Sensor of Carbon Dioxide Based on MIS Structure with Solid Electrolyte Layer

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Abstract

We present the first results on CO₂ gas detection with the help of sensors based on metal-polymer electrolyte-isolator-semiconductor structure with additional layer of proton conducting solid electrolyte – ether of phenylsulphonic acid and polyvinyl alcohol. The sensor operates at room temperature. The detection limit is shown to be of about 100 ppm of CO₂ in air.

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gas sensor; carbon dioxide; solid electrolyte; MIS structure

1. Introduction

The detection of carbon dioxide with gas sensors operating at room temperature is very important problem, because these sensors can find the application in mass production instruments, for example in air conditioning systems for the control of the ratio between air circulation inside the room and ventilation from outside. The optimization of this ratio decreases power consumption of air conditioners very much.
Recently, the most usual gas sensors, which are used for the detection of carbon dioxide in air, are the IR optical sensors. In this sensors, light absorption by the target gas at wavelength of 4.2 micron is measures and used for the calculation of gas concentration. In these devices, thermal source of light (hot spiral of lamp) or uncooled LED emitting radiation at this wavelength are used as a source of radiation. The main disadvantage of these devices is their relatively high cost (about 100 – 150 Euro) limiting their mass application. On the other hand, the sensors detecting CO\textsubscript{2} concentrations are very required by the market, especially for controllers of air conditioning systems. Therefore, it is important to design CO\textsubscript{2} sensor operating, preferably, at room temperature. The concentration range, which is the most interesting for practical application, is from ~100 to 2000 ppm, because the CO\textsubscript{2} background concentration in atmosphere is the value of 300 ppm. In this work we present the first results on CO\textsubscript{2} detection with the help of sensors based on metal-polymer electrolyte-isolator-semiconductor (MEIS) structure. The common principles of the operation of such sensor (in the case of fluorine, fluorides and hydrogen fluoride detection) are described in [1]. In such devices, the formation of additional ions taking place on the three phase interface between gas, porous metal electrode and solid electrolyte induces to the shift of capacitance-voltage ($C\text{-}V$) characteristic of the MEIS structure. The sensor operates at room temperature. The detection limit is shown to be of about 100 ppm of CO\textsubscript{2}.

2. Experimental

The scheme of the gas sensor with additional layer of solid electrolyte is shown in Fig. 1. We applied the standard MEIS structure with additional layer of proton conducting solid polymer electrolyte – ether of phenylsulphonic acid (PSA) and polyvinyl alcohol (PVA). The capacitance and capacitance-voltage characteristics of MEIS structures were measured by use of RCL meter “Agilent 4980A” connected with computer. The gas sensitivity of the sensor was investigated by use of gas mixtures of CO\textsubscript{2}:air with different ratio and relative humidity. The gas mixtures were prepared with the help of 4-channel gas flow controller “Microgas-F14” (Russia).

![Fig. 1. The scheme of the MEIS gas sensor with additional layer of solid electrolyte.](image)

3. Results and discussion

The $C\text{-}V$ curves of the MEIS structure were observed at different relative humidity 40%, 60%, 80%, and in dry air. The optimum operating voltage equal to -0.8 V was found, where the derivative reaches the maximum value. In further experiments, we used a humid air with fixed value of relative humidity (RH) as a carrier gas. $C\text{-}V$ curves, measured at different concentrations of CO\textsubscript{2} (0 ppm, 100 ppm, 200 ppm, 500 ppm, 1000 ppm) at RH40, are shown in Fig. 2. One can see from these plots that the $C\text{-}V$ curves shifted upward with an increase in CO\textsubscript{2} concentration in air. The maximal capacitance of the structure is defined by the concentration of mobile ions in polymer electrolyte near the silicon oxide layer at fixed bias voltage. The values of mobile ion concentration and flat band voltage were estimated for different CO\textsubscript{2} concentrations by means of calculation of parameters of $1/C^2$ dependencies on bias voltage (Fig. 3a, b).
The positive value of flat band voltage decreased with the increase in CO₂ concentration (Fig. 3b). It corresponded to the increase of capacitance (Fig. 2) and decrease of surface bending of energy bands and thickness of depletion layer in Si.

Fig. 2. $C-V$ curves of the MEIS structure for different CO₂ concentrations in air at RH40.

Fig. 3. (a) Mobile ion concentration and (b) flat band voltage as a function of CO₂ concentration in air at RH40.

The time response of the sensor to different concentrations of CO₂ in air was measured in a range from 50 to 1000 ppm with RH80. There was no visible response at 50 ppm and 100 ppm concentrations at this humidity. The response appeared for 200 ppm concentration, and then its value increased for 500 ppm and 1000 ppm concentrations (Fig. 4). The response time of the sensor is rather fast for room temperature. It is equal to about 1 min. The capacitance change of the sensor in dependence on CO₂ concentration is described well by a power law with value of power index near 0.6 (Fig. 4b) [2]. The mechanism of sensor sensitivity to carbon dioxide consists, probably, in the interaction of CO₂ with adsorbed water in PVA/PSA that induces to a change in concentration of hydrogen ions in polymer electrolyte.

The main problem for the measurement of concentration of CO₂ with MEIS gas sensors was strong dependence of the $C-V$ curves on air humidity. The slow change of adsorbed water in polymer electrolyte...
during the measurements induced to instability and permanent drift of zero line. Further work must be focused on improvement of this stability and optimization of sensing materials for the sensors.

Fig. 4. (a) Response of the MEIS structure to different concentrations of CO₂ in air at RH80; (b) Change of capacitance of the MEIS structure as a function of CO₂ concentration in the case of different humidity of air: RH40 (open squares) and RH60 (open circles) and the fitted power dependencies (solid lines).

4. Conclusions

At first we have demonstrated the CO₂ detection with the help of sensors based on metal-electrolyte-isolator-semiconductor structure. We have applied the MEIS structure with additional layer of proton conducting solid polymer electrolyte – ether of phenylsulphonic acid and polyvinyl alcohol. The sensor operates at room temperature. The detection limit is shown to be of about 100 ppm of CO₂ in air.

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