SURFACE ACOUSTIC WAVE SENSORS: NEW ANALYTICAL CAPABILITIES

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Surface acoustic waves (SAWs), propagating along below different crystallographic directions on anysotropic piezoelectric substrates are suggested as a tool for nondestructive characterization of thin film materials subjected by a gas phase adsorption. Facilities of the tool are demonstrated on considering H_2, CO, N_2O, and H_2O adsorption on porous (polyvinil alcohol, palladium and palladium-nickel films) and monolithic (quartz) absorbers. Difference between porous and single crystal materials is outlined. The number of the adsorbed particles, the changes in the temperature, mass, density, elastic constants and electric conductivity of the films are evaluated both for steady-state and kinetic conditions.

Introduction

Novel analytical tools for nondestructive characterization of the physical and chemical phenomena in thin film and monolithic materials upon a gas phase adsorption is of fundamental importance for many areas, such as clean biosensing, electronic materials etc. However, contemporary knowledge on these phenomena is not perfect because of limited number of reliable experimental data, complexity of foolproof experimental techniques, multiformity of the accompanied processes, etc.

Among available analytical tools, piezoelectric quartz crystal microbalance is one of the most efficient [1]. It is based on the change in resonant frequency Δf of a piezoelectric plate produced by the change in the plate mass Δm due to a gas or liquid phase adsorption. Another efficient tool is based upon the propagation of SAW along the analysed surface [2]. In comparison with quartz microbalance, operating typically at 10 MHz, the SAW tool has better resolution as its typical operation frequency is in the range between 50 and 500 MHz. However, application of the tool has till now been restricted by adsorbed mass Δm solely. Present paper demonstrates an advanced SAW tool that, on accounting Δm together with the changes in the density ρ, elasticity C_{ij}, electric conductivity σ and temperature T of an absorber, becomes more fruitful for nondestructive characterization of thin film materials.

2. Methodics

The scheme of the SAW tool is shown on Fig. 1. It consists of a set of SAW delay lines (channels) implemented on a piezoelectric substrate (1) and located around common center with pairs of interdigital transducers (IDTs) (1) in each of the channel. A test film (2) is deposited in the center of the tool. When adsorbing by the film, a test gas produces the changes in the film properties. The magnitudes of the changes depend on the type of the gas, the gas

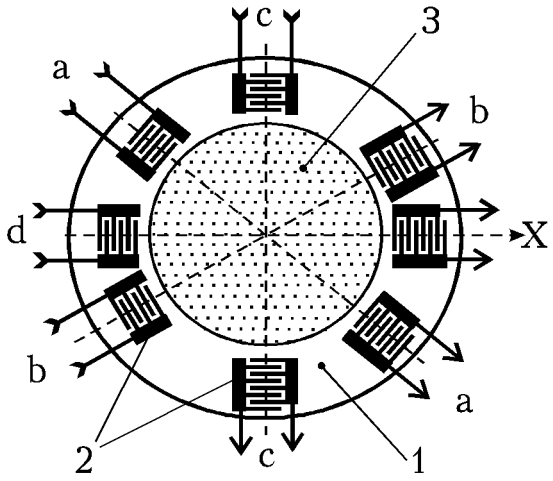

Fig. 1. The integral structure for the investigation of gas phase adsorbtion upon thin film materials: *1*—piezoelectic substrate; *2*—interdigital transducers (IDT); *3*—a film under investigation; a, b, c, and d—probing channels.

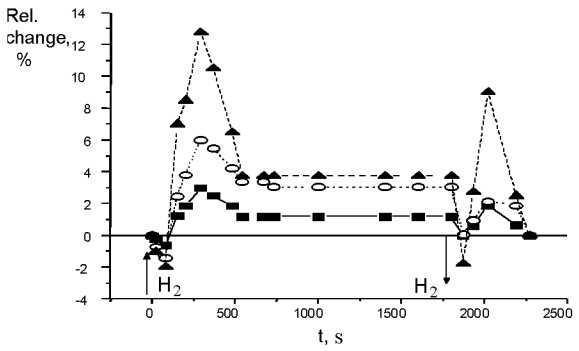

Fig. 2. Temporal changes of density $\Delta\rho/\rho$ (□) and elastic moduli $\Delta C_{11}/C_{11}$, $\Delta C_{44}/C_{44}$ of $Pd_{0.97}Ni_{0.03}$ film during hydrogen adsorbtion and desorbtion ($h = 300$ nm, 20 °C). H_2—dry air swiched off, gas mixture 1% H_2 + N_2 swiched on; H_2—gas mixture 1% H_2 + N_2 swiched off, dry air swiched on.

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concentration and the material of the film, contributing into the change in SAW velocity v_0 (SAW response $\Delta v/v_0$) in accordance with partial mechanical components of the SAW displacement for a given propagation direction [3]. Since the SAW components on anysotropic substrate are different for different propagation directions, the magnitudes of the SAW responses in different channels are distinguished each other even though the test film (2) is the one and the same for all of them.

To screen electric fields, accompanying SAW propagation on piezoelectric crystal, out the test film and to cut acousto-electric contribution from the SAW response, a metal electrode is deposited at the film/substrate interface. To analyse phenomena onto free surface of solids, a test film and a metal electrode are removed from the SAW propagation path. Usually, the SAW propagation in the structures like the SAW tool is studied by mechanical equations of motion and Maxwell's equations, together with relevant boundary conditions. However, in the most frequent case of thin isotropic film on a piezoelectric substrate of arbitrary anisotropy, the perturbation approach provides the most clear result [4]:

$$\frac{\Delta v}{v_0} = \frac{\pi h}{2\lambda}\left[-\frac{\Delta\rho}{\rho}A + \frac{\Delta C_{44}}{C_{44}}B + \left(\frac{(1-\Delta C_{44}/C_{44})^2}{1-\Delta C_{11}/C_{11}} - 1\right)C\right] - K^2\frac{\Delta\sigma}{\sigma}\,\frac{(\sigma_s^2/v_0^2C_s^2)}{(\sigma_s^2/v_0^2C_s^2+1)^2} + \mathrm{TCV}\,\Delta T.$$

Here, $\Delta\rho/\rho$, $\Delta C_{ij}/C_{ij}$, $\Delta\sigma/\sigma$, and ΔT are the changes in density, elastic modulii, sheet conductivity and temperature of the film generated by a gas phase adsorption; h is the film thickness, λ is the acoustic wavelength, K^2, TCV, and C_s are the coupling constant, the temperature coefficient of the SAW velocity, and the capacitance per length on the surface of substrate along the SAW propagation direction, respectively, A, B, and D are the coefficients related with three mutually orthogonal mechanical displacements of SAW A_x, A_y, and A_z along shear, surface normal, and propagation direction, respectively.

Taking into account, that at a constant volume of the film $\Delta\rho/\rho = \Delta m/m$, the number N of the species *adsorbed into the film* can be evaluated as [5]:

$$N = N_A\frac{\rho S h}{M}\,\frac{\Delta\rho}{\rho}. \qquad (1)$$

Here, N_A is the Avogadro number, M is the atomic mass of a gas, S is the film surface.

Finally, taking into account that adsorbed gas species produce a thin layer and, thereby, perturb the SAW propagation even on the free surface, the total number N of the species *adsorbed on the free surface* is evaluated as [6]:

$$N = N_A\frac{2S\lambda}{\pi V^2 M\,(A_X^2 + A_Y^2 + A_Z^2)}\,\frac{\Delta V}{V} \qquad (2)$$

Eq. 1 describes the following important result: the SAW response $\Delta v/v_0$ towards different aspects of a given surface process ($\Delta\rho/\rho$, $\Delta C_{ij}/C_{ij}$, $\Delta\sigma/\sigma$, and ΔT) can be enhanced or rejected by proper selection of an acoustic substrate material, its crystallographic orientation and/or SAW propagation direction (i. e., by the values of v_0, K^2, TCV, A_x, A_y, and A_z). This property is originated from anysotropic nature of the SAW propagation on piezoelectric crystals, making it possible to study partial components of a surface process either one by one or in any combination and all together, though all the aspects are obviously revealed simultaneously. Moreover, Eq. 1 is applicable both to steady-state (equilibrium) and kinetic (non equilibrium) conditions as it is valid for any step of a surface phenomenon. The only principal restrictions is that the surface of the solid has to ensure the propagation of SAW, otherwise, the application of the SAW tool is impossible as it is, for example, for liquid/solid interface.

Moreover, an important property of the SAW tool is the capability to decrease for a given test film the threshold detectable concentration n_{thr} and, thereby, thresholds of all measurants (N, $\Delta\rho/\rho$, $\Delta C_{11}/C_{11}$, $\Delta C_{44}/C_{44}$, $\Delta\sigma/\sigma$, and ΔT) by increasing the operation frequency f_0 and/or the length L_0 of the film. Indeed, since $\Delta v/v_o = \Delta f/f = -\Delta\varphi/\varphi$, where $\varphi = 2\pi(L/v_0)f$, the change in the SAW phase φ for $L = aL_0$ and $f = bf_0$ ($a, b > 1$) can be written as: $\Delta\varphi = a\cdot 2\pi(L_0/v_0)\Delta f$ and/or $\Delta\varphi = b\cdot 2\pi(L_0/v_0)\Delta f$. So that, for a given gas concentration n, the absolute value ($\Delta\varphi$) is varied proportionally to the coefficients a and b. In the same way, for a given $(\Delta\varphi)_{\mathrm{thr}}$, relevant threshold gas concentration n_{thr} can respectively be decreased by increasing L and f.

3. Experimental procedure

The novel tool was exposed to test gas concentrations of 1% of H_2, N_2O and CO in N_2 and humid air adsorbing upon Pd, Pd:Ni and polyvinil alcohol films, which physical and chemical pattern has been well explored by other analytical methods [6, 7]. The films were deposited on quartz and lithium niobate substrates by traditional technique described in [4]. There the methodics of measuring of acoustic responses $\Delta v/v_0$ and $\Delta\varphi/\varphi_0$ ($\Delta v/v_0 = -\Delta\varphi/\varphi_0$) is also presented. For Pd and Pd:Ni films tempetrature and electric changes can be neglected ($\Delta\sigma = 0$ and $\Delta T = 0$) [6],

Table 1

Properties of the tool implemented on ST-quartz substrate

Channel	Prop. angle off x-axis Θ	Phase velocity V_o (m/s)	Elecromech. coupling K^2 (%)	Beam steering Ψ	Norm. diffr. angle Φ/Φ_{iso}
A	−50°	3313	0.081	9.2°	1.71
B	60°	3415	0.045	8.4°	0.46
C	90°	4990	1.9	0°	—
D	0°	3156	0.116	0°	1.38

Table 2

Changing of elastic properties not-annealed (1) and annealed (2) Pd films under different gases ($h = 240$ nm, 20°C)

Adsorbate	$\Delta\rho/\rho$, %		$\Delta C_{11}/C_{11}$, %		$\Delta C_{44}/C_{44}$, %	
	1	2	1	2	1	2
1% H_2 + N_2	0.166	0.159	6.315	5.093	−3.507	−3.045
1% CO + N_2	0.031	0.118	−0.122	−1.592	−0.172	−1.115
1% N_2O + N_2	0.004	− 0.011	−0.184	−0.563	0.099	0.137
1% H_2O + N_2	2.688	1.494	4.675	9.835	−15.905	−13.762

so 3 film parametes were determined: relative changes of density $\Delta\rho/\rho$ and of two elastic moduli $\Delta C_{11}/C_{11}$, $\Delta C_{44}/C_{44}$. In this case the integral structure contained 3 probe channels with ST-cut quartz as a substrate. For PVA film whose conductivity σ and temperature T could be changed during adsorbtion an integral structure with 5 probe channels with a $LiNbO_3$ 128° Y-cut was exploited. Main acoustic characteristics of the ST-cut quartz based structure are presented in Table 1 as an example.

Conclusions

The novel tool provides nondestructive estimation of the steady-state and kinetic properties of thin film materials subjected by a gas phase adsorption. It allows separation of the temporal changes in the film properties produced by surface and bulk stages of an adsorption process. Six measurable parameters (N, $\Delta\rho/\rho$, $\Delta C_{11}/C_{11}$, $\Delta C_{44}/C_{44}$, $\Delta\sigma/\sigma$, ΔT) can be analysed either one by one, or in any combination and all together. At a given threshold value of the SAW response, relevant threshold values of the measurants can be reduced by increasing the length of a test film and/or operation frequency.

The tool is not applicable for liquids, because Rayleigh mode suffers high attenuation at a solid/liquid interface. Also, it is not applicable for the films deposited onto isotropic substrates, as the elastic anisotropy and piezoelectricity of the solids is inherently necessary for the operation of the tool.

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