Photovoltaic intelligent gas sensors for the detection of acetone concentration over a wide range of measurement for biomedical applications and tasks of public safety

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Abstract. This report presents experimental studies of electrical changes in photovoltaic sensitive elements based on a Por-Si: c-Si heterojunction during the adsorption of acetone molecules in a mixture of pure nitrogen. The porous silicon layer was formed by electrochemical etching on a p-type silicon wafer. The obtained samples were subjected to additional plasma-chemical treatment using hydrogen and fluoride ions after fabrication. Such surface treatment has a stabilizing effect on the electrical properties of the material and increases their adsorption sensitivity to polar molecules. The developed technology allows you to automatically change the sensitivity of photovoltaic sensors during the experiment, depending on the concentration of acetone. These photovoltaic sensors are able to expand the range of measured concentrations from 1 ppm to 10 vol%.

1. Introduction

Acetone is widely used in the chemical industry, cosmetics and biomedical researches. The most dangerous property of acetone is its high flammability. At temperatures above the flash point of acetone of -20 ºC (-4 ºF), air mixtures of 2.5 to 12.8 vol% acetone can explode or cause a flash. Static discharge can also ignite acetone fumes [1]. It is important to measure the acetone concentration over a wide range of measurements for the tasks of Occupations Safety and Health in industry [2]. Measuring the concentration of acetone in exhaled air by humans is important for the successful treatment of diabetes [3]. Acetone concentrations range from 300 to 900 ppb in healthy people and to more than 1,800 ppb in people with diabetes [4]. The acetone concentration reaches 1250 ppm in people with ketoacidosis [5]. Thus, measuring in wide range of concentrations of acetone is important for biomedical research too.

The creation of measuring systems for a wide range of gas concentration measurements is a complex technical task due to the limited range of sensor measurements. Currently, the attention of most researchers focused on nanotechnology semiconductor sensors [see, for example, 6-10]. The main advantages of such sensors are the possibility of their mass replication at their low cost and small size.

Most sensors for acetone operate at work temperatures above 175 ºC [11]. Acetone gas sensors based on Al2O3-doped ZnO has an optical excitation-enhanced sensing properties at a temperature of 64 ºC [12]. The nanorods bundles ZnO microspheres, consisting of closely packed nanorods with
widens of about 50 nm, have good response and recovery times (1s and 3s when the sensor was exposed to 100 ppm acetone at an temperature of 320°C) [13].

In recent publications [14-17], new methods for measuring acetone concentrations at room temperature are described, which greatly simplifies the design of the sensor. However, these modern gas sensors have a limited dynamic measuring range. For example, an IDE device with a nanogap has a dynamic range from 1000 to 10 ppm for acetone at room temperature. [18].

Previously, we published the results of research of photovoltaic sensors based on Por-Si-C-Si heterojunctions to detect polar molecules ammonia with dipole moment of 1.43 D in a wide range of concentrations [19]. The obtained samples underwent additional plasma-chemical treatment with fluorine and hydrogen ions after fabrication. Measurements by the method of secondary ion mass spectrometry showed that the concentration of fluoride ions on the surface of the material reaches 3–4 at%. Fluorine and hydrogen ions have a stabilizing effect on the electrical properties of the material surface. Fluorine is more active than oxygen, so contact with the air atmosphere is not accompanied by changes in the composition of the surface of the porous silicon. This operation eliminates the “aging” of porous silicon when interacting with air. Doping with hydrogen ions of the surface region of the material leads to saturation of dangling bonds of silicon and plays a significant positive role in luminescence in the visible region of porous silicon [20].

Acetone molecules have a more significant dipole moment of 2.93 D [21] compared to ammonia molecules. This report presents the results of using photovoltaic sensors to measure the concentration of acetone in an inert atmosphere of pure nitrogen at room temperature measurements. The technology of making samples and special electrical contacts to them and the methodology of the experiment are described in detail in the articles [19]. We used only acetone mixed with ultrapure nitrogen to supply the gas-dynamic generator to create an acetone gas mixture in the range from 1 ppm to 10 vol%.

This new gas detection method opens up a new way to create intelligent gas sensors in a wide range of measurements [22]. Such a developed method of measurement allows increase a measurement precision by automatically change the sensitivity in photovoltaic sensors during the experiment, depending on the gas concentration. Therefore, such sensors can extend the range of measured concentrations and the accuracy compared to known sensors.

2. Results and discussion
We used the light intensity of the samples from 2 to 200 lx when changing the concentration of acetone vapours in the mixture with high purity nitrogen from 1 ppm to 10 vol% (100,000 ppm) in a measuring chamber. Some experimental dependences the electromotive force on electrical contacts upon adsorption of acetone at different levels of illumination are shown in figure 1. Changes in light exposure lead to different ranges of acetone measurement (figure 1).

![Figure 1. Dependences of the EMF values on acetone concentration at different illumination levels of 2, 20 and 200 lx.](image-url)
So, the photovoltaic gas sensors can change sensitivities and ranges of measurement by changing illumination intensity (figure 1). Figure 2 shows a graph of light intensity and electromotive force, provided that maximum metrological accuracy can be achieved. These data can be the basis for the development of intellectual sensors for acetone with a wide dynamic measurement range and with the maximum possible accuracy of measurement.

Figure 2 includes a spline approximation of EMF-magnitude for sensors data from illumination levels based on the data of figure 1. We standardize parameter $L$ based on these measurements. In this case, we have the maximal analysis accuracy for different ranges of acetone concentrations.

The acetone concentration depends in our photovoltaic gas sensors on two parameters: the EMF magnitude ($U$) and the light intensity ($L$). The maximal precision can be achieved using Equation (2) by finding a two-parameter function $c(U, L)$ that describes the experimental data.

Fitting functions for the experimental data for acetone are been approximated using the following generalized two-parameter function:

$$ U(L) = -0.475 + 2.3739 \ln (L + 1.01) $$ (1)

Figure 2. Dependence of the EMF magnitudes on different illumination levels with maximum sensitivity to acetone.

Previously for ammonia photovoltaic sensors, we developed software modules for control of the light intensity for maximum accuracy of gas measurements using the NI LabVIEW program and National Instruments equipment [22]. In our case, these modules need to be reprogrammed taking into account the data of formulas (1) and (2) for acetone sensors, which allow us to directly calculate and display the gas concentration in real time. We can also apply the developed algorithm for similar experiments with other polar gases.

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Fitting functions for the experimental data for acetone are been approximated using the following generalized two-parameter function:

$$ c(U, L) = \alpha(L) \left( \beta(L)^{\gamma(L)} \right) \frac{\beta(L)^{\gamma(L)}}{U - \delta(L)^{\gamma(L)}} $$ (2)

We found fitting functions $\alpha(L)$, $\beta(L)$, $\gamma(L)$, and $\delta(L)$ for generalized two-parameter function from the experimental data and described them using the following relations:

$$ \alpha(L) \equiv 11 \cdot L $$

$$ \beta(L)^{\gamma(L)} \equiv 1.2 + 0.22 \ln (L - 1.3) $$

$$ \gamma(L) \equiv 0.1 \frac{0.1}{[1 + (12 \cdot L)^5]} $$

$$ \delta(L) \equiv 0.11 - \frac{0.06}{[1 + (15 \cdot L)^5]} $$ (3)
This function $c(U, L)$ (Figure 3) describes the acetone concentrations based on the experimental measurement of two signals.

Two experimental signals from our photovoltaic sensors are used as inputs to the engineered mathematical module of the NI LabView™ program. The acetone concentrations calculate under this program and output on the front panel of the NI LabView™ program in real time. The logic control module finds an optimal level of an illumination and minimizing error of the measurement. However, the maximum accuracy for analysis can be achieved in the event of slowly changing gas concentrations. In addition an iteration process increases the total measurement time.

3. Conclusions
We used the samples with a special plasma-chemical treatment with hydrogen and fluoride ions after fabrication. Such surface treatment has a stabilizing effect on the electrical properties of the material and increases their adsorption sensitivity to polar molecules of acetone. Experimental concentration dependences have been measurement for the electromotive force on contacts of photovoltaic sensors upon adsorption of acetone under different levels of illumination. We engineered special mathematical module of the NI LabView™ program for automatic control and measurement of acetone concentration in the wide range from 1 ppm to 10 vol% (100000 ppm).

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