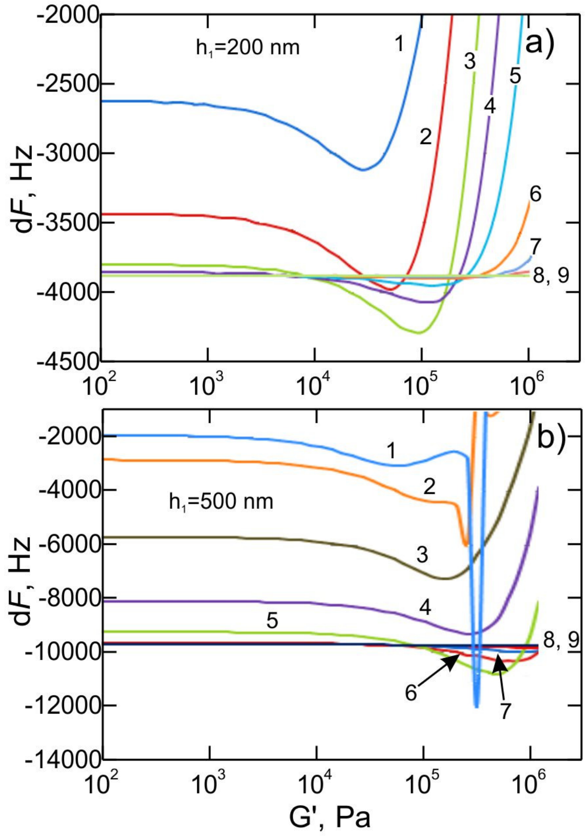

Fig. 3. Effect of the parameter *G'* on *dF* for 100 and 200 nm (a) and 300 and 500 nm (b) films and different values of *G*'': $4\cdot10^5$ (*1*), $3\cdot10^5$ (*2*), $2\cdot10^5$ (*3*), 10^5 (*4*), $5\cdot10^4$ (*5*), $2\cdot10^4$ (*6*), 10^4 Pa (*7*).

The quantitative value of changes in the frequency of crystal *dF*, when all three parameters ρ, *G*' and *G*'' are varied, can be calculated from the formula

$$dF(t)=\frac{\partial F}{\partial\rho}d\rho(t)+\frac{\partial F}{\partial G'}dG'(t)+\frac{\partial F}{\partial G''}dG''(t)\,. \tag{1}$$

We estimated the values of the derivatives in each term in the formula (1). The order of the sensitivity *dF*/*d*ρ values for films of different thickness is shown in the signatures to Fig. 1. Evaluations from Fig. 3 show that *dF*/*dG*'~ 0 in the actual part of parameters ($10^2…10^4$ Pa); the values of *dF*/*dG*'' for the data of Fig. 2 are shown in Table 2.

Table 2. The quantity *dF*/*dG''* (Hz/Pa) at the initial section of the curves in Fig. 2.

G', Pa	Film thickness, nm			
	100	**200**	**300**	**500**
	dF/*dG''* (Hz/Pa)			
400 000	6.37	16.3	24.52	36.03
300 000	6.73	21.1	26.29	33.87
200 000	9.49	20.2	81.94	28.23
100 000	5.87	12.9	16.77	15.65

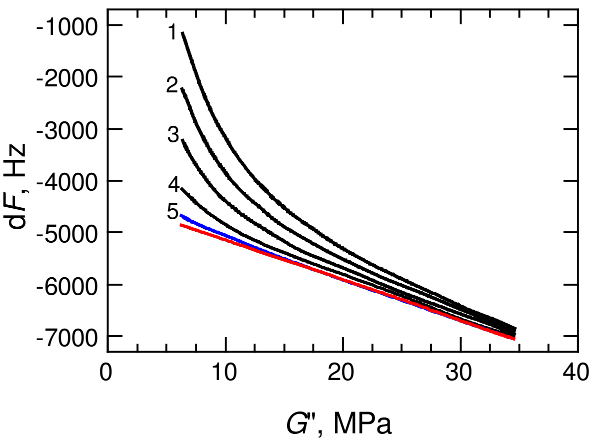

Fig. 4. Frequency change *dF vs. G''*. Density of films are linearly increasing from 1000 to 1450 kg/m^3, the value *G'* is varied: $5\cdot10^6$ (*1*), $4\cdot10^6$ (*2*), $3\cdot10^6$ (*3*), $2\cdot10^6$ (*4*), $1\cdot10^6$ Pa (*5*) and less.

It is clearly seen from Fig. 2 that at $G'' = 10^5\ldots10^6$ Pa there is a pronounced decrease in *dF*, which indicates a rapid decrease in the frequency of resonator as the "soft" film becomes "hard". It is interesting to note that the thickness film shows the greatest slope *dF*/*dG''* (about 30 Hz/Pa), and the smallest slope (6…9 Hz/Pa) is inherent to the thinnest film.

We now consider the effect of combination of the simultaneous action of two parameters, ρ and *G''* (each of these cases is shown in Figs 1 and 2). This calculation was carried out for a film with the thickness 200 nm and higher values of *G'* and *G''* (data are in the caption of the figure). This calculation is made using the formula (1) and taking into account the first and third terms. The change in ρ(*t*) occurs as follows: at the initial point, the density is 1000 kg/m^3 and linearly increases to 1450 kg/m^3 at the end of the range. From Fig. 4, it follows that for $G' < 10^6$ Pa (line *5*) the function *dF*(*G''*) is strictly linear and does not depend on *G'*. The calculated response is 0.2 Hz·cm^2/ng. This value corresponds to the usual responses of quartz microbalances and represents a natural response to the increase in the mass of quartz. At the same time, at the initial section of the curve *1* ($G' = 5\cdot10^6$ Pa) the slope is significantly increased and can be estimated as 3.5 Hz·cm^2/ng. Thus, if for some combinations of mechanical parameters inherent to the film the adsorption of volatile molecules leads to a simultaneous increase in the mass and parameter *G*, then the response can be a reaction not so much to mass as to the change in *G''*.

3. Calculation of the QCM response kinetics of adsorption in the case of a change in ρ, *G'* and *G''*

To qualitatively consider the kinetics of the response during adsorption and desorption in materials such as ionic liquids, we have chosen a material with $G' = 10^4$ Pa and a density of 800 kg/m^3. The film thickness is 1000 nm (this is typical for ionic liquids, since such films are usually obtained by drying).

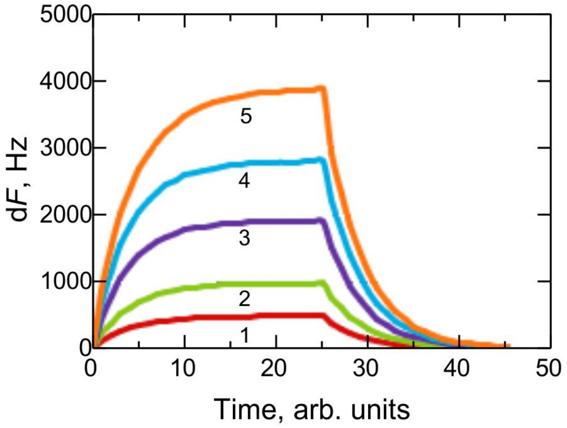

Fig. 5. Kinetics of QCM response with an exponential change in *G''* during adsorption ($G' = 5\cdot10^2$ Pa). The initial value of *G''* = $6\cdot10^6$ Pa, the value of *dG''* is: $0.66\cdot10^6$ (*1*), $1.33\cdot10^6$ (*2*), $2.65\cdot10^6$ (*3*), $3.98\cdot10^6$ (*4*), $5.3\cdot10^6$ Pa (*5*). The film thickness is 6650 Hz (1000 nm).

Let the parameter *G''* decreases by an order of magnitude during the adsorption time in the range $6.3\cdot10^5$...$6.3\cdot10^6$ Pa, according to the exponential law $G'' = 6\cdot10^5 - dG''\left(1-e^{-t/\tau}\right)$ (that is, the viscosity at adsorption decreases) and returns to the initial value for desorption, Fig. 5 shows the calculated curves *dF*(*t*) for this case. The initial value of G'' is constant and is $6.3\cdot10^6$ Pa, and the final value decreases as shown in the caption of the figure. (Such a combination of $G' \ll G''$ is typical for materials close to ionic liquids, which are increasingly used for analytical purposes and such a change *dF*(*t*) is called as the anti-Sauerbrey response.)

The opposite behavior is observed if the adsorption of molecules increases *G''*, a situation typical for materials with a normal response to adsorption (Sauerbrey-response). The combination of increasing the mass of adsorption with increasing *G''* leads to a dramatic increase in the response, which is observed, in particular, for block copolymers, where the adsorption of molecules in soft gaps can increase this parameter.

Fig. 6 shows the change in the resonance frequency of quartz in time for the 700-nm film ($F_0 = 5$ kHz), when the density increases according to $\rho = 800 + 100\left(1-e^{-t/\tau}\right)\text{kg/cm}^3$ and *G''* is *constant* for each curve, and it is indicated in the caption of the figure. The initial curve ($dG'' = 0$) is shown in the line *1*. It is clear that the response here is about 100 Hz, but with increasing *dG''*, the frequency response is sequentially increased to more than 1600 Hz, *i.e.*, 16 times. Further growth of *G''* does not lead to changes in the response.

However, if *G''* increases simultaneously, then the effect is even more significant (see Fig. 7). Here, along with the indicated increase in the density, there is an increase in *G''* according to the law $G'' = 6.3\cdot10^5 + dG''\left(1-e^{-t/\tau}\right)$.

The curve *1* in Fig. 7 is identical to the curve *1* in Fig. 6 (response is about 100 Hz). However, all the other responses far exceed the curve *1*. The maximum response

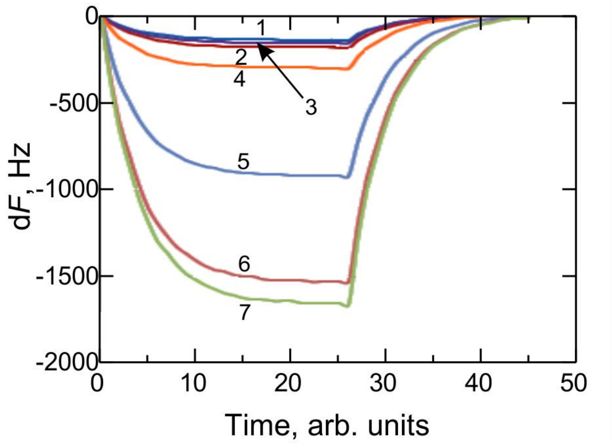

Fig. 6. QCM sensor response kinetics of the 700-nm film under changing the density: $\rho = 800 + 100 \cdot (1 - \exp^{-t/\tau})$ kg/cm^3; $G' = 10^4$ Pa; $G'' = 6 \cdot 10^5$ (*1*), $1.26 \cdot 10^6$ (*2*), $3.14 \cdot 10^6$(*3*), $6.28 \cdot 10^6$(*4*), $1.26 \cdot 10^7$(*5*), $3.14 \cdot 10^7$(*6*), $6.28 \cdot 10^7$ Pa (*7*).

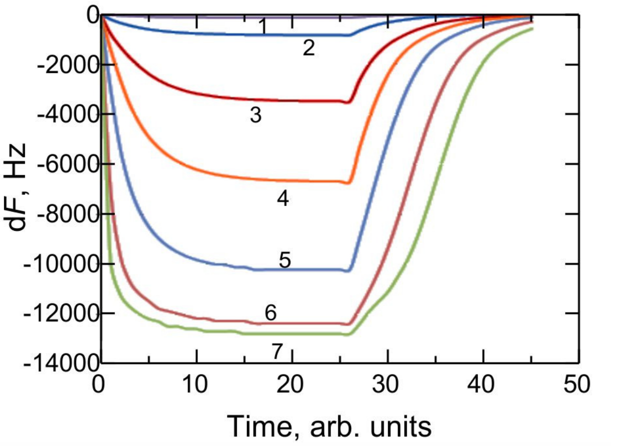

Fig. 7. QCM sensor response kinetics of the 700-nm film under simultaneous varying ρ and $G'' = 6.3 \cdot 10^5 + dG''(1 - \exp^{-t/\tau})$. Values dG'' are: 0 (*1*), $6 \cdot 10^5$ (*2*), $1.26 \cdot 10^6$ (*3*), $3.14 \cdot 10^6$ (*4*), $6.28 \cdot 10^6$ (*5*), $1.26 \cdot 10^7$ (*6*), $3.14 \cdot 10^7$ (*7*), $6.28 \cdot 10^7$ Pa (*8*).

is about 13 kHz. True, for this it is necessary that *G*'' increase during adsorption by a factor of 100, namely from $6 \cdot 10^5$ to $6 \cdot 10^7$ Pa. You should pay attention to the change in the shape of the response curve. In the absence of *G*'' variations during adsorption, the kinetics *dF*(*t*) is exponential both in the ascending and descending branches (Fig. 6). At the same time, the presence of such a variation in *G*'' leads to deformation of *dF*(*t*): the rate of changes in the frequency increases sharply in the growing branch, and the non-exponential tail appears in the falling branch.

Actual for the detected effect is a certain relationship between *G*' and *G*'', namely *G'* must be less than *G*'' approximately 30…100 times. A simple examination of Table 1 shows that the known values of *G'* and *G*'' in this range of values really “can fall”. Moreover, the data in Fig. 7 give grounds for doubts in the correct estimation of the distribution coefficient *K* for molecules between the gas phase and sorbent, especially when the *K*-values exceed 10^6, which seems overestimated [33]. Apparently, in the latter case it is necessary to speak of a change in the effective viscosity of block films due to the adsorption of molecules in soft gaps between rigid blocks.

4. Conclusion

The results of calculations presented above convince us that even in the case of sufficiently thin films (hundreds of nanometers), the viscosity effects can significantly affect the response of quartz microbalance sensors during adsorption. In the case of sufficiently thick layers, the viscosity effects can turn out to radically change the response of QCM to the adsorption of volatile molecules. Thus, utilizing QCM-based sensors in viscous medium, it is necessary to take into account not only the mass loaded (adsorbed) onto the quartz surface but also effect of viscosity on sensor response.

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Authors and CV

Z.I. Kazantseva

Z.I. Kazantseva is Ph.D. in Physics and Mathematics, Senior Researcher at V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. Her area of scientific interests includes thin organized films, LB-technology and sensory materials.

Institute of Semiconductor Physics, NAS of Ukraine

I.A. Koshets

I.A. Koshets is Ph.D. in Physics and Mathematics, Senior Researcher at V. Lashkaryov Institute of Semiconductor physics, NASU. The area of his scientific interests includes development of bio- and chemical sensors, software and electronics for sensory applications.

Institute of Semiconductor Physics, NAS of Ukraine

Yu.M. Shirshov

Yu.M. Shirshov is Professor, Doctor of Sciences in Physics and Mathematics, scientific consultant at V. Lashkaryov Institute of Semiconductor Physics, NAS of Ukraine. The area of his scientific interests includes molecular phenomena on semiconductor and insulator surfaces, optoelectronic and microelectronic chemical sensors and biosensors.

Institute of Semiconductor Physics, NAS of Ukraine

V.I. Kalchenko

V.I. Kalchenko is Academician of NAS of Ukraine, Professor, Doctor of Sciences in Organic Chemistry, Head of the Institute of Organic Chemistry, NAS of Ukraine. The area of his scientific interests includes calixarenes, organophosphorus chemistry, supramolecular chemistry, design and synthesis of novel materials.

Institute of Organic Chemistry, NAS of Ukraine