Determination of nanoscale layer thickness adsorbed water liquid by acoustoelectric methods

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Abstract. It is shown to determine the thickness of the adsorbed liquid layer, it is proposed to use surface acoustic waves (SAW). The relative change in the SAW velocity is proportional to the thickness of the adsorption layer. The constant of proportionality is depending on the acoustic parameters of the solid (adsorbent) and the liquid in the layer. The velocity of sound in an adsorbed liquid depends on the thickness of the layer. For the determination of the velocity of sound in the liquid of the adsorption layer, it is proposed to use an original method based on comparing the parameters of bi-directional (differing in velocity) SAW.

Liquid layers are an adsorption layer, a wetting film or a bulk liquid layer. Surface acoustic waves (SAW) can be used to determine the thickness of the liquid layer. The dispersion of SAW in a layered system "piezoelectric substrate - liquid layer" is described by a large system of equations and can be solved only by numerical methods. The dispersion coefficient of the velocity of SAW in the system "piezoelectric substrate - thin layer of liquid" is determined by the expression:

$$\frac{\Delta V}{V_s} = \text{Re} \left( \frac{\Delta k}{k} \right).$$

where $\Delta k$ and $\Delta V$ are changes in the wavenumber and velocity of SAW as a result of acoustoelectric interaction.

![Layered system](image)

Figure 1. Layered system.

The dispersion of the velocity of SAW in the system "thin layer of liquid - piezoelectric substrate" (Figure 1) is described by dispersion equation (1). In [1] it has been shown that by linear
approximation the relative change in velocity SAW \((\Delta V/V_s)\) can be represented by a simple expression:

\[
\frac{V_0 - V_s}{V_s} = \left( \frac{\rho_f V_f}{\rho_s V_s} \cdot \tg \theta + \pi K^2 \frac{\varepsilon_p \varepsilon'}{(\varepsilon_p + 1)^2} \right) \frac{h}{\lambda},
\]

(1)

where \(\rho_f\) and \(\rho_s\) – liquid density and solid density, \(\varepsilon_p, \varepsilon_f\) – relative permittivity’s of \((\varepsilon_p = (\varepsilon_{\psi}, \varepsilon_{\zeta} - \varepsilon_{\xi}^2)^{1/2}\) and liquid, \(\theta = \arccos (V_f/V_s)\) – the angle at which sound waves propagate in the liquid layer, \(V_f\) – sound velocity in liquid, \(V_s\) – surface wave velocity, \(K\) – electromechanical coupling coefficient.

The variation in velocity of SAW depends on the acoustic and dielectric characteristics of the layered system.

For bulk liquids, linear approximation of the velocity variance of SAW, provided \((h \ll \lambda_s)\), allows the determination of the thickness of the liquid layer from equation (1).

\[
h = \lambda \cdot \left( \frac{\Delta V/V_s}{\rho_f V_f / \rho_s V_s \cdot \tg \theta + \pi K^2 \frac{\varepsilon_p \varepsilon'}{(\varepsilon_p + 1)^2}} \right).
\]

In a vapor-gas medium, a nanoscale layer of adsorbed liquid on the surface of a solid is formed. The structure and physical properties of adsorbed liquid and liquid in the bulk state are different. Viscosity and permittivity are the most sensitive properties to changes in structure of liquid.

To exclude electrical disturbances in the propagation conditions of SAW, a piezoelectric with a metallized surface can be used. In this case, the expression for changing the velocity (1) is simplified

\[
\frac{V_m - V_s}{V_s} = \frac{\rho_f V_f}{\rho_s V_s} \cdot \tg \theta = \frac{\rho_f}{\rho_s} \left( 1 - \frac{V_f^2}{V_s^2} \frac{h}{\lambda} \right).
\]

In this equation, the thickness of the adsorption layer determines the density of the liquid \(\rho_f\) and the sound velocity in the liquid \(V_f\), which is determined from acoustic measurements.

To determine the velocity of sound in a liquid, the propagation of SAW in two different directions of an anisotropic metallized acoustic sound duct was used. The velocity of SAW depends on the direction of propagation. Therefore, it is possible to measure the relative change in velocity, which is caused by the influence of the liquid layer for different directions of the metallized sound line. The resulting system of linear equations determines \(V_f\). For two directions of propagation of surface acoustic waves in a layered system with different values of the velocity \((V_1 \neq V_2)\), we have two equations.

\[
\frac{\Delta V_1}{V_1} = \frac{\rho_f}{\rho_s} \sqrt{1 - \frac{V_f^2}{V_1^2} \frac{h}{\lambda}}, \quad \frac{\Delta V_2}{V_2} = \frac{\rho_f}{\rho_s} \sqrt{1 - \frac{V_f^2}{V_2^2} \frac{h}{\lambda}}.
\]

(3)

For different directions of SAW propagation in a layered system, the ratios \(\rho_f/\rho_s\) and \(h/\lambda\) are the same, and only the velocities \(V_1\) and \(V_2\) differ. From equations (3) we can write

\[
\frac{V_2 \Delta V_1}{\Delta V_2 V_1} = \frac{\delta f_1}{V_1} = \frac{V_2}{V_1} \sqrt{\frac{V_1^2 - V_f^2}{\frac{V_2^2 - V_f^2}{\frac{V_2^2 - V_f^2}}}}.
\]

\[
\frac{\Delta V_i}{V_i} = \frac{\delta f_i}{f_i} = \delta f_i \text{ from the interference condition } (i = 1, 2).
\]

\[
V_f = \sqrt{RV_2^2 - V_1^2}, \quad R = \left( \frac{\delta f_1 \cdot V_1}{\delta f_2 \cdot V_2} \right)^2
\]

(4)

Equation (5) makes it possible to calculate the adiabatic velocity of sound in an adsorbed liquid based on a comparison of the parameters of SAW differing in velocity in a layered system.
The position of the SAW – transducers used in this technique is shown in Figure 2. Four transducers 2 and 3, deposited on the surface of the piezoelectric substrate 1, form two delay lines. Polymolecular adsorption of polar liquid vapor out on metal film 4 is carried. Which is applied between the emitting and receiving interdigital transducers. The dotted line marks the zone of interaction of SAW with the adsorption layer.

Figure 2. The position of the SAW – transducers

To determine the change in the velocity of surface acoustic waves in a layered system, a phase-interference method is used to measure small changes in the velocity and attenuation of surface acoustic waves [2].

The density of liquid in the layer can be calculated by the formula

$$\rho_f = \frac{K}{2V_s^2} + \left(\frac{K}{2V_s^2}\right)^2 + \left(\frac{\Delta V \rho_s \lambda}{V_s h}\right)^2,$$

(6)

the resulting expression (2) taking into account the dependence of the sound velocity in the liquid $V_f^2 = 1/(\rho_f \beta)$ on its density and adiabatic compressibility $\beta$ ($E = 1/\beta$ – bulk modulus of water).

To determine the density of a liquid using formula (6), it is sufficient to measure the relative change in the velocity of SAW in any of the selected directions of propagation of SAW ($V_s = V$ or $V_s = V_2$). The sensitivity of the interference method to a change in velocity is high (~ $10^{-8}$ at a frequency of 100 MHz). Wavelength $\lambda$ is given by the dimensions of the transducer. The bulk modulus of water of the liquid in the boundary layer can be taken the same as that of the bulk liquid.

The method for determining the thickness of a nanoscale liquid layer was tested when evaluating the adsorption isotherm $h(p/p_s)T$ of water vapor on the metallized surface of lithium niobate YZ-cut (Figure 3).
Due to the use of tabular values of the bulk modulus of water, when determining the density of adsorbed water, it has an error due to structural differences. The compressibility of water in the boundary phase differs little from the compressibility of water in the bulk phase. Therefore, to determine the density of adsorbed water, one can use the value of the bulk modulus of water.

Numerical methods showed that with an increase in the density of bulk water under the influence of pressure from 0 to 2%, an increase in the bulk modulus in water is \(0 - 12\%\), an increase in the velocity of sound \(0 - 6.05\%\). The density, which is determined by formula (6), in addition to the dependence on the layer thickness and the bulk modulus, also depends on the parameters of SAW. With an increase in the density of adsorbed water to 2%, the error in determining the density increases only to 0.28%. When using the volumetric value of \(E\), for example, in the well-known equality \(\rho = \frac{E}{V_f}\), an error appears. When using the bulk value of \(E\) in equation (6), the resulting error in determining the density \(\delta\) is less than in the first case by about 10 times. The values of the variation in the acoustic parameters of bulk water during its compaction, as well as the error in determining the density \(\delta\) are given in the table. \(\Delta x = x(p) - x_0\), where \(x\) equal to \(\rho, E, V_f\). Compaction occurs under the influence of pressure \(\Delta p = (p - 1)\) atm.

The bulk modulus can be calculated using an empirical formula, which was obtained on the basis of numerical calculations of changes in density and other acoustic parameters of water under the influence of external pressure (table) [3]:

| \(\Delta \rho/\rho_f\), % | \(\Delta E/E\), % | \(\Delta V/V_f\), % | \(\Delta p\), atm | \(\delta\), % |
|-----------------|-----------------|-----------------|----------------|---------|
| 0,5             | 3,14            | 1,35            | 112            | 0,09    |
| 1,0             | 6,43            | 2,87            | 232            | 0,16    |
| 1,5             | 9,55            | 4,36            | 360            | 0,23    |
| 2,0             | 12,8            | 6,05            | 497            | 0,28    |

\[
\frac{\Delta E}{E} \approx 6,4 \frac{\Delta \rho}{\rho_f}
\]  

(7)

To minimize the error, it is necessary according to equation (6), determine \(\Delta \rho/\rho_f\) using the tabular value of \(E\) for bulk water. The found \(\Delta \rho/\rho_f\) value can be used in relation (7) to detail the bulk modulus and re-determine the density change.
To determine the thickness of the layer of adsorbed liquid, you can use one of the expressions obtained from equations (3).

$$h = \frac{\lambda \cdot \rho_s \cdot (\delta f_1) \cdot V_1}{\rho_f (V_1^2 - V_f^2)^{\frac{1}{2}}}$$  

$$h = \frac{\lambda \cdot \rho_s \cdot (\delta f_2) \cdot V_2}{\rho_f (V_2^2 - V_f^2)^{\frac{1}{2}}}$$  \hspace{1cm} (8)

Accordingly, it is necessary to determine the density of the liquid $\rho_f$ and the speed of sound in it $V_f$ from acoustic measurements using formulas (3) – (6).

Thus, it is possible to determine the thickness of the nanoscale layer of adsorbed liquid from acoustic measurements of changes in the parameters of sounding pulses of SAW. An expression for determining the thickness of the adsorption layer is obtained. The proportionality factor depends on the acoustic parameters of the solid (adsorbent) and liquid in the layer. The velocity of sound in adsorbed liquid depends on the thickness of the layer. In order to detail the velocity of sound in the liquid of the adsorption layer, it is proposed to use an original method based on comparing the parameters of surface acoustic waves which differ in velocity.

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