The development of semiconductor Fourier spectroscopy principles for the gas analysis on the example of the volatile hydrocarbons concentrations thin-film sensors on based on rare-earth elements

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Abstract. In this work the basic principles of creation of semiconductor Fourier spectroscopy for the gas analysis are formulated, that will allow us to increase selectivity, sensitivity and stability of an operation of the gas sensors. The experimental data obtained by means of semiconductor sensors on the basis of samarium sulfide made by zol-gel technology given detecting micro impurity of propane and methane in atmospheric air are given in work.

1. Introduction
Researching of mechanisms and the principles of work of semiconductor chemical gas sensors are carried out very intensively for the last 20-30 years. Nevertheless, the question of their selectivity in various gas mixes isn’t solved unambiguously. In practice it leads to restriction of their mass application though advantages of semiconductor chemical gas sensors are obvious: it is diminutiveness of sensors, low cost of their production and also availability of technologies and materials. The present stage of development of scientific research stimulates search of the new principles of detecting of the gas impurity in this area of the gas analysis, and creation of the intellectual digital systems dictates development of new approaches to methods of detecting of gas particles. The presented research and recent publications [1-4] are also directed to the solution of a problem increasing selectivity, speed and stable work of gas sensors in practice (a problem of increasing 3 "$s$").

2. Measurements technique
The offered approach to the analysis of experimental data on conductivity of sensors based on modification of optical methods of Fourier spectroscopy for tasks of the semiconductor gas analysis allows resolving unambiguously an issue of increase in selectivity of a gas sensor. The first calibration data are obtained by a researching of electrophysical characteristics of gas sensors for the purpose of the detecting of propane and methane which are contained in atmospheric air. SmS and solid solution $Sm_{1-x}Eu_xS$ [3] are chosen as materials of a gas-sensitive layer of sensors. The essence of the presented approach consists in using analogy to optical measurements, generally in infrared area of an optical spectrum, from these measurements of conductivity of a gas-sensitive element in time, for receiving of optical analog of a spectral characteristic of a sensor when detecting micro impurity of volatile hydrocarbons. It is necessary to change the procedure of work of a gas-sensitive element for this purpose. Now the most part of measurements as, however, and calibration of chemical gas sensors, are made at the fixed working temperature of the gas sensor. The novelty of the offered approach consists in receiving temperature dependence of a signal of the detector, carrying out periodically heating and cooling of a gas-sensitive element of the sensor, both at calibration, and in the course of
measurements. At the same time it is possible to receive an optical analog of spectral density of the characteristic of the gas sensor by application to the received data of transformation of Fourier. Here the relative conductivity of the detector \( (\sigma(t)/\sigma_0) \) is an optical analog of relative intensity of the absorbed radiation \( (I(t)/I_0) \), and the frequency characteristic of the sensor expressed in terms of \( kT(t) \) (in our case in \( eV \) electron-volt) is an optical analog of the frequency characteristic of the absorbed radiation that was expressed in terms of quantum energy \( h\nu \) (for example, for near IR-area an optical spectrum). It should be noted that data of preliminary calibration of a chemical sensor on binary gas mixes allow to allocate an amplitude-frequency range of concentration impact on conductivity of the semiconductor of this or that component of the measured gas mix from a useful signal of the detector (in our case of propane or methane). Selection is reached at the expense of different optimum working temperatures of detecting of molecules of propane and methane at allocation by means of Fourier's transformation of amplitude-frequency characteristics of a gas sensor. It turned out that the received frequency characteristic of the sensor is fixed for various relatives among themselves of concentrations of methane and propane, differing in the numerical value. It is confirmed experimentally by presence of optimum temperatures of detecting of these gases (see fig. 4 and fig. 5) at implementation of the procedure of calibration of sensors on testing gas mixes on the certified equipment (the gas-mixing equipment «Micro gas - FM», see fig. 1-3). The frequency characteristic received at measurements is responsible for selectivity of the detector and for stability of its work (lack of frequency shift at calibration of the sensor and at measurement). At the same time amplitude of the allocated frequency is defined by concentration influence of this or that measured component of gas mix. The process of calibration of concentration of propane in synthetic (zero) air was set by means of the certified gas-mixing equipment «Micro gas - FM» (fig. 1). TO-8 housing with the gas sensor was placed in a tight flor-plastical container, connected to gas-mixing equipment by means of the bringing and taking away gas highways (fig. 2). The useful signal from the sensor was registered by means of standard 20 digit amplitude digitizer (AD) operated from the personal computer (fig. 3). Heating of a gas-sensitive layer was carried out by means of the independent platinum closed heater in the range of temperatures from 300K to 773K with registration of the current temperature of a surface of the gas detector. It should be noted that optimum temperatures of a surface of sensors when detecting molecules of methane and propane differ essentially (in limits 40-50 °C). It allows constructing the system of selective detecting of the specified components of gas mix in rather gas environments, difficult on structure. At the same time the frequency characteristic of sensors corresponds to various working temperatures of detecting of the specified components of gas mix and is strictly fixed for each of them.

Figure 1. The gas-mixing equipment «Micro gas - FM».
3. Results of measurements
The preliminary estimates of gas sensitivity of SmS sensors were used for detecting molecules of propane and methane. It shows that the sensitivity to propane is about 3 times higher in comparison with methane molecules. Further the search of new gas-sensitive materials on the basis of rare-earth elements was crowned with success. As a result for composite material of structure $Sm_{1-x}Eu_xS$ (see work [3]) it was succeeded not only to increase sensitivity of the detector to methane, but also it is essential to lower the optimum temperature of its detecting. It approximately on 200°C is lower than temperature of ignition of methane in atmospheric air that raises an explosion protection class on temperature of ignition of gas mix according to the international classification [3, 5].
Figure 4. Spectral response of semiconductor sensor SmS at various concentrations of methane in ambient air: about 0.265 vol.% , 0.200 vol.% , 0.151 vol.% , 0.101 vol.%.

Figure 5. Spectral response of semiconductor sensor SmS at various concentrations of propane in ambient air: about 0.705 vol.% , 0.512 vol.% , 0.304.% , 0.103 vol.%.
4. Conclusion

It should be noted that the obtained experimental data on the detection of methane and propane molecules in the atmospheric air look promising (see fig. 4 and fig. 5). It made possible to formulate the basic principles of semiconductor Fourier spectroscopy in relation of detection of molecules (corpuscles) with using solid-state chemical gas sensors. This approach is an analogue of optical measurements in the absorption of radiation by a substance. The application of the developed technology consists in the construction in the future of high-selective high-speed intelligent digital detection systems for various purposes.

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