Hydrogen Sensors Based on Metal–Insulator–Semiconductor Structures with a Layer of a Proton-Conducting Solid Electrolyte*

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Received June 30, 2006

Abstract—Application of solid electrolytes as undergate layers accelerates the response of a sensor at room temperature as compared with ordinary hydrogen sensors manufactured on the basis of the metal–insulator–semiconductor (MIS) structures with a palladium gate. The proton-conducting solid electrolytes under study include NAFION, zirconium hydrophosphate, and etherified polyvinyl alcohol (PVA) with heteropolyacids and phenoldisulfonic acid, which can be deposited under the platinum gate. Sensors based on the MIS structures with these solid electrolytes show a high sensitivity toward hydrogen (~120 mV per concentration decade). The response time $\tau_{0.63}$ of a freshly manufactured sensor with a layer of zirconium hydrophosphate amounts to about 2 min. The maximum mechanical stability, especially at relative humidities in excess of 80% is intrinsic to sensors containing layers of PVA with heteropolyacids. The response time of such sensors is nearly 10 min.

DOI: 10.1134/S1023193507050096

Key words: hydrogen sensor, MIS structure, proton-conducting solid electrolyte, gas fire alarms (detectors)

INTRODUCTION

The interest in the development of hydrogen sensors operating at room temperature, which can be manufactured using silicon technology, is due to the possibility of creation of a new generation of fire alarms (detectors) that are capable of detecting the odor of the smoldering combustible material, rather than the smoke produced by fire or the temperature rise in the room caused by the flames. This possibility is specified in relatively recent standards EN54/6, ISO 7240/6, and NPB 98. One of the most important gases that are emitted by smoldering combustible materials in the early stages of a fire is hydrogen. The large diffusion coefficient of hydrogen and its low background content in atmosphere (~0.5 ppm) make hydrogen a very appealing candidate for manufacturing gas fire alarms. On the other hand, detecting this gas is of importance for fuel cells that are rapidly developing at the present time.

Sensors that are used in gas fire alarms must possess the following most important properties: low electric power consumption, high sensitivity (a value of $H_2$ concentration of 10 ppm is typical of fire), low cost, and, consequently, the possibility of manufacture with the aid of an adequate technology, preferably, the silicon technology.

To our minds, there exist two most important kinds of sensors for the application in gas fire alarms, specifically, metal oxide sensors manufactured using the technology of silicon micromachining, i.e., thin dielectric membranes of silicon oxide or nitride (“nano-permicron” technology) and sensors on the basis of the metal–insulator–semiconductor (MIS) structures.

In this paper we will focus our attention on the MIS sensors and especially on the MIS sensors with an undergate layer formed out of a proton-conducting solid electrolyte.

The principle underlying the method of measuring a gas concentration with the aid of an MIS structure with
a layer of a solid electrolyte (MEIS) was described in detail in [1, 2]. The electrochemical reaction that proceeds on the three-phase interface gas/metal/solid electrolyte with the participation of gas X is

\[ X + ne \rightarrow X^{n+}. \]

The reaction in question leads to a shift of the CV-characteristics of an MEIS capacitor along the axis of voltages. The magnitude of this shift is usually described with the aid of the Nernst equation and is proportional to the logarithm of the concentration of gas X (proportion between partial pressures). Schematics of an MEIS sensor is presented in Fig. 1.

The MIS structures with a layer of an undergate solid electrolyte are an efficient instrument for measuring low concentrations of various gases, in the first place, fluorine, fluorides, and fluorocarbons [1, 2]. Nevertheless, very important is search for a cheap sensor working at room temperature and intended for the detection of other gases. The hydrogen sensitivity of the MIS structures with a layer of a fluoride-conducting electrolyte lanthanum trifluoride was investigated in our work [3]. It was demonstrated that this sensor could be used for measuring low hydrogen concentrations in the interval 10 to 100 ppm after a procedure of “reactivation.” The procedure consisted in short-term heating in air to a temperature of about 160°C. After that, the sensor had the response time of 100 s. In order for the response time of the sensor to be stable at room temperature, the procedure of reactivation must be repeated every few hours.

Of course, it is very important to find a solid electrolyte that would allow us to avoid the procedure of reactivation and work at room temperature in a broad interval of the air humidity. In our work there was investigated the sensitivity to hydrogen of the MEIS structures with layers of the following proton-conducting solid electrolytes: NAFION, antimonic acid, zirconium hydrophosphate, and a solid electrolyte on the basis of etherified polyvinyl alcohol (PVA) and phenoldisulfonic acid (PSA) or a heteropoly acid (HPA).

EXPERIMENTAL

The measurements of the gas sensitivity of the MEIS sensors were conducted on a computer-controlled gas-mixing installation that was equipped with Model RRG-9 electronic mass flow controllers. In order to prepare a gas mixture with a required concentration of hydrogen, we used gas cylinders containing 100 ppm H₂ in a synthetic air. The gas was additionally diluted with a synthetic air in dynamic conditions. The gas was humidified by bubbling through a saturated solution of a corresponding salt (MgCl₂—33% of relative humidity (RH), KCl—84%, and so on). The capacitance of structures was measured with the aid of an RCL Model HP4284A meter (Hewlett-Packard). The measurements were conducted at a frequency of the testing voltage equal to 10 kHz and an amplitude of 10 mV. Experimental details were described in work [2].

NAFI ON was applied onto the surface of silicon covered with SiO₂/Si₃N₄ layers (20/80 nm) out of an alcohol solution and dried in accordance with recommendations of the manufacturer (du Pont de Nemours). The platinum electrode of the gate was applied onto the surface of a polymer layer by cathodic sputtering in an argon atmosphere. The time period required for the performance of the sputtering did not exceed 30 min. Within this time of residence in a vacuum, the layer of NAFION was not damaged irreversibly.

A layer of zirconium hydrophosphate was obtained by us in the form of an aqueous gel. To better the wetting of a hydrophobic surface, the gel was diluted with ethyl alcohol (~70 vol %). The liquid was applied onto the surface of silicon dioxide and dried up at a temperature of nearly 60°C. A layer of platinum or palladium approximately 30 nm thick was deposited onto the surface of a film by cathodic sputtering [4].

In addition, in our experiments we investigated a new perspective material that was developed for the application in fuel cells—polyvinyl alcohol etherified with a heteropoly acid and phenoldisulfonic acid. This material is characterized by good adhesion to the surface of a substrate and stability in a wide range of humidity of air. We investigated the following materials: PVA etherified with PSA (PVA/PSA) and materials on the basis of PVA containing 90, 75, and 40 wt % HPA (PVA/HPA).

All these compounds were obtained in the form of aqueous solutions, applied onto the silicon nitride surface, and dried up at the temperature of approximately 40°C. Solutions of polymers well wet the surface of silicon nitride. After the preparation the adhesion of these materials was good enough.
For measurements we used specimens of materials manufactured approximately two months before measuring the gas sensitivity. Specimens of the MEIS structures were manufactured directly before conducting measurements. A film of a material containing 90 wt % HPA was too rigid and, when stored in normal conditions, it cracked and peeled off the surface of silicon. A platinum electrode was deposited on the surface of other specimens there was applied with the aid of cathodic sputtering in an argon atmosphere. The thickness of the layer of platinum was equal to about 30 nm.

To measure electric and gas-sensitive characteristics of the formed MEIS structures we utilized a clamped contact to a platinum gate. The handling of such a contact in the case of a polymer layer requires certain caution, for the needle of the contact sometimes inflicts damage on the layer of polymer, the more so at elevated humidity, at which polymer turns softer.

RESULTS AND DISCUSSION

The first material we investigated in MEIS structures was NAFION [5, 6]. As far as it is known, NAFION is a tetrafluorethylene with grafted sulfonic groups. Owing to these groups, it readily absorbs water out of air. As a result, the proton conductivity of NAFION increases. The electrochemical reaction that occurs at the three-phase interface only shifts the CV-characteristics of the structure, without changing its shape. An appropriate plot is presented in Fig. 2.

Fig. 2. The CV-characteristics for an MEIS structure with a layer of NAFION: (1) pure air at RH = 33% and (2) 100 ppm H₂ at RH = 33%.

A MEIS structure is sensitive to hydrogen in a concentration range from 10 to 100 ppm. A typical response of the sensor is presented in Fig. 3. The sensitivity of the structure is shown in Fig. 4. The sensitivity of a MEIS structure with a layer of NAFION is equal to 140 ± 20 mV per decade of the hydrogen concentration. This value is considerably higher than is typical for a simple two-electron process that may flow on the three-phase interface gas/platinum/solid electrolyte. Similar magnitude of the sensitivity of a sensor to hydrogen (120 mV per decade of the hydrogen concentration) was discovered in work [7], where a layer of antimonic acid was used in a MEIS structure in the role of a proton-conducting solid electrolyte.

Fig. 3. Comparing responses of MEIS structures with a layer of NAFION to 100 and 50 ppm H₂ in air at RH = 33% and a temperature of 22 ± 2°C.
Such magnitude of sensitivity was explained in [7] by the formation of a mixed potential caused by a simultaneous electrochemical reactions

\[ \text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \tag{1} \]

\[ \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow 2\text{H}_2\text{O} \tag{2} \]

at the interface. Of importance is that the first reaction is limited by the diffusion of \( \text{H}_2 \) out of a gas phase to the electrode/proton-conducting electrolyte interface. This occurs because of a low concentration of hydrogen in the gas. An analysis performed in [7] using polarization curves for the said reactions showed that mixed potential \( E_M \) is proportional to the logarithm of the hydrogen concentration \( c_{\text{H}_2} \), specifically, \( E_M = a + b \log c_{\text{H}_2} \), where \( a \) and \( b \) are some constants.

The major problem we came across when utilizing NAFION applied onto a silicon substrate was a high sensitivity of the sensor to an alteration in the humidity of air. This alteration leads not only to an alteration in the response time of the sensor but also to the peeling of the NAFION film off the substrate, which is connected with the swelling of NAFION.

The use of a solid electrolyte manufactured by a research group from the University of Perugia (Italy) [8] became an attempt to solve that problem. Pellicular zirconium hydrophosphate is a proton-conducting solid electrolyte convenient for the application in MEIS, for it can be applied directly onto the surface of oxidized silicon in the form of a film 10–20 \( \mu \text{m} \) thick. The electroconductivity of zirconium hydrophosphate at room temperature is sufficient enough for the application in the MEIS structures of sensors and is equal to \( 10^{-4} \text{ S cm}^{-1} \). The activation energy for conduction in zirconium hydrophosphate amounts to approximately 0.3 eV [8].

The curves illustrating the response of the MEIS structures with a layer of zirconium hydrophosphate and a palladium gate are presented in Fig. 5. The sensor’s sensitivity to hydrogen in the concentration interval 10 to 100 ppm, as that exhibited by NAFION, is close to 120 mV per decade of the hydrogen concentration. The corresponding curve is presented in Fig. 6. The response time of the sensor (\( \tau_{0.63} \), which is the sens-
sor’s time constant; the time it takes the signal to reach 63% of its extreme value) with the platinum and palladium gates and a layer of zirconium hydrophosphate as a function of the concentration of hydrogen is presented in Fig. 7. In either case the response time amounts to a quantity on the order of about 100 s. In the case of palladium this quantity is marginally smaller as compared with platinum because of a higher catalytic activity of palladium in the reaction of dissociation of hydrogen.

All these results were obtained for freshly manufactured MEIS structures. The measurements were conducted no later than 1–2 h after the manufacture. That time period was necessary for preparing measurements of the sensor’s characteristics.

The major problem that restricts the application of the MEIS structures with a layer of zirconium hydrophosphate as sensors of hydrogen is their aging. The aging is connected with dehydration of the surface of zirconium hydrophosphate and, consequently, with the formation of a layer possessing a low protonic conduction at the interface between platinum or palladium and the solid electrolyte. The consequence of this is the slowing down of the sensor’s response even after a 24-h storage in air. This process is more noticeable for antimonie acid and zirconium hydrophosphate than for NAFION.

The aim of subsequent experiments was to better the properties of the MEIS structures in their role of hydrogen sensors. These experiments were conducted with use made of a proton-conducting material that was developed in the Institute of Problems of Chemical Physics, Russian Academy of Sciences, (Chernogolovka, Russia). The major problem we came across when trying to measure characteristics of sensors with a layer of the PVA/PSA polymer was insufficient mechanical rigidity of the material. As a result, the sensor’s response contained great noise. Nevertheless, the detection of CV-characteristics and a gas response was possible. Another problem we came across when investigating sensors with a layer of the PV A/PSA polymer was a complex character of the frequency dependence of the impedance of such structures, which did not admit approximation by a parallel RC circuit (the absence of one time constant). As a result, with our method of measuring, the sensor’s response formally had the opposite (!) sign as
compared with the responses of sensors with layers of NAFION, zirconium hydrophosphate, and PVA/HPA.

It should be noted that, when trying to take measurements of the capacitance of an MEIS capacitor with a layer of PVA etherified by HPA, it proved impossible to apply the 10-kHz frequency of the testing voltage which was usual for our experiments and which we used for the determination of the capacitance of structures with other solid electrolytes, probably as a consequence of a large capacitance of the electrical double layer. As a result, for measurements we used a lower frequency of the testing voltage that was equal to either 500 or 1000 Hz. At these frequencies, we obtained a low-frequency CV-characteristics for the semiconducting material (silicon) used in our experiments. Typical CV-characteristics of the MEIS structures with layers of PVA/HPA with 40 and 75 wt % HPA are presented in Fig. 8.

The sensitivity of a sensor with a layer of polymer PV A/HPA (40 wt %) was investigated in a range of hydrogen concentrations extending from 10 to 100 ppm. The response of the sensor has the sign that is typical for silicon of the $n$ type, i.e. the CV-characteristics shifts along the axis of voltages in the negative direction and, consequently, the capacitance of the MEIS capacitor increases with increasing hydrogen concentration (Fig. 9). In Fig. 9 we present the response of a sensor with a layer of polymer containing 40 wt % HPA. Similar responses were obtained also for structures with a layer of polymer containing 75 wt % HPA.

The sensitivity of a sensor with a layer of polymer PV A/HPA (40 wt %) is presented in Fig. 10. The plot presented in a semilogarithmic scale corresponding to

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**Fig. 9.** The response of an MEIS structure with a layer of PVA/HPA (40 wt %) to H$_2$. The hydrogen concentrations are pointed out in the plot in units of ppm. The frequency of the testing voltage is equal to 1000 Hz and the amplitude is 10 mV. The response was measured in synthetic air at RH = 33% and a temperature of 22 ± 2°C.

**Fig. 10.** The hydrogen sensitivity of an MEIS structure with a layer of PVA/HPA (40 wt %). The frequency of the testing voltage is equal to 500 Hz and the amplitude is 10 mV. The curves were measured in synthetic air at RH = 33% and 22 ± 2°C.
the Nernst law is nonlinear in the region of 10–100 ppm of hydrogen. Besides, the response of this sensor is considerably lower as compared with the responses of sensors with layers of NAFION, zirconium hydrophosphate, and antimonic acid [7]. This experimental fact implies that the mechanism of formation of potential at the interface gas/platinum/polymer electrolyte differs from the mechanism that was described in the foregoing and which is typical of other materials.

The response time of a sensor with a layer of polymer electrolyte PVA/HPA is approximately an order of magnitude longer that the response time of a freshly manufactured sensor with a layer of zirconium hydrophosphate (Figs. 5, 9). Nonetheless, it is necessary to mention that, after storage for a few days, the response time of the sensor with a layer of zirconium hydrophosphate becomes comparable with the response time of the sensor with a layer of polymer electrolyte PVA/HPA. The response of the sensor with a layer of PVA/HPA is sufficiently reproducible (Fig. 11).

The rise in the gas humidity exerts an influence on the response time of a sensor and barely affects the magnitude of the response. The CV-characteristics and the response of a sensor with a layer of PVA/HPA (40 wt %), measured at a relative humidity of 84%, are shown in Figs. 12 and 13, respectively. Raising the humidity of air leads to a very substantial increase in the capacitance of the MEIS structure. This is connected with an increase in the protonic conductance of
the polymer and an increase in the concentration of charge carriers, which occurs following an increase in the gas humidity.

An important problem intrinsic to measurements of properties of structures was the softening of materials with increasing humidity. As a result, the clamped electrode that was used in this work damages the surface of the polymer film, which leads to an increase in noise intensity.

In a further work it would be necessary to find an opportunity to make a polymer more rigid even at a low concentration of HPA in the polymer. This is possible when using a cross-linked polymer. Still another problem to be solved is to reduce the influence of the gas humidity on the response of a sensor.

**CONCLUSIONS**

A number of MEIS structures with layers of proton-conducting solid electrolytes fixed under the catalytic layer of the gate of a sensor were investigated. It was demonstrated that the MEIS structures with a proton-conductive layer are sensitive to hydrogen in air. The sensor sensitivity is caused by the formation of a mixed potential at the three-phase interface of the sensor (gas/metal/solid electrolyte) and is close to 120 mV per decade of the hydrogen concentration for NAFION, zirconium hydrophosphate, and antimonic acid.

Polymer layers that were manufactured by etherification of PVA with HPA at an HPA concentration of 40 wt % are perspective for application. For a sensor with a polymer layer produced by etherification of PVA with PSA, an equivalent circuit is not described by a simple RC circuit, which makes the procedure required for measuring the capacitance of the structure more complicated. A thorough scrutiny of impedance spectra for such an MEIS sensor would elucidate the nature of properties inherent in the Si₃N₄/polymer and gas/polymer interfaces.

The response time (10 min) of a sensor with a layer of polymer electrolyte PVA/HPA may be reduced if the relative humidity of air is equal to about 80%. To find other methods for reducing the response time of sensors, further investigations are required.

The bettering of mechanical properties of an electrolyte may be connected with the application of cross-linked polymers, which would make it possible to reduce their swelling upon an increase in the gas humidity.

**REFERENCES**


