Chemosorption hydrogen gas sensor based on MOSFET with optical activation

T V Stoyanova¹, V V Tomaev¹,², N D Stoyanov³, S K Andreev⁴
¹Department of Physics, National university of mineral resources, Saint-Petersburg, V. O. 21-ya liniya, 2, Russia
²LED Microsensor NT, LLC, Saint-Petersburg, Politechnicheskaya 26, Russia,
³Department of Chemistry, State University, Saint-Petersburg, Petrodvorets, Universitetskii prosp. 26 Russia
⁴Institute of Solid State Physics, Bulgarian Academy of Sciences, Sofia, 72 Tzarigradsko Chaussee Blvd., Bulgaria

E-mail: Stoyanova_TV@list.ru

Abstract. In this paper we present an approach which allows to increase the sensitivity of the sensors at room temperature. Field effect transistors with SnO₂ gate in combination with optical activation of the adsorption centres on the surface were utilized. Studies of photosensitivity were carried out using a set of LEDs in the visible spectral range by the method of impedance spectroscopy. Optical activation of the adsorption centres in the SnO₂ gate leads to the additional accumulation of positive charges on top of the gate H⁺. Positive charge caused broadening of the channel in MOSFET sensor, resulting to lower real component of the impedance. These results show that optical activation allows to detect significantly lower concentrations of the hydrogen contained gases.

1. Introduction

Gas detectors and sensors based on chemisorption are widely used in practically all branches of industry, transport and medicine. In some industries without gas detectors and sensors it is impossible to provide the required level of human safety, including ecology and technogenic safety. According to the principle of the chemical sensitivity, sensors can be divided into two large groups:

1. Chemically sensitive optical sensors. Their selective sensitivity to certain chemicals is based on characteristic absorption of electromagnetic radiation in a gaseous environment. Main advantage of the optical sensors is that measured chemicals do not affect the sensor module. However, they cannot be used for measurement of many important chemicals, including hydrogen and oxygen due to the lack of strong enough absorption bands.

2. Chemically sensitive sensors based on direct effects of the environment on the sensor module. In this group sensors, chemical or physico-chemical reactions in the volume or on the surface of the sensitive element lead to changes in the electrical parameters. Such types are catalytic and electrochemical sensors. They have good sensitivity but poor performance (speed of response), high operating temperature (up to +400 - +450 °C) and short lifetime of the working cell.

Created later adsorption sensors have significantly better performance and lifetime. Generally in such sensors catalytic layers based on Pd, Pt, or SnO₂, deposited on ceramic or silicon are used.
The main mechanism of detection in such sensors is based on registration of changes in the electrical parameters during adsorption of molecules of the measuring environment on the surface of the sensor (change in conductivity or capacitance of the sensing element). The mechanism of the hydrogen sensitivity in the Schottky diodes with palladium contacts was described by Ludstrem [1, 2]. In Schottky diodes the dark current and capacitance are proportional to the concentration of hydrogen in the environment. In the n-type structures current increases, in the p-type structures, current decreases [3]. Pd layer catalyzes the dissociation of hydrogen-containing compounds to ions of hydrogen and other radicals. The selectivity of the sensor to the hydrogen is due to the higher solubility of hydrogen in the palladium in comparison to the other substances.

At room temperature, a small change of the electric characteristics is observed that not provide the required sensitivity. Effect of hydrogen influence on the electrical characteristics of the diodes and MOS structures with Pd or Pt layers increases with increasing temperature primarily due to the more active dissociation of the molecules. In the modern miniature adsorption sensors a heater is integrated in the sensor cell.

SnO$_2$ also catalyzes the dissociation of hydrogen-containing compounds. There are two main mechanisms of change of the concentration of charged carriers in the surface layer of the semiconductor due to gas adsorption:

1. Chemisorption of gases in the charged form which causes near-surface band bending of the semiconductor, described in the Schottky model [4]. This process leads to a change in the charged carrier concentration in the surface region of the semiconductor. Acceptor gases (with a large electron affinity) during chemisorption lead to negative charging of the surface layer. Their surface electronic states are located below the Fermi level of the semiconductor. Acceptor gases are O$_2$, Cl$_2$, F$_2$, NO$_2$, etc.. In donor gases, surface electronic states are located above the Fermi level of the semiconductor, so they lead to positive charging. Donor gases are H$_2$, CO, NH$_3$ and others. They reduce the resistance of the SnO$_2$ layers.

2. Direct interaction of gases with electrically active defects on the surface, which also changes the concentration of charged carriers in the semiconductor. High operating temperature of the sensors significantly limits the scope of applications. In this paper we present an approach which allows to increase the sensitivity of the sensors at room temperature, using field effect transistors with SnO$_2$ gate (figure 1) in combination with the optical activation of the adsorption centers on the surface.

2. Materials and methods

Field-effect transistors with a tin dioxide gate were fabricated in the Institute of Solid State Physics, Sofia. Their sensitivity to hydrogen-contained gases was investigated [6 - 8]. Dielectric SiO$_2$ layer with 20 nm thickness was deposited on a silicon substrate. Source and drain areas were formed by diffusion of donors through the windows in the dielectric layer. A layer of tin dioxide with thickness of 60 nm and resistance of 10 to 100 ohms / square was deposited on the gate dielectric layer.

The influence of the NH$_3$ concentration in the range of 19 - 52,000 ppm on the drain current at different voltages on the drain and gate was investigated. Using of pulse mode of operation allowed to obtain repeatable results. Measurements have shown that the change in drain current in the presence of ammonia is strongly dependent on the drain-source voltage $V_D$. This fact can not be explained only by change in the work function in SnO$_2$ layer. Model, which allowed not only to explain qualitatively but also to calculate the current change in the presence of NH$_3$ was developed [8].

When the drain-source voltage $V_D$ and a positive gate voltage $V_G$ are applied, a conductive n-channel in silicon under the gate is formed (figure 2). The potential distribution in the channel and, accordingly, the transverse field $E_x$ and $E_y$ depend on the ratio of voltages $V_D$ and $V_G$.

In the presence of moisture atoms, on the surface of SnO$_2$ take place dissociation of NH$_3$ + H$_2$O to NH$_4^+$, positive ions and negative ions OH-. Due to the influence of the distribution of the transverse field, positive ions migrate toward the source (to a negative area), and the negative ions migrate toward the drain.

The redistribution of ions changes the effective value of the gate voltage. Positive ions NH$_4^+$ make
an additional positive contribution $\Delta V_p$ in the gate potential $V_G$. Similarly, negative ions $\text{OH}^-$ give an additional negative contribution $\Delta V_n$ in the gate potential $V_G$. Thus, the total change in the gate potential $\Delta V_G$ determined by the influence of two types of ions, and can have both positive and negative sign:

$$\Delta V_G = \Delta V_p - \Delta V_n.$$

Created sensor structure based on a field effect transistor with a SnO$_2$ gate demonstrated sensitivity to hydrogen-containing gas at room temperature. This structure was used in carrying out experiments on the optical activation of adsorption centers, with the purpose to further improve the sensitivity and selectivity. These experiments were made in St. Petersburg.

Activated adsorption (requires activation energy) is usually accelerated by heating, but the concentration of adsorption centres can be also increased by illumination of the surface with light of appropriate wavelength. Illumination of the structures affects both the adsorption level of equilibrium and the kinetics of adsorption. Experiments [5] had shown that illuminated semiconductor showed a significant increase in the adsorption ability of the adsorbent, as was detected by a pressure drop in the adsorption volume. Maximum sensitivity with respect to the adsorption properties of semiconductor correspond to the maximum internal photoelectric effect.

Studies of photosensitivity were carried out using a set of LEDs in the visible spectral range by the method of impedance spectroscopy which is based on the study of the electrical response of a system imposed by electrical field with variable frequency.

Impedance measurements were carried out using impedancemeter Z-500P. The device allows to explore the properties of electrically conductive materials by recording the impedance spectra (complex resistance to the sinusoid current) at a constant polarizing voltage. Impedancemeter measures the real $Z'$ and imaginary $Z''$ components of the complex resistance when AC (sinusoidal) voltage with an amplitude value of 10 mV was applied to the sample. The voltage was applied between the drain and source of the MOSFET. The gate voltage was not applied. Activation of the adsorption centers in the SnO$_2$ gate was provided by electromagnetic radiation with wavelengths in the visible range. Red, yellow, green, blue LEDs were used as a source of electromagnetic radiation (table 1).

The measurement results were obtained in the form of hodograph curves of the impedance - plots of $Z(\omega)$ in the coordinates $Z'$ and $-Z''$, corresponding to the resistive and capacitive properties of the system, respectively (figure 3).

As a rule, the impedance spectrum of polycrystalline materials in the complex plane has two semicircles, indicating the contribution to the overall conductivity of the material volume of the grains and their boundaries.
Table 1. Main parameters of the LEDs used in the experiment.

| Parameter                  | LED model         |
|----------------------------|-------------------|
|                            | LEDis625-R5-A30   | LEDis590-R5-A30 | LEDis505-R5-A30 | LEDis470-R5-A30 |
| Color                      | Red               | Yellow          | Green           | Blue            |
| Wavelength, nm             | 623-657           | 588-592         | 503-507         | 467-473         |
| Brightness (20 mA), mCd    | 3500-5500         | 3500-5500       | 6500-8500       | 2500-4500       |
| Electrical power, mW       | 35-65             | 35-65           | 60-95           | 60-95           |
| Forward voltage, V         | 1.8-2.2           | 1.8-2.2         | 3.0-3.2         | 3.0-3.2         |

The presence of only one circle indicates a high degree of homogeneity of the sample. In the analysis of the experimental results it is common to use an approximation of equivalent circuits. Obtained frequency dependences of \( Z' \) and \( Z'' \) are compared to the known characteristics of the basic impedance model circuits. Received during the experiments results (figure 4) can be associated with a parallel circuit consisting of resistor \( R_p \) and capacitor capacity \( C_p \). The equation describing the graph can be written as:

\[
\left( Z' - \frac{R_p}{2} \right)^2 + Z''^2 = \left( \frac{R_p}{2} \right)^2,
\]

that is a circle with the coordinates \((Z'\) and \(-Z''\)). The point at which the arc intersects the axis (on the right site) corresponds to the active impedance \( Z' \) in the "volume" of the sensor.

The dependence of the complex dark impedance versus frequency has two main regions: low frequency (less than 10 kHz) and high frequency (more than 20 kHz) (figure 5 (a)). In the low-frequency region the main contribution to the complex impedance makes the active component \( Z' \). When electromagnetic radiation from the visible LEDs exposes the surface of the MOSFET structure, at high frequencies both real \( Z' \) and the imaginary \( Z'' \) components of the complex impedance region remain without change.

But at low frequencies we recorded significant changes in the components of the impedance. Significant reduction of the real component was obtained, while the imaginary component increased. Hodograph curves shifted up along the axis \( Z'' \), which corresponds to a change in capacitance of the system. The complex impedance increased about 2 times for the blue and green LEDs and a little less for the red and yellow ones.
This difference may be explained by differences in the energy of the LED radiation (table 1). In the future experiments effect of radiation in ultraviolet and infrared range will be investigated.

Optical activation of the adsorption centres in the SnO$_2$ gate leads to the additional accumulation of positive charges on top of the gate H$^+$. Positive charge caused broadening of the channel in MOSFET sensor, resulting to lower real component of the impedance. These results show that optical activation allows to detect significant lower concentrations of the hydrogen contained gases.

3. Conclusion
Studies have shown the ability to create sensors for hydrogen and hydrogen contained gases, operating at room temperature with a sufficiently low threshold. This result was achieved using field effect transistor with a tin dioxide gate in combination with original technique of optical activation of the adsorption centers.

References
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**Figure 5.** Dependence of the complex impedance vs. frequency without radiation (a) and with radiation from yellow LED (λ=590 nm) (b).