Calculation of self-consistent electrophysical parameters of semiconductor gas sensors based on samarium sulfide for semiconductor Fourier spectroscopy of volatile hydrocarbons contained in atmospheric air

S A Kazakov¹, M A Grevtsev¹, G D Khavrov¹,², S M Solov’ev¹, N V Sharenkova¹, M M Kazanin¹ and V V Kaminski²

¹Laboratory of physics of rare-earth semiconductors, Ioffe Institute, Saint Petersburg 194021, Russia
²(SPbPU) Peter the Great St. Petersburg Polytechnic University, Saint Petersburg 195251, Russia

Abstract. The developed method of semiconductor gas Fourier spectroscopy is based on the relationship of the obtained calibration characteristics of the concentration sensors for volatile hydrocarbons contained in atmospheric air (in our case, it is methane and propane), with electrophysical parameters of the gas sensitive layers. The study used gas sensors based on samarium sulfide with reproducible and stable calibration characteristics. The working layers of hydrocarbon concentration sensors were obtained by two different methods: the explosive spraying method and the sol-gel coating technology. In this paper we present a system of equations that includes the main electrophysical characteristics of a gas-sensitive film which is solved by numerical methods. These equations reflect a unique relationship between the Debye screening length \(L_d\), film thickness \(d\), Fermi level \(E_F\), concentration of impurity levels \(N_d\), dielectric constant of the medium \(\varepsilon\), crystal lattice constant \(a\), and mobility of the main charge carriers \(\mu\) with the observed data on the change in the conductivity of thin films of samarium sulfide in the processes of adsorption of methane and propane molecules on their surface. In the present work, we obtained the first calculated data of such parameters for the current prototype images of gas sensors of methane and propane.

1. Introduction

As shown in our previous studies [1,2], gas sensors based on samarium sulfide have stable metrological and electrophysical characteristics. The sensors were calibrated in different composition of calibration gas mixtures of methane (or propane) in atmospheric air. The sensor topology, the technology of applying gas-sensitive layers by the sol-gel method (from a polymer matrix) and the explosive spraying method [3] were developed and the optimal temperature and time conditions for the formation and annealing of gas-sensitive layers of sensors were selected. It should be noted that in sintered films of both metal oxides and chalcogenides bridges are formed between crystallites during the annealing of the semiconductor material and the formation of conductive channels (“conductive networks”) throughout the entire volume of a thin semiconductor film. In this case the value of potential barriers arising during the current transfer in such a film turns out to be less than the thermal
energy $kT$, which ensures unhindered movement of the main charge carriers in the semiconductor when measuring its direct current conductivity. A model of barrier conductivity of polycrystalline samarium sulfide was considered in [4]; this model was described in more detail in [5] for sensor semiconductor materials.

2. Calibration and processing of experimental data
We calculated the Debye charge screening length, and we also calculated the concentration and mobility of conduction electrons for a number of samples of thin SmS films used as working material for concentration sensors in the framework of the barrier conductivity model [4]. For this purpose the MathCAD program was used, in which a system of equations was compiled and solved that relates electrophysical parameters of samarium semiconductor sulfide and the experimentally obtained values of the temperature change in the electrical conductivity of thin sintered SmS films during the detection of methane (or propane) molecules contained in atmospheric air. We chose the solutions of the Poisson equation given in [5] for the case of adsorption of donor particles on the surface of an $n$-type semiconductor polycrystalline under stationary conditions as the initial equations of the system. This corresponds to our case where methane (or propane [1]) in the atmospheric air is detected by sensors based on samarium sulfide - an $n$-type semiconductor. The calculated value of the SmS crystal lattice constant is in good agreement with the crystal lattice parameter obtained by us from the X-ray spectra of the samples (figure 1); the calculated value of the dielectric constant of the medium also agrees with the literature data for semiconductor samarium sulfide [3].

3. Measurements and calculations
Below are the equations of system (1), which were used in the calculations when constructing the gas analysis system using Fourier transforms. The equations are derived in the framework of the model of barrier conductivity, see in more detail in [5]. A feature of the temperature regime of the semiconductor gas-sensitive element was the recording of data during the scanning of the temperature of the working layer of the sensor. When calculating the electrophysical parameters of methane and propane concentration sensors, not only expressions were used for the stationary values of the conductivity parameters of the sensors, but also for their derivatives with respect to temperature. The calculated data for the SmS constant lattice, $a = 5.971 \, \text{Å}$, are in good agreement with the data of the X-ray spectra of the samples, $a = 5.974 \, \text{Å}$ (figure 1). The value of the dielectric constant of the medium for samarium sulfide ($\varepsilon \sim 18–20$ from [3] and our calculation result $\varepsilon = 19.362$), which is also consistent with published data, was obtained.

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\begin{align*}
\sigma_0 - \left( \frac{1}{d} \right) q \mu \sqrt{2 \cdot N_d} \left( \varepsilon_\text{e} \varepsilon_\infty k \frac{T}{q^2 N_d} \right)^{0.5} \left( \sqrt{\varepsilon_\infty + \xi_0 - 1} \right) & = 0, \\
\left( \sigma_0 - \sigma \right) + q \mu \sqrt{2 \cdot N_d} \left( \varepsilon_\text{e} \varepsilon_\infty k \frac{T}{q^2 N_d} \right)^{0.5} \left( \sqrt{\varepsilon_\infty - \xi + \xi - 1} \right) & = 0, \\
\frac{\left( \sigma_0 - \sigma \right)}{\sigma_0} + d \sqrt{N_d} \left( \varepsilon_\text{e} \varepsilon_\infty k \frac{T}{q^2 N_d} \right)^{0.5} \left( \sqrt{\varepsilon_\infty - \xi + \xi - 1} \right) & = 0, \\
A - \left( \frac{\varepsilon_\text{e} \varepsilon_\infty k \frac{T}{q^2 N_d}}{\left| \xi \right| + \xi_0 \cdot 1.69} \right)^{0.5} & = 0 \quad (1)
\end{align*}
\]
where $\sigma$ and $\sigma_0$ – conductivity in the medium and vacuum respectively, $\mu$ – the mobility of charge carriers, $N_d$ – the concentration of donor centers in the surface layer, $\varepsilon$ and $\varepsilon_0$ – permittivity of the medium and vacuum respectively, $k$ – Boltzmann constant, $T$ – the absolute temperature, $q$ – electron charge, $A$ – lattice constant of SmS, $d$ – the film thickness of SmS, $\xi_0$ and $\xi$ – the dimensionless value of the potential barrier before and after adsorption respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{smsspectrum.png}
\caption{Standard spectrum of polycrystalline SmS powder used in the manufacture of gas-sensitive sensor layers.}
\end{figure}

4. Results and discussion

The further construction of the previously proposed [1,2] new method of gas analysis, semiconductor Fourier spectroscopy, is based primarily on the analogy with optical measurements and at this stage is associated with the search for the calibration function of one parameter (concentration of the measured component of the gas mixture) for each gas-sensitive item. In particular, the processing of experimental data for methane from [1] in dimensionless terms of the change in the conductivity of a gas-sensitive element (all curves for different methane concentrations were normalized to the obtained maximum value of the change in the conductivity of the sensor at a given methane concentration) is shown in figure 2. Figure 3 shows one of the temperature sections ($T = 492^\circ C$) of the dependences shown in figure 2. Obviously, there is a linear relationship between the dimensionless electrical conductivity of the gas-sensitive element in the presented coordinates (called the adsorption value in [3]) and the methane concentration in atmospheric air. This is fully consistent with the mechanisms and ideas about the adsorption of active particles, considered in detail in [5].
Figure 2. Normalization of data on the temperature dependence of the conductivity change for different methane concentration:
1 – 0.265 vol.%; 2 - 0.200 vol.% ; 3 - 0.151 vol.%; 4 - 0.101 vol.%. 

Figure 3. A linear relationship between the concentration of methane contained in atmospheric air and the adsorption value in dimensionless terms of a change in the conductivity of a gas sensor at a given cross section for a detector temperature of 492°C.
5. Summary
In the course of the work, the semiconductor sensors of methane and propane based on SmS were calibrated. The obtained data on the temperature dependence of electrical conductivity were used to calculate the electrophysical parameters of the sensors according to equations compiled taking into account ideas about the mechanisms of adsorption of active particles. A good agreement between the calculation results and the published data indicates the promising new method of gas analysis, namely, semiconductor Fourier spectroscopy.

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