



Quartz crystal microbalance in the active mode as a tool to modify sensor surface for higher selectivity and sensitivity



Fedor N. Dultsev^{a,b,*}

^a Institute of Semiconductor Physics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 630090, Russia

^b Novosibirsk State University, Russia

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ABSTRACT

Oscillating quartz crystal microbalance (QCM) surface was used to increase the rates of reactions on this surface. It is demonstrated that the rate of the formation of chemisorbed monolayer increases when the surface oscillates, so the time necessary for surface modification decreases from 20 h to 20 min. During surface oscillation, the molecules bound non-specifically get detached from the surface, but more specific bonds are formed between nano-objects and the surface, which allows us to enhance the sensitivity and selectivity of sensors based on affine interactions. With the help of oscillatory treatment, we carried out the separation of oligonucleotides from the mixture containing fully complementary oligonucleotides and those having mismatches.

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Introduction

To achieve high sensitivity and selectivity of a biosensor, it is necessary to immobilize a recognizing layer (e.g. antibodies) on the surface of the device. Immobilization methods are diverse, for example, passive adsorption of antibodies is widely used. However, in this case immobilization occurs in a random manner, not necessarily in the functionally active orientation. Another method is surface modification resulting in the attachment of special functional groups, for example carboxylic groups. Then these carboxylic groups are bound to antibodies through their amino groups. Surface modification is carried out by forming a monolayer. One of the methods to form a monolayer is adsorption of organosulfur compounds, in particular thiols, from solution or from the gas phase, onto a substrate made of gold or silver [1–9].

The formation of chemisorbed self-assembled monolayers (SAM) on the surface is limited by thiol diffusion to the surface. The formation of SAM often takes 24–48 h, depending on solvent and on thiol concentration. Diffusion may be accelerated by increasing the flow rate and concentration. Numerous studies [10–13] showed that the kinetics of monolayer formation is rather well described by Langmuir's model; it was demonstrated that the formation of a

monolayer involves alignment of molecular axes along the perpendicular to the surface [14,15].

Thus, the formation of a monolayer includes several structural transitions: a rapid stage in which about 80% of the monolayer is formed within several seconds, and the second stage taking much longer time, which includes rearrangement on the surface and the formation of a dense monolayer. The possibility to accelerate the second stage substantially by means of surface stress created by surface vibration was shown in Ref. [16] with the help of a micromechanical cantilever-based chemical sensor. In addition, high-frequency oscillation leads to a decrease in surface roughness. For example, in Ref. [17] the roughness of metal surface was shown to decrease during oscillation.

One of the promising analytical methods is based on the quartz crystal microbalance (QCM) using the advantages of its oscillating surface.

The major advantages of QCM include its small size, high sensitivity, good stability, fast response and low cost. The resonator consists of a thin AT-cut quartz disc. The cut in the quartz crystal was specially chosen to provide the zero first-order temperature coefficient of shear oscillations, which is necessary for the temperature stability of sensing devices. Flat metal electrodes were deposited on each side of this quartz disc. Alternate voltage applied to the electrodes creates a strong electric field within the quartz volume. Due to the piezoelectric effect inherent to quartz, the electric field generates mechanical shear strain and displacement. Because of the small temperature coefficient and high mechanical Q factor, the AT-cut QCM is widely used at present as a sensitive element in

* Correspondence address: Institute of Semiconductor Physics, Siberian Branch of the Russian Academy of Sciences, Novosibirsk, 630090, Russia.

E-mail address: fdultsev@isp.nsc.ru

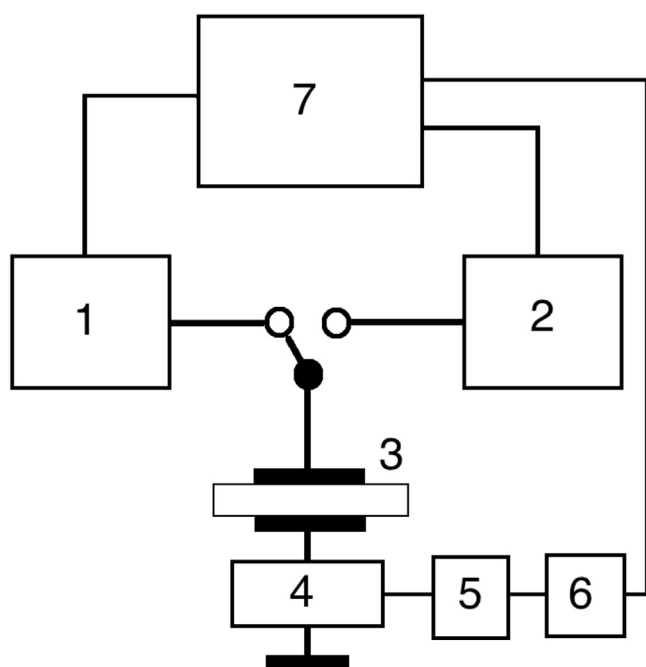


Fig. 1. Diagram of the set-up to study the effect of oscillations on the formation of ordered monolayer.

gas sensors, chemical and biological sensors [18–20]. In our works, we use the QCM in the active mode [21]. For this purpose, alternate voltage with the QCM resonant frequency is supplied. Varying the voltage amplitude, we thus set the amplitude of QCM surface oscillations. When definite amplitude is achieved, a particle gets detached from the QCM surface. This moment is detected with the help of the same QCM [21]. This procedure can be used not only for sensing but also for separation of the particles bound specifically and non-specifically. For example, separation of two bacterial species was demonstrated in Ref. [22].

In the present work, we describe how the QCM can be used to accelerate chemical processes involved in the formation of a monolayer (surface rearrangement). The same QCM is further used as a sensor; it helps to follow the kinetics of monolayer formation. The use of the oscillating surface to accelerate the interactions with agents characterized by different affinities to the analyte will allow one to accelerate the process taking place on the surface, and also to increase the selectivity of the sensor in general. As another example, we demonstrated how fully complementary oligonucleotides can be separated from the solution containing a mixture of oligonucleotides, both having and having no mismatches.

2. Materials and methods

2.1. Procedure and setup

All the experiments were carried out in solution. The AT-cut QCM 8.5 mm in diameter manufactured by KVG was used. The electrodes were 4 mm in diameter, chromium/gold 10/80 nm, the resonance frequency of the QCM was 14.3 MHz.

The set-up is shown schematically in Fig. 1. The amplitude of surface oscillations is preset by the voltage supplied from generator (1) GS-80 to QCM (3). To measure the eigen-frequency of the QCM, we used a separate generator (2) for excitation at the fundamental harmonic. For gravimetric measurements, the QCM is disconnected from the generator and connected to the measuring generator (2), from which the frequency signal is given to the frequency meter to measure the frequency of the natural oscillations

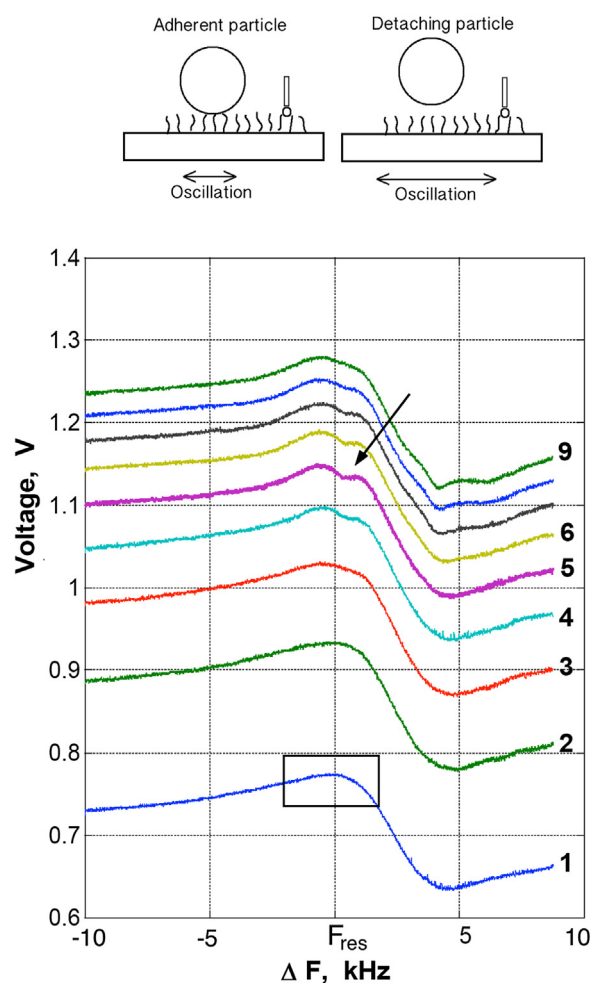


Fig. 2. Voltage–frequency dependences for different voltage values. Scanning was carried out over frequency near the resonance ± 10 kHz. Rupture moment is indicated with an arrow. The top image shows schematically how the rupture from the surface occurs. Large particles are the first to get detached. With further increase in the amplitude, smaller particles are detached. In the case of identical size and mass, weaker bound particles are the first to get detached.

of QCM. The moment of particle detachment was detected using the voltage–frequency dependence; for this purpose, we used the current transformer (4), logarithmic amplifier (5), and ADC (6). Data were collected with the help of computer (7).

2.1.1. Rupture force measurement procedure

To study the detachment of molecules from the surface, we used the method described in Ref. [21], modified as described in Ref. [23]; the distortions of the voltage–frequency dependence at the moment of rupture were followed. This procedure allows us to distinguish between the molecules bound with the surface specifically and non-specifically. The use of this procedure allows not less than 2 orders of magnitude increase in sensitivity [21]. The essence of the method is detachment of a particle under shear oscillations with smoothly increasing amplitude; the voltage value at which detachment occurs is measured. Bond strength is calculated from this voltage value. Voltage–frequency dependences for different voltage values are shown in Fig. 2. To obtain the voltage–frequency dependence, frequency scanning was carried out near the resonance ± 10 kHz. At the moment of molecule detachment from the surface, distortions appear on the curve (marked with the arrow).

For the surface filling degree less than 1%, frequency change dF/F is much lower than the background of temperature inhomogeneity of QCM material, so it is impossible to detect the presence of

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