Atomic-molecular and acoustoelectronic processes in a rarefied gas medium

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Abstract. The features of the interaction of surface acoustic waves with a rarefied gas medium are considered. The relationship between acoustoelectronic and atomic-molecular phenomena accompany the processes of adsorption and desorption of atoms and molecules on the surface of a solid is analyzed. Two types of sorption processes are discussed: adsorption and desorption of gas on a solid surface; adsorption and vapour desorption. In the first process, the temperature of the adsorbent is higher than the boiling point of the corresponding liquid. In the second, the adsorbent temperature corresponds to the area of coexistence vapour and liquid. In each case, the use of vacuum technology in the processes under investigation is noted.

1. Introduction
Thermal, elastic, and atomic-molecular processes in the area of localization of the surface energy of a solid are interrelated. The absorption by the surface of a solid of atoms or molecules from the gas phase is determined by the processes of adsorption and desorption. At present, the main advances in the study of adsorption have been obtained in installations that ensure the creation of an atomically clean surface under conditions when the number of gas or vapor molecules interacting with the surface is limited. Usually, the most modern methods of studying adsorbed molecules and ultrahigh vacuum technology are used [1]. Atomic-molecular and acoustoelectronic processes on the surface of a solid are also interrelated. Therefore, new original opportunities for studying adsorption-desorption processes and other atomic-molecular processes on the surface of a solid are provided by surface acoustic waves (SAW) the used. To create sorbent coatings for various sensors, it is important to study adsorption in a low vacuum or in a gas medium [2].

The formation of an adsorption bond between a surface atom and an adsorbed atom (adatom) is preceded by relatively slow energy exchange processes [3]. The most effective in the relaxation of thermal vibrations of adsorbed particles is the phonon mechanism of energy exchange of high-frequency vibrations for the energy of low-frequency vibrations. When the vibration frequency of an adatom falls within the range of vibrations of atoms of a solid, a one-phonon relaxation mechanism is realized, which is the simplest and most probable. The rates of one-phonon relaxation processes are in the range $10^{12} - 10^{13}$ s$^{-1}$. The one-phonon energy transfer process as the adsorption potential decreases (descending to the bottom of the potential well) proceeds sequentially as a two-, three-, and four-phonon relaxation process. The characteristic times of energy exchange in multiphonon relaxation are 4–5 orders of magnitude longer than in the case of a one-phonon process. During the adsorption of particles on the surface of metals and semiconductors, a significant contribution to the relaxation of
thermal vibrations is made by the processes of energy transfer to the electronic subsystem of a solid [5]. The exchange times in these processes are from $10^{-9}$ to $10^{-11}$ s.

2. Interaction of surface acoustic waves with a gas medium

In case, when the surface of a solid is loaded with a liquid or gas, Rayleigh waves are transformed into leaky surface waves [4]. Leaky waves are elastic disturbances that propagate along the boundary of a solid and continuously re-emitting energy from the solid into a liquid medium or gas medium. Usually, the speed of sound in the loading medium and its density is less than the velocity of the SAW and the density of the solid. This allows us to consider the influence of the loading medium as a small disturbance.

In the case of a gas load, the parameters of the leaky waves can be determined from an approximate theory. According to [5], the attenuation due to the gas load, $\alpha$ [dB/cm] is determined by the expression:

$$\alpha \approx 8.686 \left( f \rho / \rho_S V_S \right) \frac{\sqrt{M/RT}}{f} ,$$

where $M$ and $p$ are the molecular weight and pressure of the gas, $T$ and $R$ are the temperature and the universal gas constant, $f$ and $V_S$ are the frequency and velocity of the saw, $\gamma = C_p/C_V$ is the ratio of the isobaric and isochoric heat capacities of the gas, and $\rho_S$ is the density of the solid.

To register the attenuation of surface waves as a function of the gas pressure, the interference method was used to measure small changes in the parameters of SAW [3]. From the output of the high-frequency generator, passing through the SAW delay line, a signal is fed to the amplifier input. Simultaneously with the RF generator, a signal weakened by the attenuator is fed to the amplifier input. The amplitudes of the attenuated direct signal $U_1$ and delayed $U_2$ signal are balanced. The direct and antiphase delayed signals interfering. The resulting difference signal, after passing through the amplifier, enters the input of an oscilloscope or other recording device (figure 1). Due to interference, the value of the resulting signal $\Delta U$ depends on the ratio of the phases and amplitudes of the interacting signals. Amplitude balance is achieved by regulation the attenuator, and phase balance by tuning the frequency of the generator. The generator is regulated to the frequency of the interference minimum.

![Figure 1. Block diagram of an experimental setup for measuring the SAW attenuation due to a gas environment.](image)

![Figure 2. Dependence of the attenuation of SAW on the pressure of argon (1) and air (2). Quartz $XY$-cut, $f = 200$ MHz, $T = 293$ K.](image)

A change in the state of the surface and the near-surface area of the substrate as a result of the influence of the gas medium will lead to a change in the conditions for the propagation of SAW. In the general case, the velocity and amplitude of the SAW will change, therefore, the frequency of the interference minimum will change. The change in the velocity of the SAW is determined from the condition $\Delta V/V = \Delta f / f$. The SAW attenuation is determined by the value of the residual signal,
which is balanced by the attenuator. The attenuation value change is determined by the attenuator scale. With a small change in attenuation \((\Delta U \ll U_0)\), the value \(\alpha\) [dB/cm] is determined by the formula [3]:

\[
\alpha = (20/f) \cdot \log_{10}(1 - \Delta U/U_0),
\]

where \(U_0\) is the half-amplitude of the resulting signal, determined from the condition \(2U_0 = U_1 + U_2\).

The piezoelectric substrates used were lithium niobate with a YZ-cut with a size of \(5 \times 0.7 \times 0.1\) cm and crystalline quartz with an YZ-cut with a size of \(10 \times 2 \times 0.2\) cm. An 80 nm thick aluminum film was deposited on a polished quartz or lithium niobate surface by thermal evaporation, and two interdigital transducers were fabricated by mechanical engraving. The number of electrode pairs in the interdigital transducers is 30 on a quartz substrate and 10 on lithium niobate. The aperture of the transducers varied within 50–100 SAW lengths, and the distance between the centers of the emitting and receiving transducers was ~3–5 cm.

The linear dependence of the SAW attenuation on the frequency and pressure of gases was experimentally confirmed. The slope of the \(\alpha(f)\) dependence during the propagation of SAW in an argon atmosphere (at a pressure of 1 atm and a temperature of 298 K) is \(6.8 \cdot 10^{-4}\) dB/(MHz·cm). The results of measuring the dependence of SAW attenuation on gas pressure are shown in figure 2. The slope of the curves depends on the molecular weight of the gas. The data obtained are in good agreement with the results of work [5].

3. Gas adsorption and desorption on a solid surface

Even in ultra-vacuum conditions, the solid surface cannot be shielded from residual gases. Because of the high energy density of the surface wave, it can effectively initiate desorption of gases from the surface of the sound duct under the action of acoustic waves [6]. The experiments were carried out in a vacuum of ~5 \(\times 10^{-7}\) mm Hg. Using low-intensity SAW pulses, reproducible results were obtained for a wide range of gases. In those cases, when the SAW amplitude was kept constant and the power increased due to an increase in the pulse duration at a constant repetition rate, a linear dependence of the desorption rate on the acoustic power was observed. If the power increased due to the amplitude of the signal, the rate of desorption increased according to power law. The obtained experimental results [6] can be explained on the basis of the acoustic desorption theory proposed in [7].

In the area of contact between the two phases, under the influence of the difference in their molecular force fields, a nonhomogeneous transitional surface layer is formed. The most common form of adsorption can be expressed through Gibbs surface excess

\[
\Gamma_i(d\sigma)_r = -\sum_j \Gamma_j d\mu_j,
\]

where \(\sigma\) is surface tension at the interface, \(\mu\) is chemical potential [8]. It is important to correlate \(\Gamma_i\) with the number of molecules that have passed into the surface phase.

Let the semi-infinite solid be confined to a flat surface. It is necessary to select a volume \(V\) in a solid, which cuts out on the surface an area equal to the area \(S\). Let us define the surface excess of a certain value as the difference between the values of this value in the presence of a surface and in its absence of a surface. The most important is the surface excess of the number of molecules \(N_i^c\) and the excess of the corresponding concentration

\[
\Gamma_i = N_i^c / S.
\]

In the case of an inert solid adsorbent, a rarefied adsorbate monolayer can be regarded as a two-dimensional analog of an ideal gas. To describe a given system "adsorbate – adsorbent", in addition to temperature \(T\), surface concentration \(\Gamma\), a third main variable is required – surface pressure. It is the difference between the surface tension \(\sigma_0\) of the pure component 1 and the surface tension of the two-component system \(\sigma\) [3]. For a two-component system, surface tension is the rate of decrease in the Helmholtz free energy \(F\) with an increase in the surface area \(\sigma = -(\partial F/\partial S)_{T,V,N}\). The surface pressure at the "gas – solid" interface for a given gas pressure \(p\) can be determined from the adsorption data using the Gibbs equation.
where

\[ \sigma_0 - \sigma = - k_s T \int_{p=0}^{p} \Gamma \cdot d \ln p. \] (2)

We now analyze the effect of adsorption on the propagation of elastic surface waves. It is obvious that the decrease in free energy surface, which occurs during adsorption, is accompanied by a change in the elastic parameters of the surface lattice, which leads to a decrease in the velocity \( v_R \) of Rayleigh waves. To identify this dependence, taking into account the fact that \( v_R = \omega(k)/k \), let us use the well-known universal ratio of the change in the frequency of the conservative oscillatory system [3]

\[ \Delta \omega/\omega_0 = \Delta E/E_0 = \Delta V/V_R. \]

Here \( \Delta E \) is the change in the total mechanical energy of the allocated volume \( V \) during adsorption, \( E_0 \) is the unperturbed energy value, and \( k \) is the wavenumber.

For the selected volume \( V \) of a semi-infinite solid, we will not make a distinction between internal and free energy, assuming that the absolute temperature is close to zero. In this case, a change in the total mechanical energy during adsorption can be identified with a change in surface tension \( \Delta \sigma = \sigma - \sigma_0 \), therefore \( \Delta V/V_R = \Delta \sigma/\sigma \). Taking into account (2), we can finally write

\[ \Delta V/V_R = (k_s T/\sigma) \int_{p=0}^{p} \Gamma \cdot d \ln p. \] (3)

The last relation is interesting in that it allows one to determine the surface tension of a solid using the experimentally measured adsorption isotherm \( \Gamma(p/p_s) \) and the corresponding change in the SAW velocity. Estimates of the expected change in the SAW velocity as a result of adsorption give the value \( \Delta V/V_R \sim 10^{-6} \), which can be measured with an accuracy of about 0.5% [3].

4. Polymolecular adsorption of vapors of polar liquids

One of the most complex and interesting surface processes is the polymolecular adsorption of liquids vapors on the surface of a solid. There are significant differences in the formation of the adsorption layer of polar and non-polar liquids. The physical properties of polar substance in the bulk liquid phase and in the boundary state differ significantly [9].

To study the adsorption of liquid vapors, a measuring cell (figure 3) with two sealed sections was developed. A piezoelectric substrate 1 was fixed on the cover of the upper section, on which (as in figure 1) SAW transducers 2 and a rectangular aluminum film 3 with an adsorbing surface area \((a \times b)\) were formed. The adsorbing surface was an aluminum oxide layer on a metal film. A glass capillary with an inner diameter \( d \), sealed on one side, partially filled with an evaporating liquid 6, was placed in the lower section of the cell through a hole in a heat-insulating Teflon gasket 4. The change in the height of the liquid column in the capillary \( \Delta L \) during vapor adsorption was recorded with the cathetometer 5. It was assumed that the densities of the bulk and adsorbed liquid are identical. In this case, adsorption can be expressed through the change in the average thickness of the adsorption layer

\[ h = \pi d^2 \cdot \Delta L/(4a \cdot b). \]

The adsorption layer on a solid surface is formed as a result of the dynamic equilibrium of the processes of adsorption and desorption of liquid molecules. The layer thickness depends on the vapor pressure at the surface of the solid (adsorbent) and on the temperature of the adsorbing surface. The parameters of the adsorption process can be changed by varying the temperature of the evaporating liquid or the temperature of the adsorbing surface of the metal film. The relative vapor pressure \( p/p_s \) in the adsorption zone can be calculated using the Clausius – Clapeyron relation

\[ \ln(p/p_s) = (Q_L/R) \cdot (T_1^{-1} - T_2^{-1}), \]

where \( Q_L \) is the latent heat of vaporization of the liquid. By varying the temperature of the evaporating liquid \( T_2 \) and maintaining a constant temperature of the adsorption layer \( T_1 \), the adsorption isotherm \( h(p/p_s) \) can be obtained. The use of surface acoustic waves as probing pulses makes it possible to study the complex of physical properties of an adsorbed liquid [3].

At a fixed temperature of the evaporating liquid (therefore, \( p = \text{const} \)) and variations in the temperature of the adsorbing film \( (T_1 \geq T_2) \), we can study the adsorption isobar. In figure 4 shows the
temperature dependence of the change in adsorbed water at a fixed vapor pressure $h(T)_p$. To exclude the influence of diffusion processes on the time of establishment of thermodynamic equilibrium in the adsorption zone, air was preliminarily evacuated from the upper section with a foreline pump.

**Figure 3.** Diagram of the measuring cell for studying the adsorption of liquid vapors.

**Figure 4.** Isobar adsorption of water vapor on the surface of the oxide layer of the aluminum film.

**5. Conclusions**

Thus, in the interaction of SAW with a gas medium, the attenuation of these waves depends on the frequency, pressure, and molecular weight of the gas. High sensitivity to gas pressure changes allows using the measuring system as a microphone. This microphone can convert acoustic vibrations into an electrical signal in a wide frequency range from infrasound to ultrasound. It is shown that gas adsorption on a solid surface is accompanied by a decrease in the velocity of SAW. An equation is obtained that corresponds to this decrease. This equation makes it possible to determine the surface tension of a solid using the experimental adsorption isotherm obtained and the measured decrease in the velocity of SAW. It is important to note that in the acoustic study of molecular processes in a sparse gas environment, the use of vacuum devices in experimental plants is of great importance. The ability of Rayleigh waves to stimulate the desorption of gases from a solid surface may be of interest for degassing flat samples in a vacuum, when their significant heating is unacceptable.

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