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New Photovoltaic Gas Sensors for Detecting of Ethanol and Mercaptoethanol

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Keywords

Gas sensors, Porous and Crystalline Silicon, Heterojunction, Photovoltaic Effect

The purpose of this experimental study is an extending the number of detectable gases, based on the observed photovoltaic gas sensitivity effect between porous and crystalline silicon at a room temperature of experiment. We researched these smart sensors for detections of ethanol and mercaptoethanol molecules in wide range of the measurement concentrations with the maximum possible accuracy. The sensitivity properties of these photovoltaic ethanol and mercaptoethanol sensors in dependence on light intensities and gas concentrations were analyzed. Photo-EMF sensitivities corresponding to gas concentrations in the range from 1 ppm to 900 ppm can be maximized by controlling the intensity of illumination light under NI LabView software modules. Our sensors can be useful for the detection of ethanol and mercaptoethanol in a mixture with pure nitrogen.

Introduction

A new type of ammonia gas sensor that uses electrical contacts to measure photo-EMF at a heterojunction between porous and crystalline silicon at a room temperature of experiment was discussed in [1]. This new technology increases sensitivities over a wider concentration range than typical ammonia gas sensors. This gas detecting method opens a new way for creating of new intelligent gas sensors. We can control sensitivities and metrological specifications of the photovoltaic sensors during experiment under NI LabView program and National Instruments hardware [2].

Selectivity properties of gas sensors are very important in practice. Unfortunately, porous silicon has an electrical sensitivity to numerous gases. The purpose of this experimental study is an extending the number of detectable gases, based on the observed photovoltaic effect [1]. Practical interest has gases with a significant dipole moment. For example, such polar molecules can be molecules of ethanol. Ethanol molecules have a significant dipole moment equal to 1.69 D [3]. A world ethanol market is huge (around 100 bln liters) and fast develops [4].

In the literature there are numerous publications on ethanol sensors In this short report we mention only some of it. Sensors for ethanol detection from the company Figaro are well-known. Now the Figaro TGS 2620 sensor has a high sensitivity to alcohol and organic solvent vapors [5]. The sensing element is comprised of a metal oxide semiconductor layer formed on an alumina substrate of a sensing chip together with an integrated heater. Typical detection range of the TGS 2620 sensor is 50÷5000 ppm. Micro ethanol sensors fabricated using the commercial 0.18 μm CMOS consists of a sensitive zinc oxide film, a heater and interdigitated electrodes [6]. Experiments showed that the best working temperature of the sensitive zinc oxide film was 350°C. The experimental results showed that the resistance of the ethanol sensor varied from 6.18 to 5.1 MΩ as the ethanol concentration increased from 0 to 250 ppm at the working temperature. The sensitivity of the ethanol sensor with the inverting amplifier circuit was 0.35 mV/ppm. Synthesis and ethanol sensing properties of novel hierarchical Sn_3O_4 nanoflowers with high response at lower temperature (190°C) is described in [7].

Currently, ethanol sensors at room temperatures working on the base of new materials and methods of gas detection intensively investigated. For example, a light-controlling, flexible, transparentand working at room-temperature ethanol gas sensor by using commercial ZnO nanoparticles is described in [8]. The fabricated sensor not only exhibits fast and excellent photoresponse, but also shows high sensing response to ethanol under UV irradiation. The SnO_2-doped poly-diallyldimethylammonium chloride sensor has a detection limit of 10 ppm at the room temperature and shows good selectivity to ethanol [9]. Flexible ethanol sensors on glossy paper substrates operating at the room temperature is investigated in [10].

Fabrication of a grapheme field effect transistor array on microchannels for ethanol sensing is shown in [11]. Such sensors have a significant advantage in design compared to sensors having heater. We did not find any publications in the literature on similar photovoltaic ethanol sensors, described in [1].

Other points of interest for our research can be mercaptoethanol molecules. Mercaptoethanol molecules have a dipole moment equal to 2.8 D. A world mercaptoethanol market also develops actively [12]. Detection of 2-mercaptoethanol using gold-coated micromachined cantilevers is described in [13]. In the literature there are no data on its detection by other methods.

Development of new smart sensors on the base the achievements of nanotechnology, electronics, computer signal processing and monitoring of gas concentrations by wireless sensors network is very relevant now. See, for example, [14, 15].

Thus, researches on improving the smart photovoltaic gas sensors parameters of ethanol and mercaptoethanol are relevant now as a new method of gas detection. In this short report we present the experimental results for a using of such sensors for detecting of these molecules in an inert atmosphere of pure nitrogen.

Results and Discussions

Porous silicon for this study was formed by anode electrochemical etching of (111) oriented p-type silicon wafer within a resistivity of 10 Ωcm at a current density of 10 mA/cm^2 using HF-based solution. During etching an additional illumination and an ultrasonic processing was applied to the silicon surface. The thickness of porous silicon layers is found from cross-section scanning electron microscopy (approximately 12 μm at 5 min etching time). Thin porous film from aluminum was manufactured on a surface of porous layer (gas and light transparent contact. This thin layer was transparent to illumination and gas molecules and creates electrical contact to porous silicon (electrical contact C on Fig. 1 (b)).

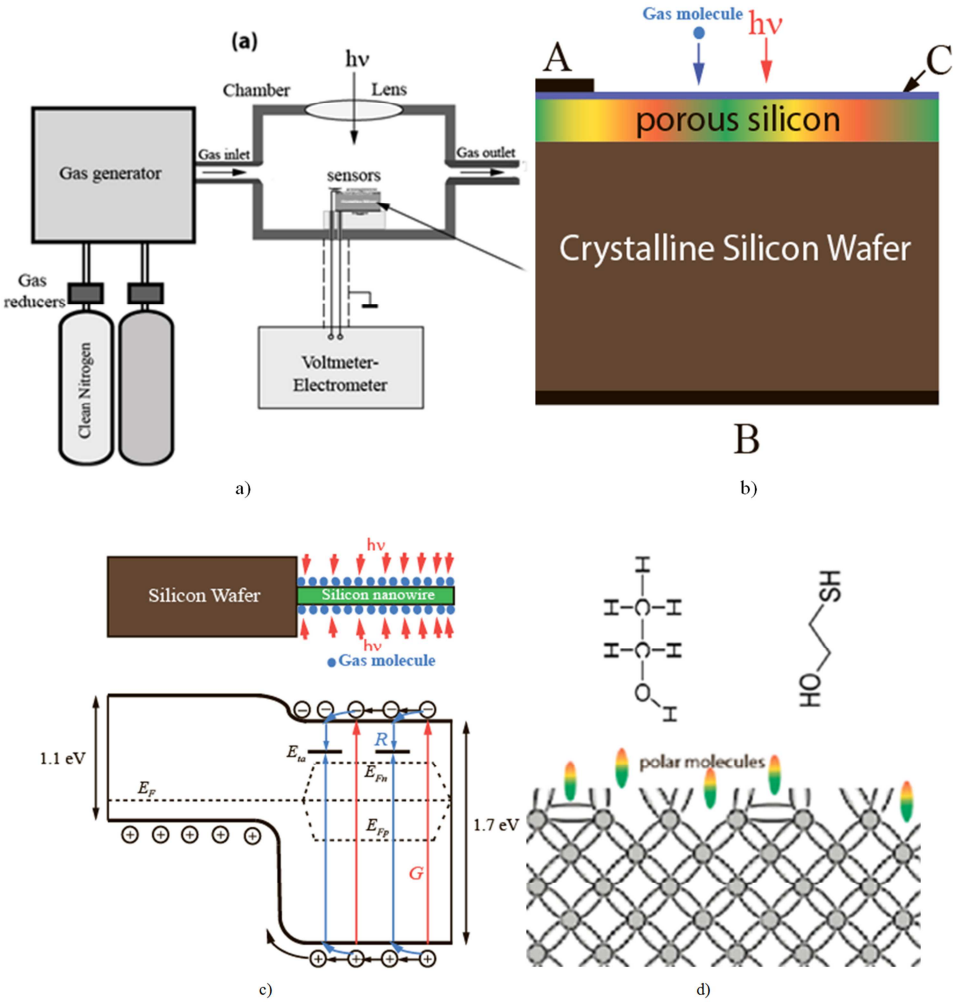

Fig. 1. *Experimental setup (a) and a cross-section of photovoltaic gas sensor structure with porous silicon on crystalline silicon wafer (b) (A and B are standard electrical contacts, C is a special contact, which is transparent to molecules of gases and photons). A physical model of a heterojunction energy diagram between silicon nanowire and crystalline silicon wafer under light absorption and gas molecules adsorption (c); a surface adsorption model (d).*

The photo electromotive forces between A and B contacts of samples were studied in a special measuring chamber Fig. 1). We used voltmeter-electrometer for a Photo-EMF registration. Composition of gas atmosphere was changed by gas generator under dynamical mixing clean nitrogen with a researched gas (Fig. 1). The surface of samples was illuminated at different intensity and wavelengths of light. Illumination levels were measured by Luminance meter T-10 of Konica Minolta. The photo-EMF-based gas sensors work at a room temperature.

Fig. 1, c, d shows a physical model of a heterojunction energy diagram between silicon nanowire and crystalline silicon wafer under light absorptions and adsorptions of gas molecules.

Fig. 2 shows the concentration dependences of the Photo-EMF under ethanol adsorption at different levels of illuminations. In our experiment maximal changes of the Photo-EMF magnitudes ranged under levels of illuminations from 1 ppm to 10000 ppm (200 lx), from 10 ppm to 1000 ppm (20 lx) and from 1 ppm to 100 ppm (2 lx). These ranges show that variation of light exposure permits operation of Photo-EMF sensitivities at different gas measuring ranges for ethanol.

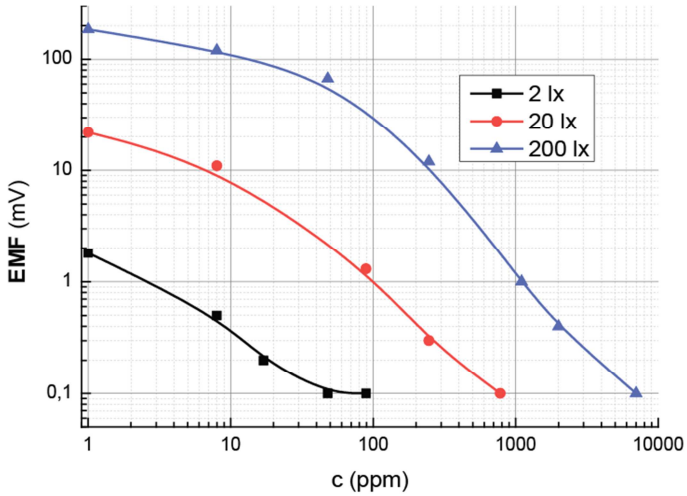

Fig. 2. *Dependences of the Photo-EMF of sensors on ethanol concentration under different Illumination levels 2, 20 and 200 lx.*

Fig. 3 shows a graph of the light intensity and the electromotive force at the condition, at which can be achieved the maximum metrological accuracy. These data can be the basis for the development of intellectual sensors for ethanol with a wide dynamic measurement range with the maximum possible accuracy of measurement. Fig. 3 includes a spline approximation of EMF-magnitudes for sensors data from illumination levels based on the data of Fig. 2. We standardize parameter *L* based on these measurements. In this case, we have the maximal analysis accuracy for different ranges of ethanol concentrations. The approximation of the calibration curves can be described by the formula:

$$U(L)=-1.7493+185.561\exp(L/155.27) \quad (1)$$

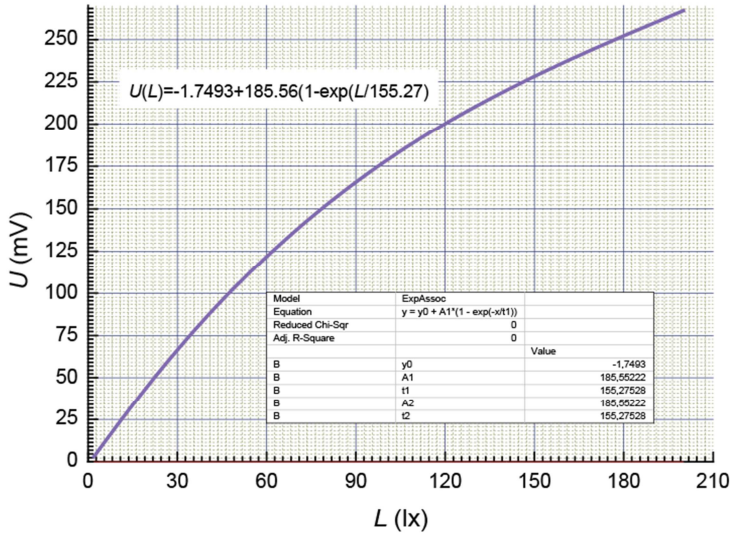

Fig. 3. *Dependence of EMF-magnitude on sensors contacts at different illumination levels with maximal sensitivity to ethanol.*

The photo-EMF-based gas sensors can change sensitivities and ranges of measurement by changing illumination intensity (fig. 2). We can determine the ethanol concentration in a measuring chamber under different illumination levels. For example, an ethanol concentration of 100 ppm could be measured under the levels of 2, 20 and 200 lx respectively (fig. 2). However, for the limiting levels 2 and 200 lx the measurement errors are maximal because we have measurements near the thresholds of sensitivity and the saturation ranges for the 100 ppm ethanol concentration (fig. 2). The measurement at 20 lx is more precise in comparison with 2 and 200 lx, but not optimal according to Equation (1). For a minimization of the measurement errors we have to change continuously the intensity of light during real-time measurements. We have to match an optimal magnitude of illumination level L at a coincidence of a real sensor signal Us and a calculation magnitude Uc under the equation (1).

A control algorithm of parameter L for optimal measurement of ammonia concentration with photo-EMF-based semiconductor sensors is realized with modules in LabView program. We have developed LabView software modules which optimize the experiment with maximal accuracy of measurement. If the signals Us and Uc are not equal, a light intensity controller increases or decreases the parameter L by the step L depending on the conditions $Us > Uc$ or $Us < Uc$. An iteration cycle should be stopped if two signals are equal ($Us = Uc$). In our experiment it is realizable in the gas measurement over a concentration range from 1 ppm to 900 ppm.

Similar results were obtained under the adsorption molecules mercaptoethanol.

We have developed software modules controlling the intensity of light for maximum accuracy under NI LabView program and National Instruments hardware under the calibration curve. We engineered separately specific modules in the NI LabView program for dynamic control of sensitivity in a wider concentration range, communications, collection and processing of data of the photo-EMF gas sensors in real-time measurements. The main advantage and performance for ethanol and mercaptoethnol detection by photovoltaic gas sensors is the expansion of the dynamic range of measurements.

Conclusions

Based on our results, we conclude that photo-electromotive force on heterojunction between porous silicon thin layer and crystalline silicon wafer depends on concentration of polar molecules of ethanol and mercaptoethnol in the measurement chamber at the room temperature of experiments. Photo-EMF sensitivity corresponding to ethanol concentration in the range from 1 ppm to around 900 ppm can be maximized by controlling the intensity of illumination light. New intelligent photo-EMF-based gas sensors can change measurement sensitivity and concentration range by changing illumination. The NI LabView program and modern National Instruments hardware are very useful to develop a dynamic control measuring system for a wide range of ethanol and mercaptoethanol concentrations. ■

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