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SURFACE ACOUSTIC WAVE MONITORING OF THIN Au FILM DEPOSITION ON GaAs SURFACE

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Abstract. Deposition of thin Au films with thermal evaporation in vacuum is widely used in the technology of the GaAs microwave and optical devices. The film formation in fact is a multi-stage process, including various physical and chemical transformations, that is interpreted as thin-phase epitaxial growth. It was studied by many authors, mostly by observation of the results of metal deposition with optical or electron microscopy, Auger spectroscopy and other methods. In this paper we introduce results of *in situ* monitoring of the metal (Au) deposition process with surface acoustic waves. SAWs at frequencies near 100 MHz were exited at the (100) surface of the semiinsolating GaAs with interdigital transducers. Phase velocity and attenuation of the SAW was precisely measured and analyzed as a function of the film deposition time (film thickness). Specific time-domain responses and results of Fourier analysis give information about surface and near-surface transformations during the deposition and give new opportunities to control this process [1-2]. SAW diagnostics can be applied to monitoring and control of any epitaxial growth processes, if SAW propagation in the substrate is provided.

1. Introduction

Thin Au films are widely used in the technology of the GaAs devices. The metal film formation is a multi-stage process, including various physicochemical reactions which is studied usually by optical or electron microscopy, Auger spectroscopy and so on.

In particular, as was reported in [2], the surface acoustic waves (SAWs) velocity reduction is due to mechanical loading changes besides connected to the SAW electric component screening with the metal film deposition. At the same time, it was found [4] that internal friction changes *in situ* with increasing of the temperature annealing and determined by the physicochemical processes at the Au/GaAs interface. For this reason, the SAW propagation parameters (amplitude and phase) variation with Au deposition time with the Au-GaAs interaction and the surface GaAs layer reconstruction is interest so from the point of the view of SAW diagnostics possibilities as the SAW effects on the reaction going. Specific time-domain responses and results of Furrier analysis give information about surface and near-surface states and show new opportunities to control this process [1-2].

In this paper we introduce results of *in situ* monitoring of the metal (Au) deposition process with the surface acoustic waves. SAWs at frequencies near 100 MHz were exited at

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the (100) surface of the semiinsolating GaAs with interdigital transducers. Phase velocity and attenuation of the SAW was precisely measured and analyzed in details as a function of the film deposition time (film thickness).

2. Experimental

The gold layer evaporated on the GaAs surface was studied in a vacuum chamber at a pressure of ~ 10^{-5} Pa. A narrow tungsten strip incandescent to 1200 °C was used as a vaporizer. The temperature of the GaAs surface did not exceed 80 °C during deposition. The samples were plates of semi-insulator (111) GaAs 30 x 23 mm in size. For excitation and detection of the SAWs, thin-film aluminum interdigital transducers (IT) operating at a central frequency of 65 MHz were deposited onto the GaAs surface (Fig. 1). Prior to the experiment, the GaAs surface was cleaned with isopropyl alcohol. The surface of irradiation was 10 x l5 mm^2, the IT aperture was W= 3.5 mm, and the distance between the IT was L = 15.5 mm. The amplitude and phase of the SAW output signal were measured every 0.5 s.

The technique of measuring the parameters of the SAWs propagating between the IT allowed determination of the SAW amplitude accurate to ±0.01 dB, phase, to ±1 °, and time count interval, to ±10 ms. The loss in all the measurement cycles prior to the start of action was 32 dB, the maximum output signal of the frequency synthesizer was 0.7 V, and the path impedance was 50 Q.

The SAW parameters (amplitude and phase) were measured directly during deposition of a 2000 Å - thick gold film. The films were deposited sequentially from two vaporizers (1000 Å each). The SAW diagnostic results were compared to the data obtained by optical microscopy at layer-by-layer etching.

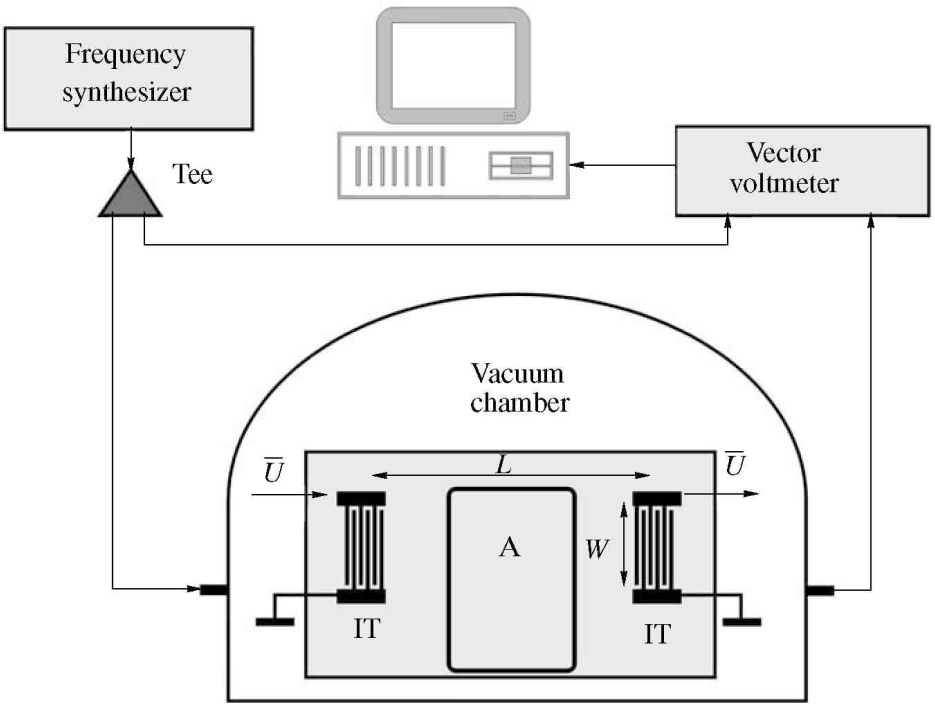

Fig. 1. The experimental facility. *A* is the region under study, *W* is the IT aperture, and *U* is the input and output voltage.

3. Experimental results

The results of the measurements of the parameters of SAW propagation in the GaAs surface layer as a function of gold deposition time are presented in Fig. 2. One can see that the

amplitude and phase variations with time are not interrelated. The jumps of the amplitude and phase dependences may imply the phase transformations in the GaAs surface layer during deposition of evaporated gold and the recrystallization processes [5, 6, 7].

The surface of the Au/GaAs samples after etching in a solution HCl + $HN0_3$ was investigated with an optical microscope. In the micrograph (Fig. 3), one can observe large fused metal islands, which were electrono-graphically determined to be the alloy Au + Ga, and the GaAs islands extended perpendicularly to the surface (Fig. 3, region *A*). In the electron diffraction patterns of the sample surface, rings from cubic gallium arsenide are present, in addition to the reflections from the single-crystal solution Au + Ga.

The substructure in the micrograph (Fig. 3, region *B*) represents the GaAs islands extended along the surface and covered with a thin layer of the solid solution Au + Ga (in the electron diffraction patterns, there are reflections from the GaAs hexagonal phase). It follows from Fig. 3 that, in our case, the growth stages coincide with the known stages of gold film growth on GaAs. If one takes into account, that the time intervals of the phase transformations are much longer than the period of the propagating SAWs, the SAW parameter variations can be considered to occur under quasi-equilibrium conditions.

4. Discussion

Physicochemical processes in the Au-GaAs system. The studies of the layer-by-layer growth of gold films on GaAs as a function of Au thickness (up to ~2000 Å) by optical, scanning, and electron microscopy, X-ray microanalysis, Auger spectroscopy, and electron diffraction [3, 6] show that, at the Au/GaAs interface, the following processes occur as the Au film grows:

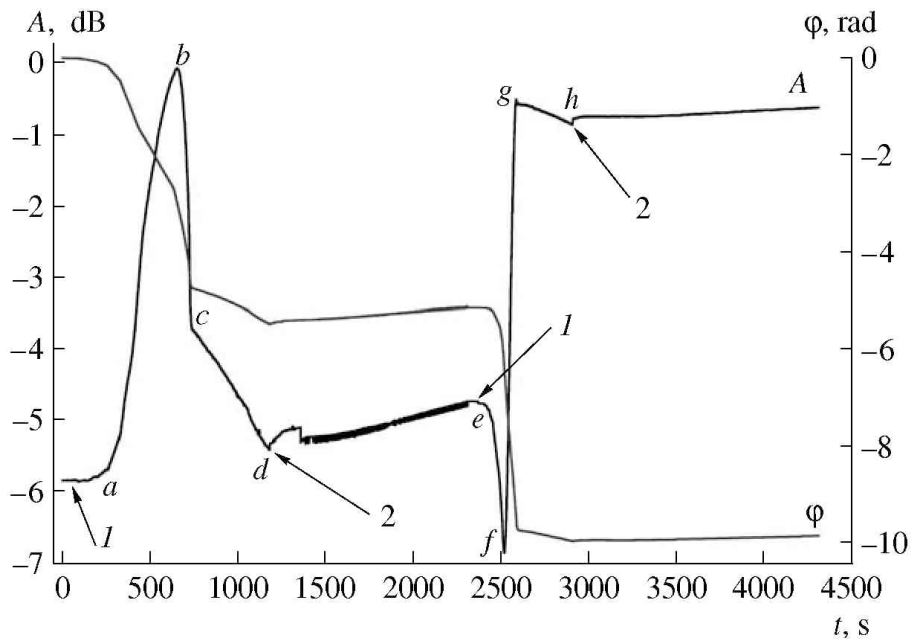

Fig. 2. Dependences of the SAW propagation parameters on gold deposition time with the vaporizer on (7) and off (2). *A* is the amplitude and *φ* is the phase.

(1) Transformation of a loose layer of the natural gallium arsenide oxide to a dense layer (0 - 300 Å) with granular structure and occurrence of free (unbound with the gallium arsenide lattice) gallium atoms at the surface (the surface oxide layer possesses the block structure.
(2) Formation of microislands of Au_3Ga and Au_7Ga_2 compounds (100 - 500 Å).

(3) Deformation and destruction (fining) of the dense oxide layer accompanied by the occurrence of free Ga and As atoms, dilution of the Au_3Ga and Au_7Ga_2 compounds (100 - 500 Å), and sedimentation of the GaAs hexagonal phase islands extended along the substrate surface and covered with a thin dendrite layer of the Au-Ga solid solution (530 Å).
(4) Sedimentation of the GaAs islands with the cubic and hexagonal structures rotated relative to one another and extended along the normal to the GaAs surface (750 Å).
(5) Dilution of the islands of GaAs whiskers extended along the normal to the surface and formation of the solid solution of polycrystalline phases Au + Ga + As (750 - 1000 Å).
(6) Crystallization of the diluted solid gallium solution in gold from the solution in melt at the surface of the GaAs islands of the hexagonal phase covering the gallium arsenide surface and secondary sedimentation of the GaAs whiskers extended along the normal to the substrate surface and oriented relative to one another in a complex way in the region surrounding the crystalline gold area (1325 - 2000 Å).As was shown erlier [7], during deposition of gold, the following multilayer structure forms at the GaAs surface (Fig. 4a):

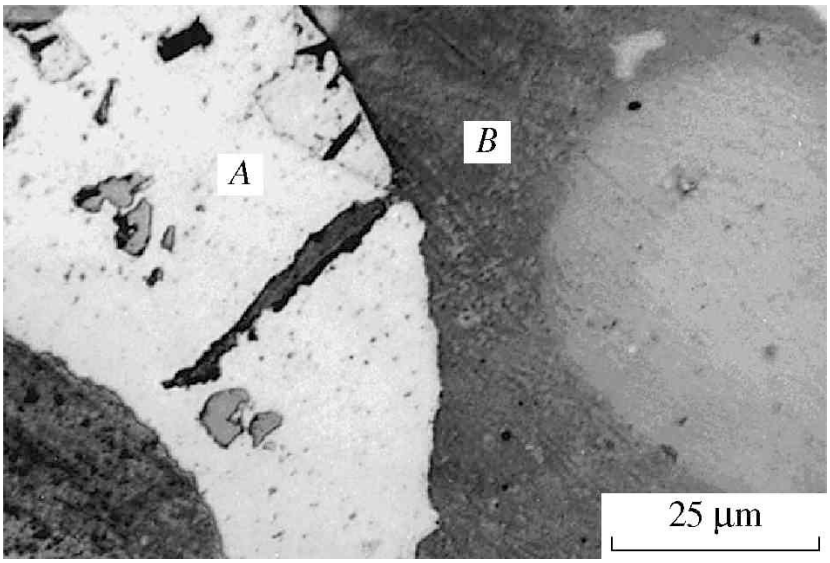

Fig. 3. Micrograph of the Au/GaAs surface after selective etching.

—Thin layer of recrystallized GaAs with the structure from the hexagonal phase islands extended along the surface of the basic gallium arsenide.
—Thin continuous metal layer on the basis of the Au_7Ga_2 compound with the dendrite structure.
—Island (dendrite) gold layer with small gallium impurities (gold grows from the solution in melt) with the gallium arsenide islands extended perpendicularly to the GaAs surface and located along the gold island boundaries.

The Au/GaAs layers under study are inhomogeneous not only in composition but also in stress. Since the crystallites grow at the gallium arsenide surface in the vapor-liquid-crystal way, the stresses appearing at the interfaces between the layers during the gold layer growth are similar to those typical of wetting effects. In this case, the stress vectors along the gallium arsenide surface and perpendicular to it are different both in value and in direction (Fig. 4b). As is known, the variation in geometrical microrelief of the surface (curvature, roughness, etc.) influences the crystal surface energy, surface tension, electric potential, etc., as well as the intracrystalline fields in the crystal volume, which causes not only phase transitions but also the change in orientation of the GaAs layer. From this, one can expect that, as gold is deposited, deviation from the main deformation axes specified by the passing SAW occurs.

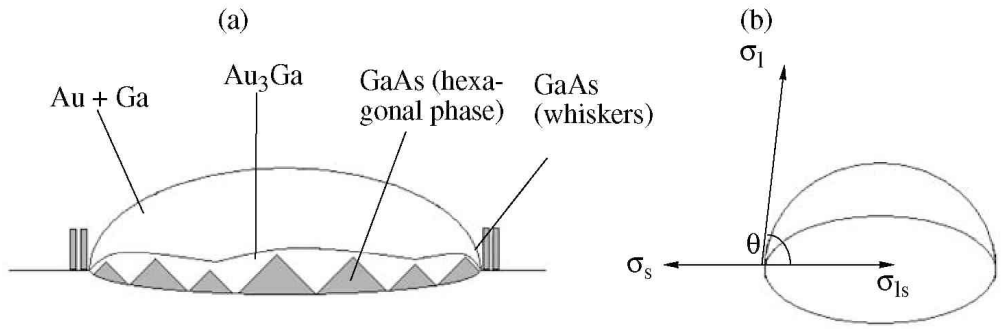

Fig. 4. Surface scheme: (a) the surface layers in the Au-GaAs system and (b) the distribution of interphase energy at the interface Au + Ga (σ_l)/GaAs(σ_s).

SAW diagnostics. According to the processes occurring at the Au/GaAs interface, known concepts on the SAW dynamics [3-8], and the considered variations in the SAW parameters during gold deposition onto gallium arsenide, the following conclusions were presented:

1. The variation of SAW amplitude *A* with deposition time is shown in Fig. 2; wave absorption power *P* calculated from the amplitude is shown in Fig. 5. The amplitude of a wave propagating over the gallium arsenide surface is similar to the sound absorption curves near a critical point, i.e., the point in the state diagram which corresponds to the critical state. The critical point is a special case of a phase transition and characterized by the loss of thermodynamic stability in density or substance composition. In this case, the change in wave absorption is determined, as is known, by the degree of crystallinity of a material $\Delta V_C / V$, where ΔV_C is the total volume of the crystal phase and *V* is the layer volume. The wave amplitude can change as follows:

$$A = A_0 \exp(\alpha C x),$$

where α is the absorption coefficient of a material and *C* is the concentration of sediments of this material:

$$C = C_0 \exp(-U/(RT)),$$

where *U* is the energy of the formation of sediments [9].

In the amplitude curve (Fig. 2), one can see at least three peaks (special points are *b,f,* and *g*). To all appearances, the increase (decrease) in wave amplitude follows that in quantity of crystal islands in the gold-based film near the phase transition point. The occurrence of Au-Ga, GaAs, and Au crystal islands is caused by closeness to temperatures of the formation or sedimentation of these compounds. In the deposition time dependence of the amplitude (Fig. 2), there are both exponential *(a-b)* and linear *(c-d)* portions. The exponential character appeared to be determined by the rate of a chemical reaction of the formation of such compounds as Au_7Ga_2 and Au_3Ga. The activation energy of the change in amplitude, in this case, corresponds to the energy of their formation, whereas the linear character of the curve is determined, most likely, by nonthreshold diffusion caused by plastic deformation with the subsequent dilution (sedimentation) of the GaAs and/or Au islands [9].

Thus, the change in wave amplitude (absorption) with time is caused by the phase transformations in the surface layer, mainly in the plane perpendicular to the GaAs surface. This is explained by the fact that, during propagation of Rayleigh waves, the vector of a vibrational shift of particles lies in the plane perpendicular to the interface (vertical plane). In

this case, the traveling wave either grows or attenuates owing to the variations in composition and concentration of inclusions in which it is absorbed and/or scattered [5].

2. The dependence of SAW propagation velocity v on gold deposition time (Fig. 6b) indicates that the SAW velocity decreases with an increase in deposition time. Since the vector of the phase (group) wave propagation velocity lies in the GaAs plane, the SAW velocity variation is determined by the phase transformations in the plane parallel to the gallium arsenide surface. One can see that the dependence of the wave propagation velocity on deposition time is a broken line whose envelope changes almost exponentially. As is known, the variation in velocity is determined mainly by the state of the medium (including its charge properties) when

$$E_1 - E_2 = ln(v_1/v_2).$$

Here, E_x is the energy of the first state and E_2 is the energy of the second state [6]. In our case, the activation energy of the variation in velocity calculated from the curve envelope appeared to correspond, in general, to the Ga melting (solidification) energy.

The linear portions of the dependence of the velocity on deposition time have different slopes and, probably, correspond to the rates of the chemical reactions occurring near the temperature of the phase transformations caused by plastic deformation stresses. In this case, the rate of the chemical reactions is determined by the quantity of incoming atoms, which, in turn, is determined by the constant pressure time.

Motion of Ga and As atoms and vacancies in GaAs occurs, at first, mainly in the direction perpendicular to the surface under the action of the stresses caused by pressure of a surface, for instance, oxide, layer. A further increase in gold deposition time results in the motion of GaAs structural units in the plane parallel to the substrate

During gold absorption, as was shown above, the surface microrelief changes. Considering the wave velocity to be the velocity of motion of the compression-tension areas in the surface plane space, one can relate the change in the SAW velocity to the change in surface curvature. Then, $v_1 = v_2 tan\theta$, where $tan\theta$ is the ratio of the slope to the initial crystal side. Taking into account that $\varepsilon = v_x/v_2$, we obtain the relative deformation rate $\varepsilon \sim Q/t$. The change in the increment of the velocity of a propagating wave to the initial velocity value with deposition time indicates the change at the newly forming surface of the crystallographic direction with the maximum SAW velocity; i.e., it allows judging the system geometry whose coordinate lines are as though frozen in the medium and deformed together with it. The intensity of deformation, i.e., the magnitude determining the change in angle between the chosen directions equally sloped relative to the main axes of deformation at a point due to deformation, changes.

3. The dependence dv/dt on deposition time is presented in Fig. 6. As is known, $dv/dt = d^2\xi/dt^2$ and $m\, d^2\xi/dt^2$ is the general equation of motion, where ξ is the shift of a particle with mass m from the equilibrium position and U is the potential energy of the system. First of all, it is noteworthy that dv/dt undergoes step changes and pulsing. There are portions that differ from each other in value. The selected portions $dv/dt \sim const$ correspond to a constant rate of relative deformation. Note two peaks in the dependence of dv/dt on deposition time that slightly lag relative to the amplitude peaks. The observed peaks correspond to the reactions of sedimentation (dilution) of the GaAs islands along the normal to the surface. At the first deposition stage, the equal-acceleration portions can be related to the changes (phase transformations) in the GaAs layer caused by pressure of the oxide layer on the surface.

Since the gold-based layer is elastic, the surface strength is mainly affected by layers of dense oxide (in the beginning of deposition), recrystallized Au layers, and GaAs islands extended perpendicularly to the surface and rotated irregularly relative to the substrate.

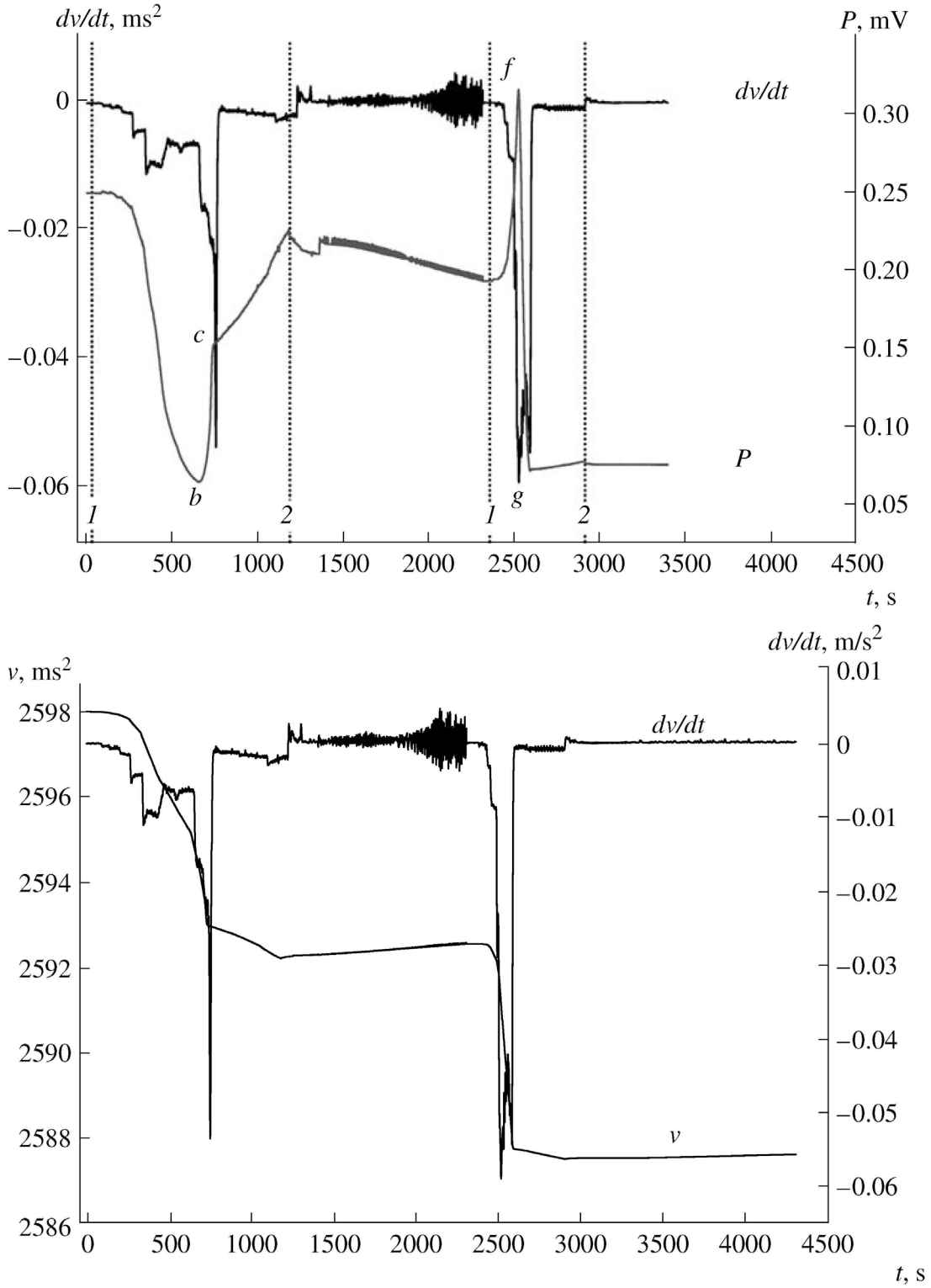

Fig. 5. Dependences of the SAW parameters (*v* is the velocity, *dv/dt* is the derivative of velocity, and *P* is the absorbed power) on Au deposition time.

For a given stress value, the corresponding diffusion creep occurs, which determines the *dv/dt* value and the rate of chemical reactions. If particle shifts are small as compared to the typical size of an acoustic wave, the equation of motion of particles under the action of elastic forces of a medium is

$\rho dv/dt$ = -grad (P) or

$dv/dt = P/\rho_0 h,$

which is known from acoustics of microinhomogeneous media.

At the same time, upon harmonic oscillations of a plate and its contact with a medium, viscosity forces transfer its motion deep in the medium as a viscous wave of a sort. In this case,

$dv/dt = vd^2 v/dx^2,$

where v is the kinematic viscosity coefficient.

The surface GaAs layer experiences shear stresses, such as tension, compression, and rotations; the layer itself presses the underlying gallium arsenide layer, thus favoring diffusion creep and gallium accumulation at the interface with gallium arsenide. The areas of constant *dv/dt* correspond to equal pressure of the surface layer on GaAs.

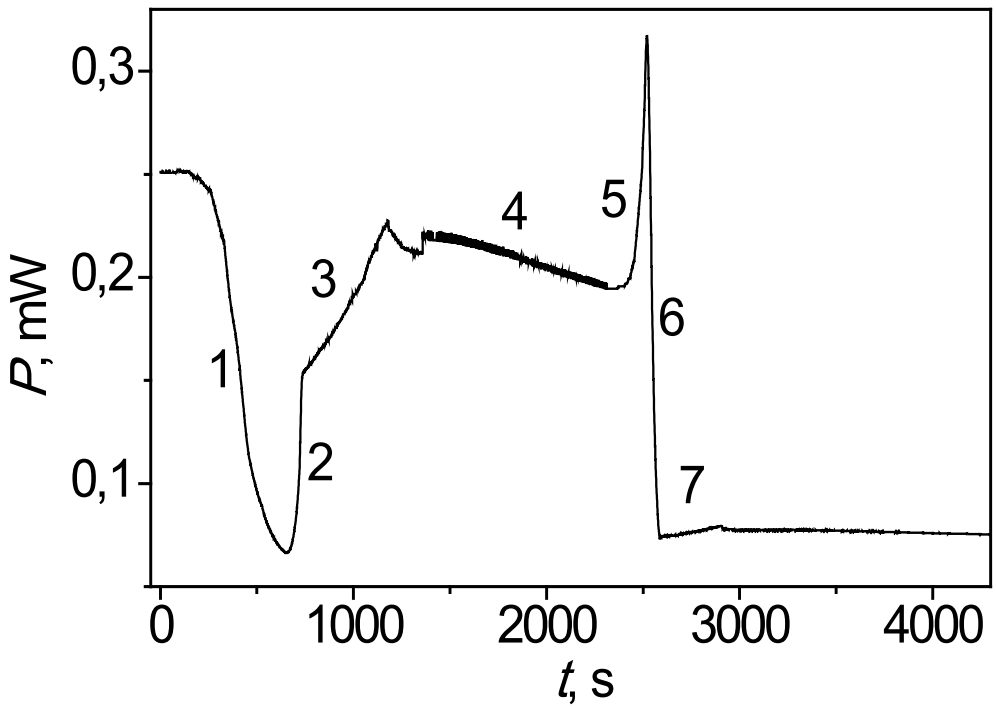

Fig. 6. Dependences of the SAW absorbed power *P* on Au deposition time.

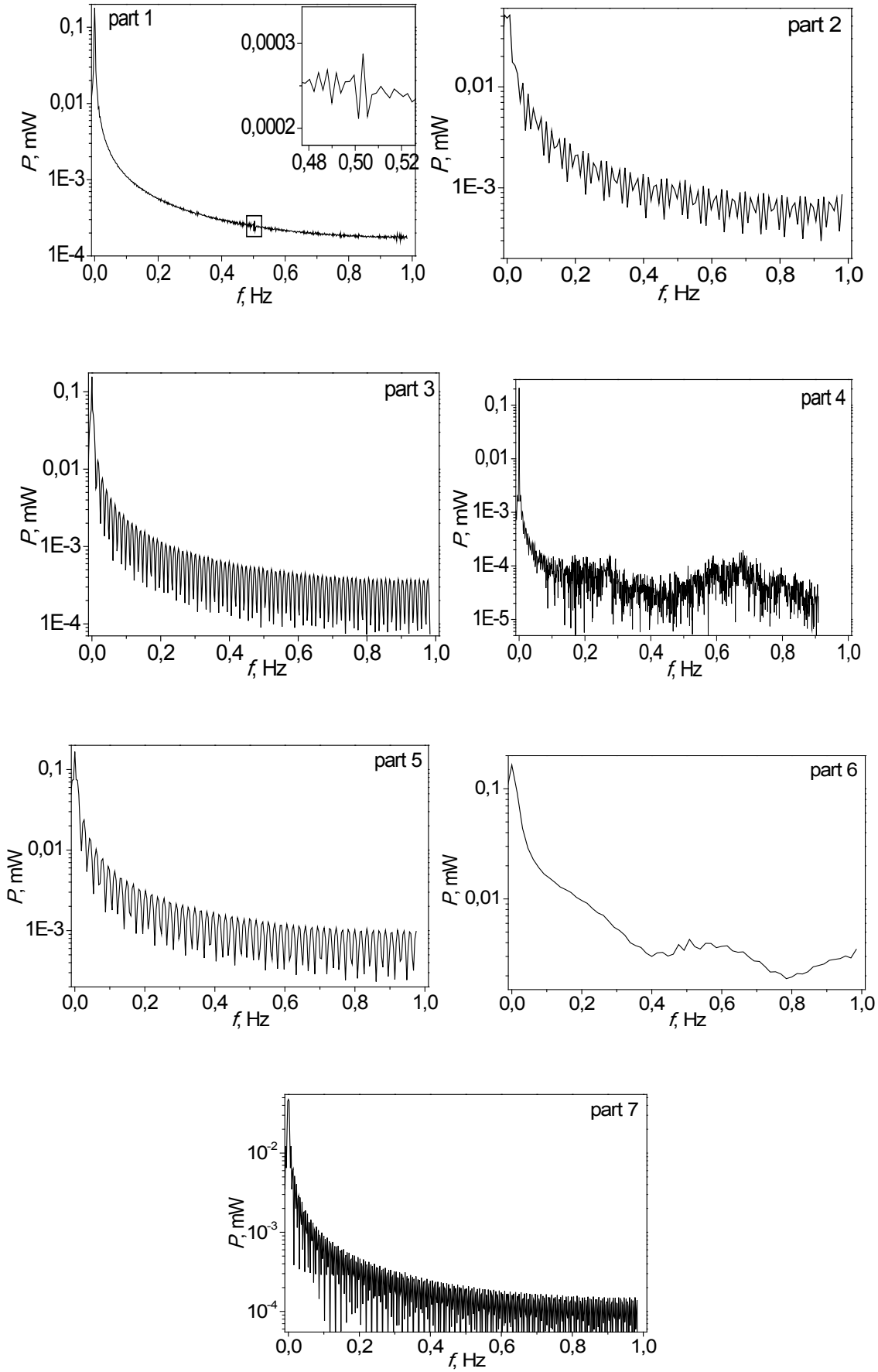

Fig. 7. Fourier transforms *P(f)* of *P(t)* for parts: 1, 2, 3, 4, 5, 6, and 7 presented at Fig. 6.

Owing to the effects of piezoelectricity and electrostriction, electric fields appear in both the dielectric and the surface layer; i.e., in gallium arsenide, shear deformation occurs which causes rotations and reconstructions of the GaAs surface, specifically, the transformations (111) —- (110) —► (100). The envelope characteristic corresponds to the tangent of the angle of rotation of the surface layer. The critical angle is 54 °.

The spectral response of the scattering power corresponding to different time interval parts of gold deposition (i.e., gold layers thickness) is shown at Figs. 6, 7. The spectral characteristics above all indicate as found the aggregate state of the near-surface layers and chance of rotation for the crystallized islands under electric field intensities line and/or mechanical stress forces in the near-surface layer. The magnitude of the acoustic power losses as occurred are determined by number of precipitated islands and connected to the near-surface deformation type.

The time dependence behavior of the velocity deviation is presented at Figs. 8, 9. It gives useful information about magnitude of viscosity changing. The oscillation spectrums of the velocity deviation show the features of the phase transforming including such reactions as micro-discharges, the liquid phase forming and GaAs islands precipitation at the metal-semiconductor boundary.

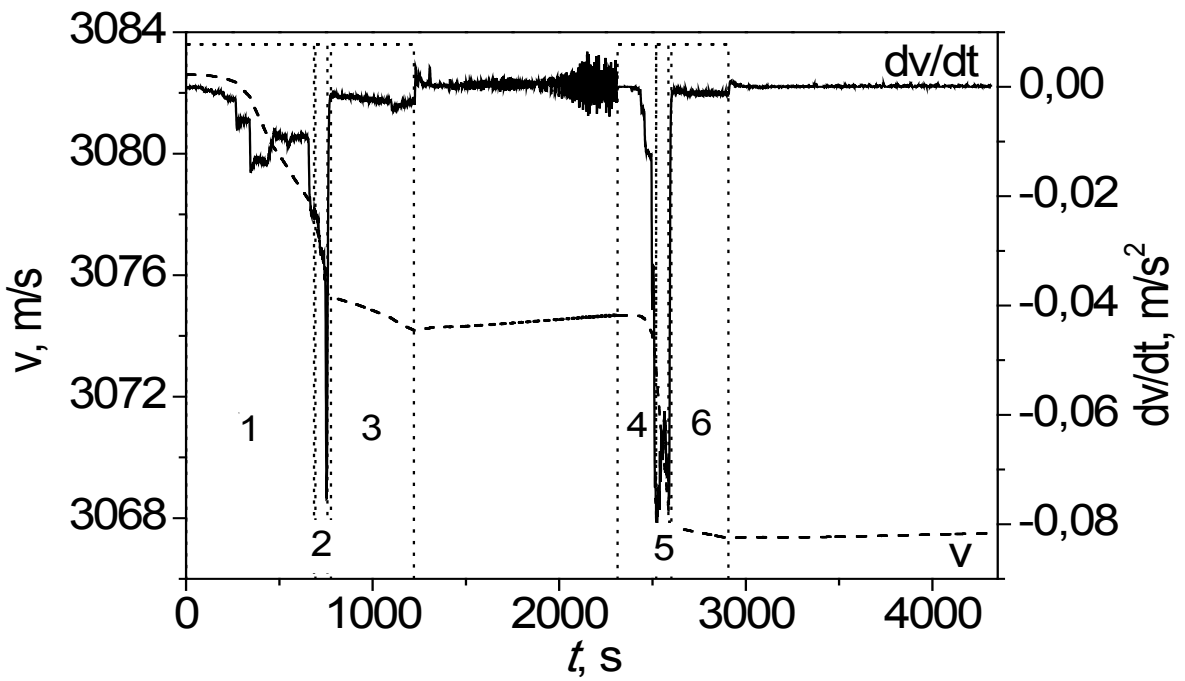

Fig. 8. The SAW velocity (v) and derivative of velocity *(dv/dt)* dependences on Au deposition time.

Thus, the SAW propagation parameters substantially depend on the physicochemical reactions at the interface between the Au and GaAs contact layers and can be used for their detection and identification. Furrier analysis gives information about the surface and near-surface transformations during deposition and give new opportunities to control this process [1-2]. SAW diagnostics can be applied to monitoring and control of any epitaxial growth processes, if SAW propagation in the substrate is provided.

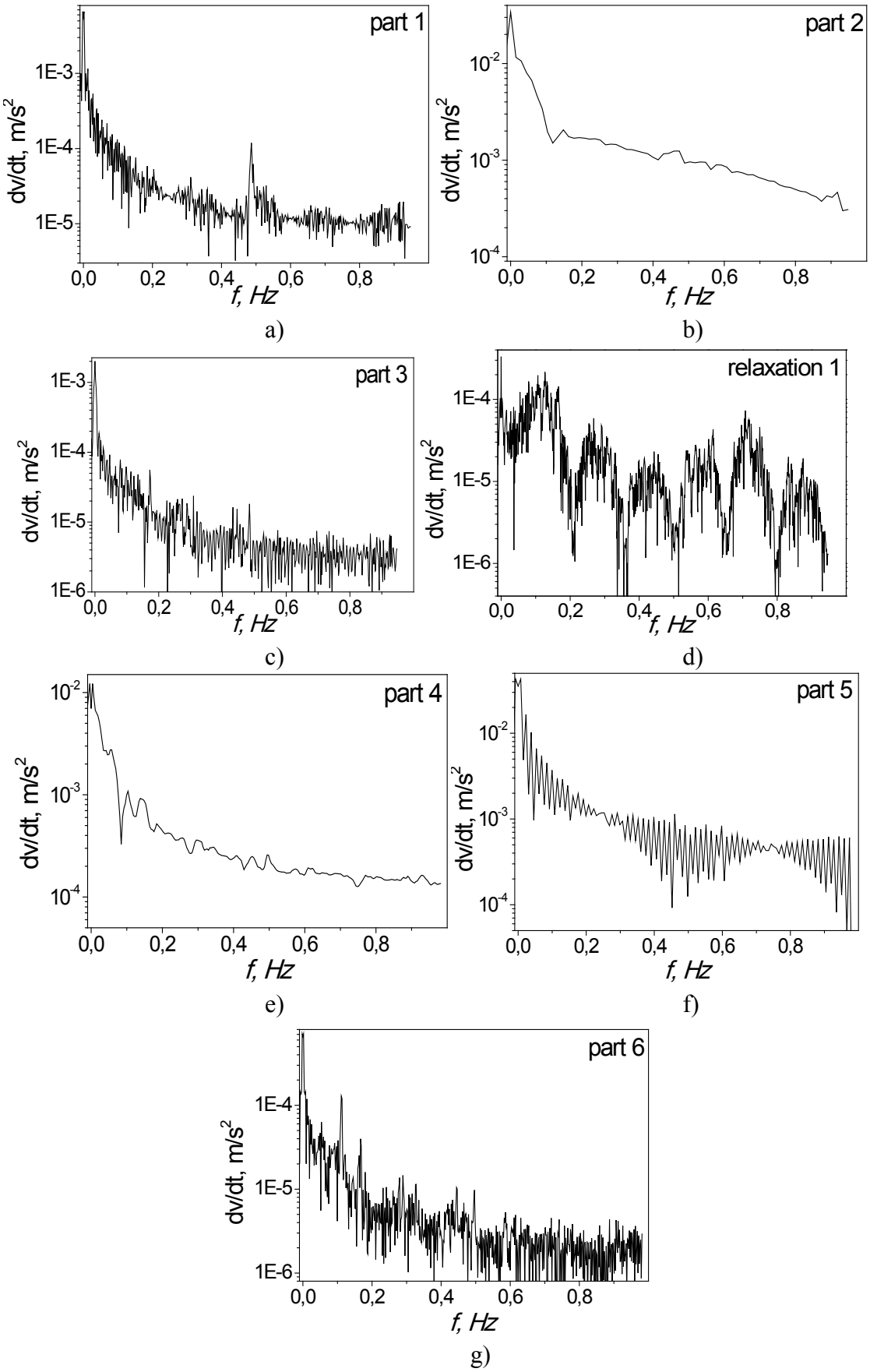

Fig. 9. Fourier transform of the parts (1-6) (see Fig.8).

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