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Fluctuation-enhanced gas sensing

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Abstract

The sensitivity of gas sensors was earlier measured by classical method-comparison the resistance of sensors in gas media and air. Here we reported results of the study of low-frequency noise characteristics of sensors. We compare data for different Figaro TGS sensors as well as our sol-gel H_2 tin dioxide and porous silicon sensors. The study was performed in dry air and in a mix of dry air with carbon monoxide, hydrogen and alcohol of different concentrations. Higher sensitivity of spectral dependence of noise (SDN) to gas concentration in comparison with classical method of the measurements of gas sensing by a change in the Ohmic resistance part of current-voltage characteristics of samples allows using such SND powerful method for determination of gas concentration in the air or environment.

Keywords: Sensor; hydrogen; metaloxide; porous silicon; sensitivity; noise

1. Low-frequency noise measurement set-up

It is known that porous silicon (PS) is rather promising material for creating on its basis different types of gas, humidity, and chemical sensors. Note also that metaloxide semiconductor sensors are now widely applied for characterization of gas media. Results of previous investigations of authors in the field of metaloxide and porous silicon gas sensors can be found in [1-3]. Here we analyzed current situation with gas sensitivity of different sensors and shown that measurements of SDN allowed investigate possibilities to increase the sensitivity of sensors.

The low-frequency noise measurement set-up comprised a specially designed bias supply employing an ultra-low-noise operational amplifier (REF102 and OPA37 from Texas Instruments and Burr Brown) having ultra low noise (3,8 nV/Hz$^{1/2}$) and high input resistance (2 GΩ), a gas chamber, for the samples, made of thermal glass, an ultra-low-noise/high-resistance access port and wide-band preamplifier based on an operational amplifier (OP27 from Precision Monolithic Inc., USA), a Fast Fourier Transform (FFT) analyzer (the adapter to the computer HANDYSCOPE (2) from TiePie Engineering), and a computer. The frequency range of the measuring set-up was from 1 Hz to 10 kHz. Details of the input electric circuit and preamplifier are given in [3]. The input circuit and preamplifier had a self-contained power supply based on accumulators. The set-up was encapsulated in a Permalloy shield. The hermetic chamber was used for determination of the influence of gaseous media; it provided adequate shielding of the samples against extraneous influences as well as a controllable interaction between the analyzed gas and the sample. To remove adsorbed residuals of a previous gas before a new measurement, the gas chamber was purged with clean air. Room temperature measurements were performed in the current generator mode.

2. Noise spectra

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Figure 1 shows the spectral dependence $S_U(f)$ for the 50%-porosity sample exposed to dry air (a), dry air + alcohol vapour (b), and dry air + 1.7 % CO, and Fig. 2 shows data normalized according to $S_U(f)/U^2$ for exposure to dry air (a), dry air + 0.4 % CO (b), and dry air + 1.7 % CO (c). Figure 5 shows spectral dependence $S_U(f)/U^2$ for the73%-porosity sample exposed to dry air (a), dry air + 0.4% CO (b), and dry air + 2.0 % CO. Sharp drop, by several orders of magnitude, of $S_U(f)/U^2$ with the change in concentration of carbon monoxide in air allows suggesting a possibility to estimate precisely the gas content in air, i. e., we can offer a new method of estimation of the concentration of gases in environment - the noise spectroscopy.

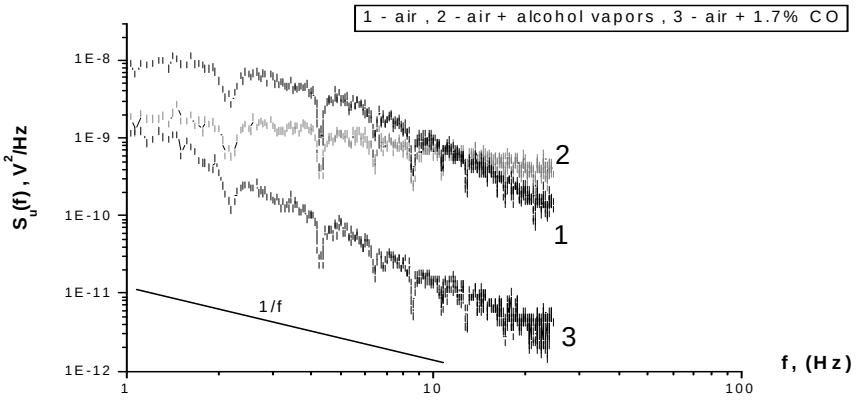

Fig. 1 Noise spectra for samples with the 50%-porosity PS layers exposed to the indicated gases at a current of 0.1 mA. The straight line refers to “classical” 1/*f* noise. Samples were placed in air (1), air + ethyl alcohol vapour (2), and air + 1.7 % CO (3).

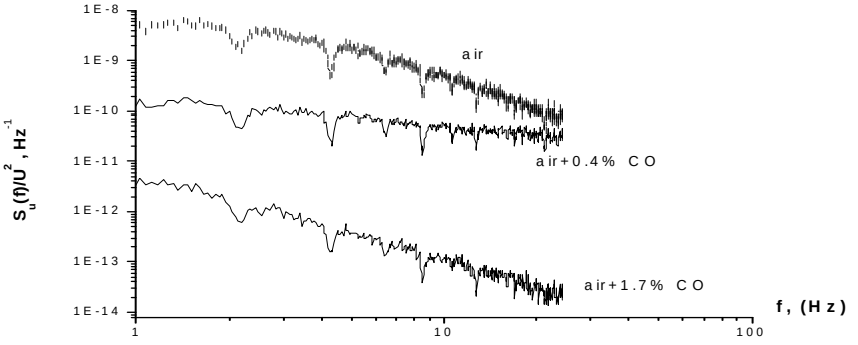

Fig. 2 Normalized noise spectra for samples with the 50%-porosity PS layers exposed to the CO gas at a current of 0.1 mA. Samples were placed in air, air + 0.4 % CO, and air + 1.7 % CO.

3. Sensitivity of gas sensors

It is seen from our measurements that value of the spectral density of the noise voltage is remarkable changed when samples were placed in different gas media and air. Therefore we decided to compare the gas sensitivity of sensors. Below we compare data for Figaro TGS 2443, 2511, 3870, and 821 sensors as well as our sol-gel H_2 and porous silicon sensors. The sensitivity of above-mentioned sensors was earlier measure by classical method-comparison the resistance of sensors in gas media and air. Here we reported results of the study of low-frequency noise characteristics of the metal – porous silicon – silicon single crystal – metal structure with different porosity of porous silicon. The study was performed in dry air and in a mix of dry air with carbon monoxide, hydrogen and alcohol of different concentrations. Calculation of the sensitivity of the investigated porous structures was carried out using results obtained by us during experiment for changes in target gas media and air of resistance $G_{dc} = R_{sa} / R_{tg}$ (in the Ohmic part of CVC) and of the spectral density of noise (SND) $G_{NOISE} = \frac{S(f)_{SA} / U_{sa}^2}{S(f)_{tg} / U_{tg}^2}$ due to voltage fluctuations. Here R_i is the sensor resistance, $S(f)_{noise}$ is the spectral density of

the noise of the sensor. We introduce results of measurements of the sensitivity of the Figaro sensors and our samples made of SnO_2 (Fig. 3) and porous silicon (Fig. 4).

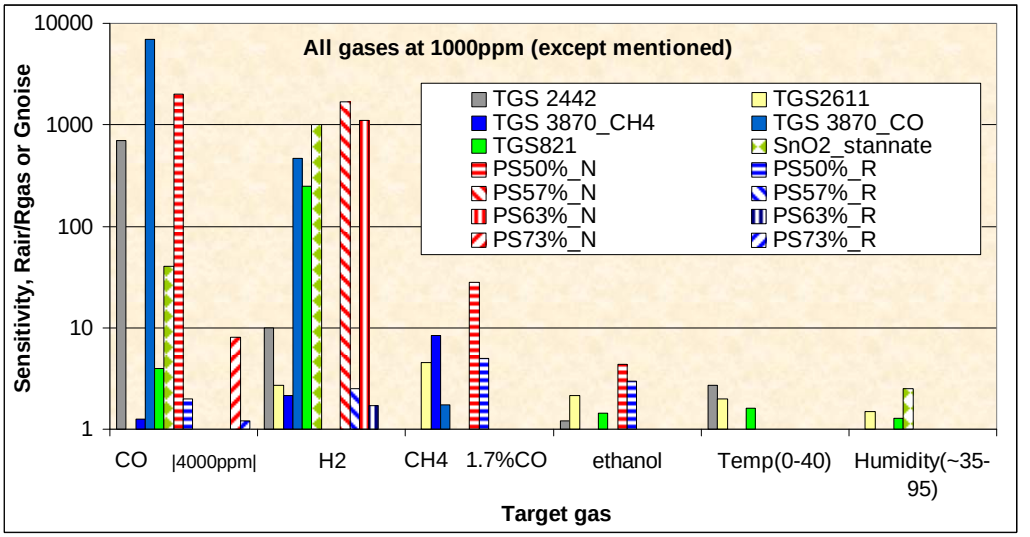

Fig. 3 Sensitivity of different sensors to gases.
We compare data for Figaro sensors TGS 2442, 2611, 3870, and 821 as well as our sol-gel H_2 and porous silicon sensors.

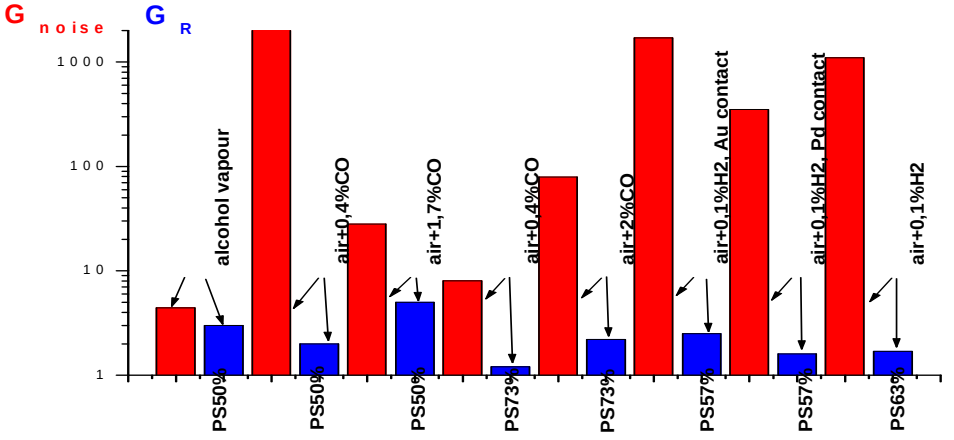

Fig. 4: Comparison of the sensitivity of different sensors obtained by measurements by classical and noise methods.

We see from Fig. 4 that the dc resistance sensitivity G_{dc}, which is measured by classical method of measurement, gives lesser values in comparison with the SND sensitivity. It allows carrying out fluctuation-enhanced measuring of the sensitivity of sensors (see also [4]).

Below we will discuss changes in different gas media of parameter α_H in empirical Hooge's formula

$$\alpha_H = S_U N f^{\gamma} / U^{\delta} .$$

Here S_U is the spectral density of the noise voltage, N is the number of free carriers in a sample, α_H is the dimensionless Hooge parameter, U is the voltage applied to the studied structure, γ is the frequency index which usually is approximately equal to unity, and $\delta \approx 2$. The values of S_U, U^{δ}, and γ were determined experimentally from the obtained by us spectra using data of the thickness of PS layer and the resistance of the sample.

In particular, for 73%-porosity samples introduced in carbon oxide and air, the parameter γ in the frequency dependence of spectral density of the voltage noise grows since γ (air) = 0.5; γ (air + 0.4 % CO) = 1 to γ (air + 2 % CO) = 1.3. So, α_H increases with increasing concentration of CO in air. We explain this as follows. With the increase in the concentration of gas molecules the number of molecules (ions) adsorbed on a surface increases and therefore the density of traps located at the PS/SCS interface increases. The heterobarrier height at gas adsorption decreases with increasing the adsorbate concentration. Therefore, the effect of a potential barrier, in comparison with increasing concentration of surface traps, becomes less important.

Comparison of α_H values shows that α_H for crystal materials is several orders of magnitude higher than for non-crystalline structures. As was noted in [5], in the disordered structures including PS, α_H can take values from 1 up to 10^4. One of the reasons of this is the low mobility of charge carriers in disordered materials to which belongs also porous silicon. The non-uniformity of the current density in the sample may also cause a large value of α_H [6]. In our case, this can probably be caused by nano-crystalline structure of the PS layer. The non-uniform density of the current in the nano-crystallite arises for several reasons: a) coral-like systems of variable cross-section silicon strings, b) the presence of the depletion region around each pore, and c) inhomogeneity of the density and mobility of free charge carriers.

4. Conclusion

The spectral dependence of noise $S_U(f)$ grows with the increase in porosity of silicon and in the concentration of polar CO molecules in air. Correspondingly, the noise parameter α_H varies also. Noise spectra of the investigated structures in various gas media in the low frequency range were different quantitatively and displayed different characteristics.

Higher sensitivity of spectral dependence of noise (SDN) to some gas concentration in comparison with classical method of the measure of gas sensing by a change in the Ohmic resistance of samples allows using such SND powerful method for determination of gas concentration in the air or environment.

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