Investigation of MIS-sensor sensitivity to vapor of unsymmetrical dimethylhydrazine in air

D V Filipchuk\textsuperscript{1,2}, A V Litvinov\textsuperscript{1}, M O Etrekova\textsuperscript{1,2} and D A Nozdrya\textsuperscript{2}

\textsuperscript{1}Department of Solid State and Nanosystems, National Research Nuclear University “MEPhI”, 115409, Russia, Moscow, Kashirskoe highway, 31
\textsuperscript{2}OOO NPF “INKRAM”, 109341, Russia, Moscow, Lyublinskaya st., 151, room 222

E-mail: dima_filipchuk@mail.ru

Abstract. The sensitivity of MIS-sensor to the products of thermal decomposition of unsymmetrical dimethylhydrazine was investigated. It is shown that MIS sensor is able to detect the concentrations of the test substance by the means of the certain products of its thermal decomposition (ammonia and nitric dioxide).

1. Introduction

This article is devoted to the investigation of the sensitivity of a MIS-sensor to vapor of unsymmetrical dimethylhydrazine (UDMH) in air. UDMH is one of the components of rocket fuel, which is actively used in Russian space industry. This substance is extremely dangerous for human organism. Even its small concentrations can cause a disruption in the work of internal organs and central nervous system.

There is no simple, affordable and automatic (without human participation) method of detecting the concentrations of UDMH. Available methods (chromatography, ion mobility spectrometry) are very complex and have to use an expensive equipment and high qualification of personnel.

A MIS-sensor can be used to detect concentrations of UDMH for some reasons. It has very high sensitivity to ammonia and nitric dioxide (at the level of parts of ppm [1,2]), which are some of products of thermal decomposition of UDMH [3,4]. If, during the thermal decomposition of UDMH, concentrations of ammonia and nitric dioxide are formed and its values exceed the minimum detectable by a MIS-sensor, then the MIS-sensor can be used to detect the vapor of UDMH in air.

2. Scheme of MIS-sensor

Scheme of MIS-sensor is shown in Figure 1. A silicon plate of KEF-15 (4) coated with a $\text{SiO}_2$ film (3) is used as a basis of the structure. A $\text{Ta}_2\text{O}_5$ film (2) is applied to $\text{SiO}_2$ film. Its thickness is about 100 nm. Palladium film (30 nm) is applied to $\text{Ta}_2\text{O}_5$ film. The MIS-structure is maintained at a constant temperature of 100-150 $^\circ$C. Its temperature is measured by thermistor (10) and stabilized by the electronic circuit of the gas analyzer.

A MIS-structure is a capacitor whose capacitance depends on the voltage applied to it (gate voltage). This dependence is called volt-farad (C-U) characteristics. When a certain gas appears above the palladium film, C-U characteristics shifts to the left or right along the voltage axis. It becomes possible to detect the change of MIS-sensor capacitance at a fixed gate voltage (Figure 2) [5,6].
3. Description of the experiment
An experimental facility was assembled to conduct experiments on thermal decomposition of UDMH. Its scheme is shown in Figure 3.

![Figure 3. Scheme of facility. 1 – glass container for dilution of UDMH, 2 – reactor, 3 – MIS-sensor, 4 – electric pump, 5 – electronic circuit, 6 – PC.](image)

An experimental facility worked as follows. The concentrations of UDMH was created by dilution in the air of the glass container. Liquid UDMH was used in the work, which was injected into glass container by chromatographic syringe. Liquid UDMH evaporated in the container and then gas mixture of UDMH appeared. By means of the pump the gas mixture was supplied from the glass container to a heated reactor (2). Reactor is a quartz tube wrapped with nichrome wire. When the current passed through the nichrome wire, the air inside the quartz tube was heated to a temperature of 800 °C (precisely at this temperature the pyrolysis of UDMH proceeds most efficiently [3]). All products of thermal decomposition were removed by means of airflow to the MIS-sensor (4). The signal from MIS-sensor was processed using the electronic circuit (5) and PC (6).
Before carrying out all experiments, calibration curves of two MIS-sensors for ammonia and nitric dioxide was obtained.

4. Results and its discussion
The ammonia concentration at the outlet of the reactor as a result of the thermal decomposition of UDMH should depend on the concentration of UDMH created in the glass container. To determine the relationship between these values, the following experiment was carried out. In the glass container, concentrations of NDMH 0.015, 0.06 and 0.12 ppm were created, and then the response of the MIS sensor was measured. The values of the sensor response were recalculated into ammonia concentration values using a calibration curve. The results of the experiment are shown in Figure 4.

As can be seen from the graph, as the concentration of UDMH in the glass container increases, the ammonia concentration at the reactor outlet also increases. This confirms the fact of the pyrolysis of UDMH, and also the fact that with the help of a MIS-sensor it is possible to detect concentrations of UDMH by the means of the one of its thermal decomposition products (ammonia).

![Figure 4. Dependence of ammonia concentration at the outlet from the reactor on the concentration of UDMH, created in a glass container.](image)

The article [4] describes a method for detecting the concentration of UDMH from one of its thermal decomposition products (nitric oxide) at a temperature of 600-1000 °C in the presence of nickel as a catalyst. When nitric oxide is released, it is oxidized to nitrogen dioxide, to which the MIS sensor exhibits a high sensitivity.

Several tubes of nickel foil were installed in the reactor. Then it was heated to 800 °C, and through it a gas mixture was passed from a glass container containing a certain concentration of UDMH (0.06 and 0.12 ppm), and the response of the MIS sensor was measured. Using the calibration curve for nitrogen dioxide, the response values were recalculated to values of nitrogen dioxide concentration. The results of this experiment are shown in Figure 5.
Figure 5. Dependence of nitric dioxide concentration at the outlet from the reactor on the concentration of UDMH, created in a glass container.

As can be seen from the graph, as the concentration of NDMH in the glass container increases, the concentration of nitrogen dioxide at the reactor outlet also increases. This confirms the fact of the pyrolysis of UDMH, and the fact that with the help of a MIS-sensor it is possible to detect concentrations of UDMH by the means of the one of its thermal decomposition products, nitrogen dioxide.

5. Conclusion
Both experiments show that a MIS sensor can be used to detect UDMH vapor by the means of the two products of its thermal decomposition, ammonia and nitrogen dioxide (last one appears only in the presence of nickel), whose concentrations during pyrolysis of UDMH can be easily detected by used MIS-sensors.

References
[1] Emelin E V, Nikolaev I N and Sokolov A V 2005 Sensitivity of MIS-sensors to concentrations of different gases Sensors and systems 10 37-9 (in Russian)
[2] Bolodurin B A, Borisenkov I L, Korchak V Yu, Litvinov A V, Nozdrya D A, Pomazan D V, Filipchuk D V and Etrekova M O 2016 Comprehensive research of sensitivity of MIS-sensors with Pd-SiO2-Si, Pd-Ta2O5-SiO2-Si structures to the content of various gases in air Russian chemistry journal 3 96 (in Russian)
[3] Ushakova V G, Shpigun O N and Starygin O I 2004 Peculiarities of chemical transformation of UDMH and its behavior in environmental objects Polzunovskij vestnik 4 3-6 (in Russian)
[4] Rounbehler D R 1984 Detection of hydrazine compounds in gaseous samples by their conversion to nitric oxide-yielding derivatives US4775633
[5] Nikolaev I N, Litvinov A V and Emelin I N 2006 Model of sensitivity of MIS-sensors to concentrations of different gases Sensors and systems 7 66-73 (in Russian)
[6] Nikolaev I N, Kalinina L I and Litvinov A V 2007 New type of shallow traps for molecules with dipole moments in dielectrics Solid State physics 6 1065-9 (in Russian)