

Acoustoelectric gas sensor with cassiterite film

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The application of surface acoustic wave (SAW) devices has recently been extended from signal processing to various sensor compatibilities. Most SAW chemical sensors rely on variations of the SAW phase velocity with the adsorption and desorption of gas on chemical interfaces. These interfaces are films on which SAWs propagate and which adsorb gas molecules [1,2]. Usually, the films are different organic polymers [2], or porous ceramics [1]. The other types of gas sensors are semiconductor-type gas sensors in which the change of resistance is measured.

The purpose of this paper is to present the surface acoustic wave gas sensor with semiconductor tin oxide film. The sensing activity is based on the SAW acoustoelectric interaction in semiconductor and the change of acoustoresistivity and longitudinal acoustoelectric current measurements.

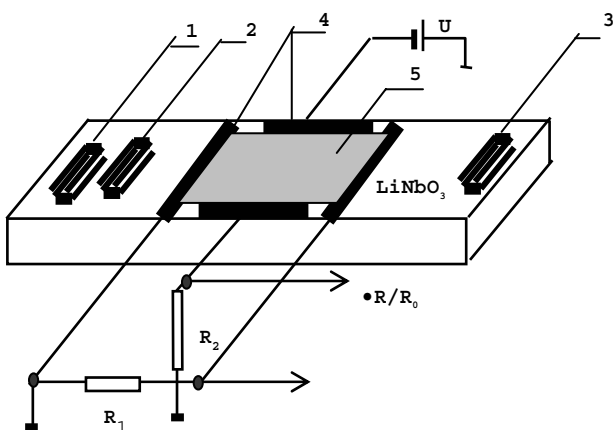


Fig.1. Schematic configuration: 1,2,3- SAW interdigital transducers, 4-metal electrodes, 5- polycrystalline cassiterite

The main element of the sensor is the cassiterite (tin oxide) film / lithium niobate layered structure (Fig. 1). The structure is placed in a chamber, which can be filled with various gases or vented out. As a rule, semiconductor-type gas sensors have been fabricated mainly by sintering tin oxide powder [3,4]. In our case the tin oxide film on the surface of lithium niobate was formed by acoustochemical oxidation of metal tin film in the oxygen atmosphere using our created method [5]. Using such method, it is easy to control the properties of the film. Polycrystalline tin oxide film made by this method distinguishes in acoustoelectric interaction. An enormous acoustoresistive effect is observed in it too and the film sensitively reacts to exterior influence including an ambient gas.

Cassiterite is n-type semiconductor. The conduction electrons of tin oxide play a major role in gas sensing, since the concentration of conduction electrons changes as the surface of polycrystalline tin oxide is exposed to

the gas to be detected. Some gases are electron-accepting particles (For example O₂) and are decreasing the conductivity and some – electron-donating (For example H₂) and increasing the conductivity. For the polycrystalline film, the neck size connecting adjacent grains is also an important factor in determining the gas sensitivity. The neck size not simply can be controlled; since it can be changed by various experimental conditions such as the parameters of continuous mode SAW, the oxidation temperature and acoustoelectrochemical transition time. Polycrystalline thin films also seem suitable for gas sensing, because they have a large surface – to – volume ratio and good possibilities of fast adsorption-desorption processes on their surfaces. Furthermore, the use of SAW in continuous mode increases the adsorption ability of the surface [5,6]. SAW propagating in the structure changes the parameters of surface states and creates new states [7] and it can change the adsorption equilibrium between solid and gas phase. SAW during wave period induces the additional charge δQ [8]

$$\delta Q = \frac{\epsilon \epsilon L_D |E_s|^2}{24\pi T}$$

so the relative surface adsorption ability will be:

$$\frac{\Delta N}{N} = (1 - \eta_0)(\pm \kappa |E_s|^2 - 1 + \sqrt{\kappa^2 |E_s|^2 + 1}),$$

where $\kappa = \frac{\epsilon \epsilon L_D}{48\pi T S N_0 (1 - \eta_0)}$; e is the electronic charge, ϵ is

the dielectric constant of semiconductor, $|E_s|^2$ is the SAW electric field on the semiconductor surface, T is the temperature in energy units, S is the area of the film surface, $N = N_0(T, P)$ is the equilibrium concentration of adsorbed particles on the surface, L_D is the Debye screening length. The sign “+” corresponds donor and “-” corresponds acceptor particles adsorption.

Acoustostimulated adsorption and chemisorption causes the change of conductivity in the necks connecting adjacent grains:

$$\sigma = \frac{eMn}{NT} \exp\left(-\frac{e\Delta\phi}{T}\right),$$

where N is the concentration of barrier in the 1cm length of film, M is the coefficient which depends on barrier form, n is the concentration of charge carriers close to barrier and $e\Delta\phi$ is the height of the barrier.

The change of conductivity, caused by adsorption, completely defines the change of the barrier height. An optical absorption index γ linearly depends on free carriers concentration in the conduction band and the absorption of gas changes this concentration and the index γ :

$$\gamma = \frac{e^3 \lambda^2 n}{\pi c^2 n_e \mu_n m_n^*},$$

where n_e is the refractive index, c is the light velocity, λ is the wavelength, m_n^* is the effective electron mass, μ_n is the electron mobility.

The change of barrier height causes the change of conductivity, consequently the absorption index of SAW, the acoustoconductivity and the longitudinal acoustoelectric current.

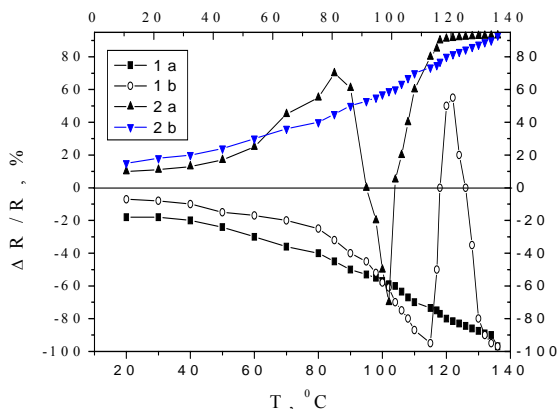


Fig. 2. Acoustoresistivity as a function of operating temperature in oxygen atmosphere (curves 1a, 1b) and in air with hydrogen (hydrogen concentration 1000ppm, curves 2a, 2b)

The change of the acoustoresistivity versus temperature when the acoustostimulated adsorption of oxygen (electron-accepting particles, fig.2, curves 1a, 1b) and the acoustostimulated adsorption of hydrogen (electron-donating particles, curves 2a, 2b) take place on the surface of cassiterite film. (Curve (a) with increase of temperature and (b) with the decrease). If the adsorbed molecules are acceptors on the polycrystalline cassiterite surface, we can observe a little negative acoustoresistivity (about -7%, curve 1a) and with the increase of temperature the negative acoustoresistivity increases. In the temperature interval from 20°C to 115°C the negative acoustoresistivity $\frac{\Delta R}{R_0}$ increases to -

93% then falls down and as the temperature reaches 117°C acoustoresistivity disappears, later changes to the positive and at the 121°C temperature reaches the maximum value +57%. The further acoustostimulation of the adsorption process changes the sign of acoustoresistivity to “-” and the effect increases to -96% and saturates. When the SAW in continuous mode is turned off (the temperature decreases) and the test gas vented out of the chamber the monotone decrease of acoustoresistivity until -18% is observed within 7-8 minutes and it needs an hour to reach an initial value. The increase of negative acoustoresistivity in the temperature interval from 20°C to 115°C can be explained by acoustic cleaning of the semiconductor film surface, i.e. acoustostimulated desorption of oxygen (curve 1b). The positive peak in the temperature range

115-127°C is caused by acoustostimulated adsorption on the cassiterite film surface. Usually, with out SAW the adsorption maximum of oxygen is at 500°C temperature but continuous mode SAW change the surface potential and, consequently, increase the adsorption ability of the surface and decrease the adsorption temperature.

When the adsorbed molecules are donors on the polycrystalline cassiterite surface (fig.2, curve 2) we can observe a little positive acoustoresistivity (about 10%, curve 2a) and with increase of temperature it increases as in the first case. The negative peak of acoustoresistivity in the temperature range 90-103°C is caused by acoustostimulated adsorption of hydrogen and maybe oxygen-hydrogen addition reaction. Usually, hydrogen molecules have a sticking coefficient of one and dissociate completely at 300°C on SnO₂ films [9] and the maximum sensitivity is in the temperature range 290-310°C. Continuous mode SAW change the adsorption ability and the catalytic activity [10] at the semiconductor surface and it seems that decrease the temperature of sensitivity. When the continuous mode SAW is turned off and the test gas complete vented out of the chamber the monotone decrease of acoustoresistivity to 15% is observed within 5-7 minutes as in the first case.

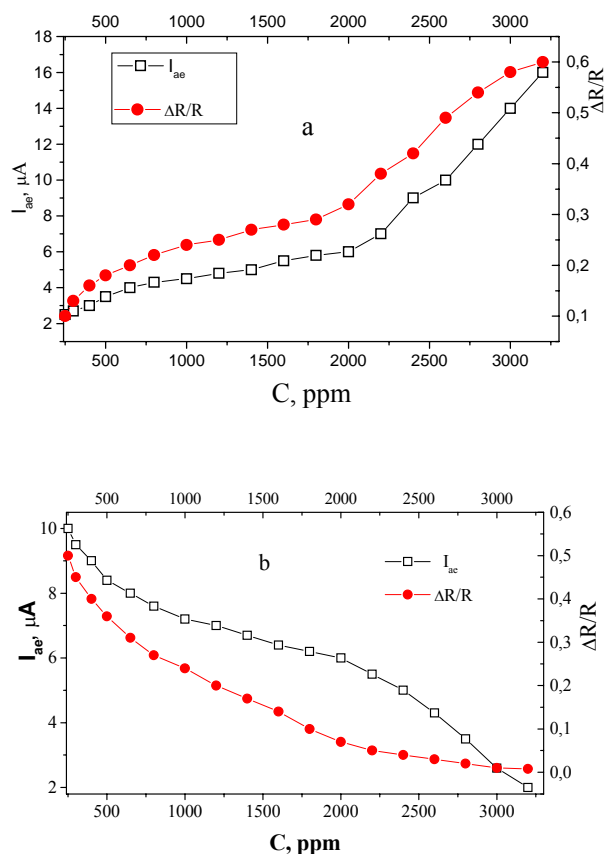


Fig. 3. The longitudinal acoustoelectric current I_{ae} and the peak of the gas sensitivity $\Delta R/R$ versus the oxygen concentration (a) and the hydrogen concentration (b) in chamber

The sensor was tested with some gases: hydrogen, oxygen, carbon monoxide and carbon dioxide and hydrogen peroxide, water, ethyl alcohol vapors. Fig. 3 shows the longitudinal acoustoelectric current I_{ae} (curve 1) and the peak of the gas sensitivity $\Delta R/R_0$ (curve 2) versus (a) the hydrogen

concentration and (b) the oxygen concentration in the chamber. The current form change and sensitivity are similar and the sensitivity is good enough even for a small concentration of hydrogen.

In conclusion, from the sign of acoustoresistivity we can determine the type of adsorbed gas (donor or acceptor), the temperature of sensitivity peak indicates what the gas it is and the sensitivity is good enough for the hydrogen concentration less than 500 ppm.

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Akustoelektrinis dujų jutiklis su kasiterito plėvele

Reziumė

Šiame darbe aprašytas dujų jutiklis, kurio jautrioji medžiaga yra polikristalinė kasiterito plėvelė, o jo veikimo principas – paviršinių akustinių bangų sąveika su krūvininkais, esančiais kasiterito sluoksnyje. Polikristalinė kasiterito plėvelė suformuota ličio niobato paviršiuje, akustocheminiu būdu oksiduojant metalinę alavo plėvelę deguonies atmosferoje. Taip pagaminta kasiterito plėvelė pasižymi akustoelektrine sąveika, joje aiškiai reiškiasi akustorezistinis efektas, ir ji jautriai reaguoja į išorinius poveikius, įskaitant ir ją supančias dujas. Jutiklis buvo išbandytas keliose dujinėse aplinkose. Akustorezistiniais matavimais galima nustatyti, kokios tai dujos, o akustoelektrinės srovės matavimais jų koncentraciją.

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