Indication and identification of hazardous substances

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Sensitivity of MIS Capacitors with Palladium Electrode to Aromatic Nitro Compounds Vapor

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Abstract – The temperature and time modes of the high-energy aromatic nitro compound vapor pyrolysis have been studied. The optimal conditions for reliable concentration measurement of gas-phase decomposition products of nitro compound molecules using MIS capacitors based on palladium-dielectric-silicon structures were determined. It has been established that the sensitivity of MIS sensors to nitroaromatic compound vapor appears when a gaseous sample is exposed to a temperature of 400°C and reaches a maximum at 500 – 550°C with an average duration of vapor heating of 1 s.

Keywords: MIS capacitors, gas concentration, ppb-level gas sensor, pyrolysis, nitrogen dioxide.

Индикация и идентификация опасных веществ

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Чувствительность МДП-конденсаторов с палладиевым электродом к парам ароматических нитросоединений

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Аннотация – Исследованы температурный и временной режимы пиролиза паров высокоэнергетического нитросоединения ароматического ряда. Определены оптимальные условия надежного измерения концентрации продуктов газофазного разложения молекул нитросоединения с использованием МДП-конденсаторов на основе структур палладий-диэлектрик-кремний. Установлено, что чувствительность МДП-сенсоров к парам ароматического нитросоединения появляется при воздействии на газообразную пробу температуры 400°C и достигает максимума при 500 – 550 °C при длительности нагрева паров в среднем 1 с

Ключевые слова: МДП-конденсаторы, концентрация газа на уровне ppb, газочувствительный датчик, пиролиз, диоксид азота.

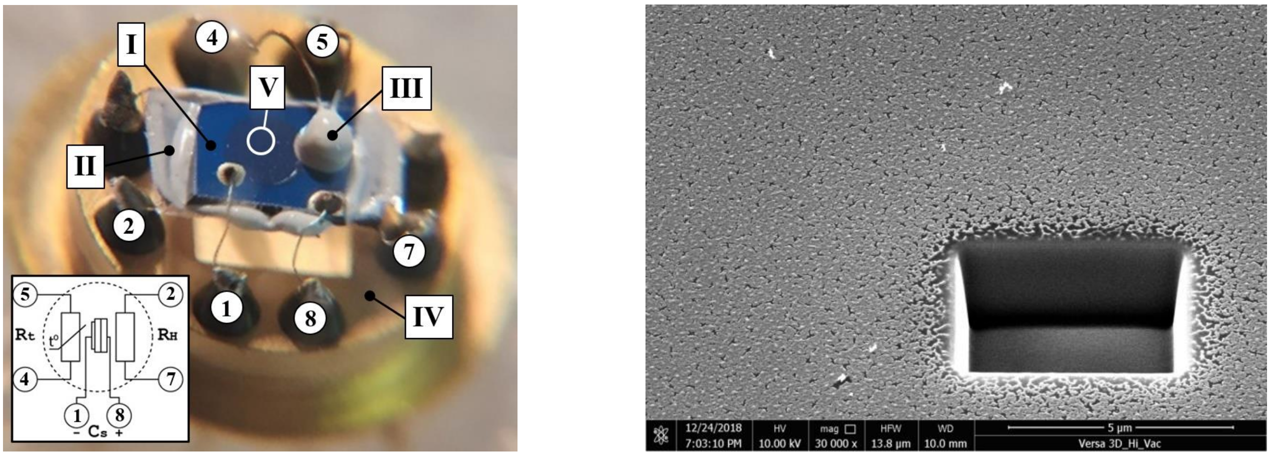
INTRODUCTION

To ensure the safety of critical infrastructure facilities (transport, enterprises and places of mass residence of people), various methods and means are used, which include systems and devices for the rapid detection of high-energy chemical compounds and mixtures based on them, which pose a potential danger to life and health. An example is 2,4,6-trinitromethylbenzene, which can be detected even at low vapor concentrations (on the level of several ppb, or about 10^{-11} g/cm^3 at room temperature [1]) using the dogs of mine search service [2] or special technical means [3–7]. There are commercially available devices based on various physical and chemical methods: nuclear physics, activation analysis, spectroscopic, chemical rapid tests and chemoluminescence. For example, devices based on mass spectrometry and ion mobility spectrometry have nitro compounds vapor sensitivity thresholds on the order of ppt units (10^{-14} g/cm^3) and an operating mass range from 10^{-11} to 2×10^{-7} g [4, 5, 8], which is enough for the rapid detection of traces of hazardous substances. However, one of the disadvantages of such devices is their relatively large weight and size parameters. Due to alternative physical measurement methods, analytic instruments, based on microelectronic sensors, can be reduced in size and weight [9 – 11]. However, relatively high sensitivity thresholds (tens and hundreds of ppb) still limit the usage of such instruments for the detection of low concentrations of gases and vapor of organic nitro compounds. Most solid-state gas sensors [9, 12, 13] operate at elevated sensor temperatures, requiring the use of heating elements and temperature sensors to control the process temperature. One of the ways to miniaturize and improve the metrological characteristics of semiconductor gas sensors, as well as gas analytical instruments and systems based on them, is the creation of integrated sensors (including the integration of sensors themselves, heating elements and thermosensitive elements). Among semiconductor gas-sensitive sensors, MIS capacitors and MIS transistors have the best technological compatibility with integrated circuit elements. Since the 1990s, NRNU MEPhI has developed and researched both discrete and integrated gas-sensitive sensors based on capacitors and transistors with various MIS structures. Many years of international experience in the development of semiconductor gas-sensitive sensors based on sensitive elements with MIS structures allow us to trace the stages of improving the metrological and operational characteristics of MIS sensors in the process of developing micro and nanotechnologies [14–18]. In particular, within our research the sensitivity thresholds have been reduced from tens of ppm to tens of ppb [18, 19], the stability of responses has been increased [20] and sensor housing improved [21].

In order to assess the possibility of using MIS capacitor sensitive elements (hereinafter MIS sensors) for measuring low concentrations of nitro-containing gases and detecting traces of high-energy compounds, a number of theoretical and experimental studies were carried out [22, 23]. Nevertheless, studies of the design and technological parameters influence of such elements on the metrological characteristics of sensors and devices based on them, as well as the development of methods for their practical use, remain in demand. This paper presents the results of the temperature and time modes study of aromatic nitro compound vapor pyrolysis to achieve and optimize conditions for reliable measurement of low concentrations of nitro-containing gases (as a nitroarenes molecules products of gas-phase decomposition) by means of MIS capacitors with a Pd electrode.

EXPERIMENTAL

The object of research during experiments in this work is MIS sensor with a control electrode made of porous palladium with a thickness of 150 – 200 nm deposited on a dielectric by means of pulsed laser deposition (PLD) [18]. Appearance, connection diagram of MIS sensors and a photograph of the Pd surface are shown in Fig. 1. Pores in a palladium film 5 – 15 nm in size tend to merge into large pores up to 500 nm long and 50 nm wide (Fig. 1, *b*).



a) *b*)

Fig. 1. (*a*) Appearance and connection diagram of the MIS sensor: I – gas-sensitive MIS capacitor with capacitance C_S; II – resistor heater with resistance R_H; III – thermistor with resistance R_t, the value of which depends on temperature; IV – metal-ceramic house; V – area of the SEM photograph, see next. (*b*) SEM photograph of the Pd electrode surface with a 4×5 μm dimple.

Such morphology allows gas molecules to easily penetrate up to the metal-insulator interface, adsorbed on active trapping centers (“traps”) formed due to the high energies of deposited particles in the PLD process, and change the distribution of charges and electric field in the MIS structure. As a result, there is a “deformation” of the capacitance-voltage characteristic (CVC) of the MIS capacitor, while the magnitude of the shift of the CVC along the voltage axis is proportional to the gas concentration. The operation principle of MIS sensors, methods for setting operating modes and measuring the useful signal are described in detail in [24].

The sensors were calibrated for low nitrogen dioxide concentrations using a NO_2 microflow source and a thermal diffusion type gas and vapor generator equipped with auxiliary gas flow controllers for additional dilution with a flow of up to 15 L/min. The calibration results are shown in Fig. 2.

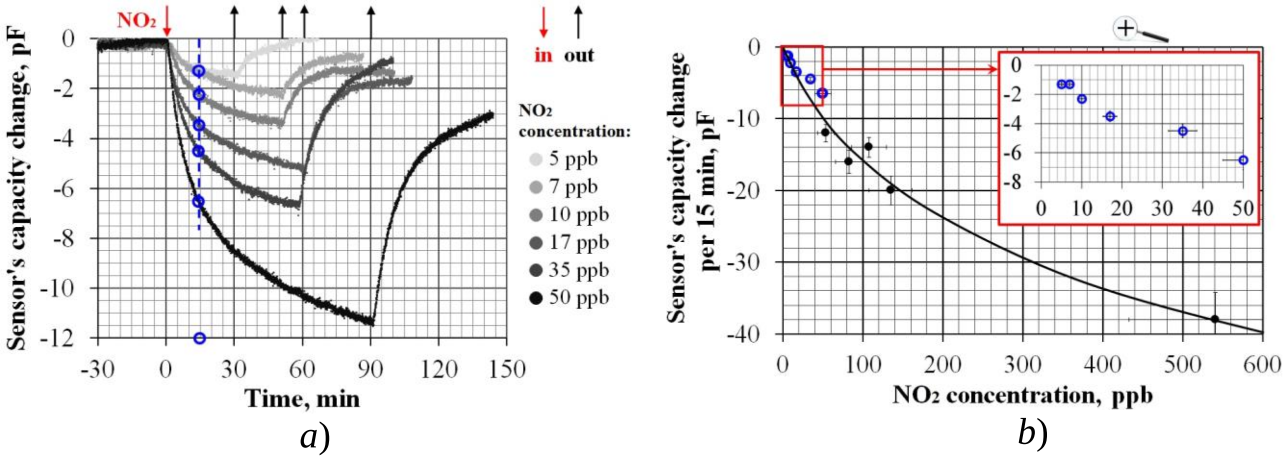


Fig. 2. Calibration results of MIS sensor sensitivity to NO_2 with operation sensor's temperature 100°C (type of MIS structure Pd-SiO_2-Si): (*a*) dynamics of the sensor's capacity change over time when concentration is established ("in") and removed ("out"); (*b*) calibration curve of the sensor's capacity change depending on NO_2 concentrations per 15 min of gas "in".

Relatively long values of the response time parameters (Fig. 2, *a*) are typical for adsorption-type gas-sensitive sensors operating in the range of ppb concentrations [25, 26]. For further experiments on the nitro compound vapor thermal decomposition, a calibration curve was consciously applied corresponding to incomplete responses for 15 min after establishing various NO_2 concentrations (Fig. 2, *b*). This is due to the peculiarities of experiments with nitro compound samples, which will be described below.

The scheme of experimental installation, on which the MIS sensor's sensitivity to nitro compound vapor was studied, is shown in Fig. 3. A photograph of the installation was shown earlier in the publication [22].

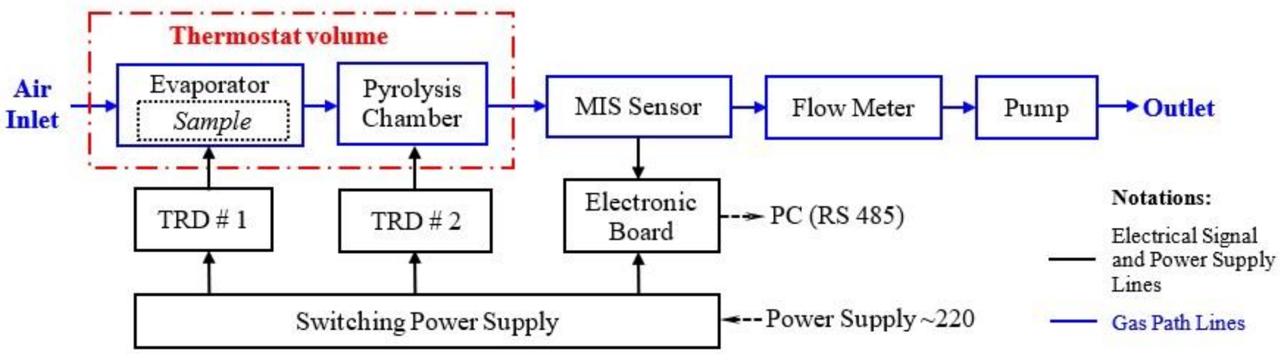


Fig. 3. Structural-functional diagram of the experimental setup for studying the sensitivity of MIS sensors to aromatic nitro compound vapor. TRD are thermoregulation devices to maintain and control the evaporator's and pyrolysis chamber's temperature.

A sample of nitro compound traces on the foil was placed in the evaporator, where the sample was heated up to 40 – 80°C in a controlled manner to increase the vapor pressure and create a stable concentration of the nitro-containing gas. In the pyrolysis chamber the evaporated sample was heated to 400 – 700°C, after which it fed to the MIS sensor to detect the concentration of pyrolysis products. The operation principle of the installation was described in more detail in [22]. Nitro compound samples were prepared by the method of controlled sample dissolution of the starting material in high purity acetone using a laboratory electronic scales CAUW-120D (RMS ≤ 0.02 mg) and a pipette dispenser (no worse than ± 3%).

The first series of experiments was aimed at establishing the nitro compound samples' productivity (with a substance mass of at least 1 mg) depending on the evaporator heating temperature and evaporation area (Fig. 4). The evaporator temperature of 70°C was taken as the optimal value, which is sufficient to maintain the sublimation rate at the level of 1.7 ± 0.3 μg/min from an area of 5 ± 1 cm^2, which, at a sampling flow of 0.5 L/min, corresponds to the concentration nitro compound vapor at the level of 3.5 ng/cm^3 (≈ 380 ppb). As can be seen from Fig. 4, data on the evaporation rate of nitro compound are confirmed in several samples at different temperatures, and the experimental measurement error decreases as the evaporation area of the nitro compound samples increases. The pyrolysis chamber design described in [22] at a sampling flow of 0.5 L/min allows exposing nitro compound vapor to high temperatures for about 1 s.

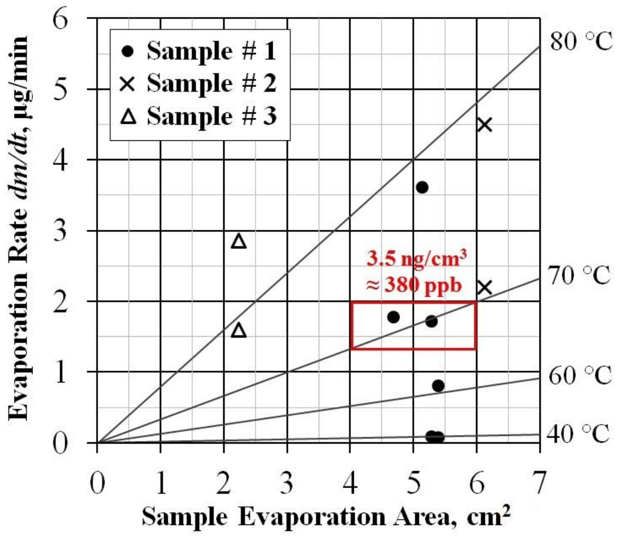


Fig. 4. Experimental data on the evaporation rate of the samples *dm*/*dt* with an initial mass of a substance for samples #1–3 of at least 1.4 ± 0.2 mg depending on the evaporator heating temperature and evaporation area of the sample (sampling flow rate 0.5 L/min).

The next step was to determine the pyrolysis chamber's optimal heating temperature to maintain an efficient process of nitro compound vapor's pyrolysis in the gas phase according to the radical mechanism with the NO_2 group's elimination. The efficiency criterion in this case was the dynamics and magnitude of the MIS sensor's response (electric capacity change) to pyrolysis products. The experimental results are shown in Fig. 5 and Fig. 6.

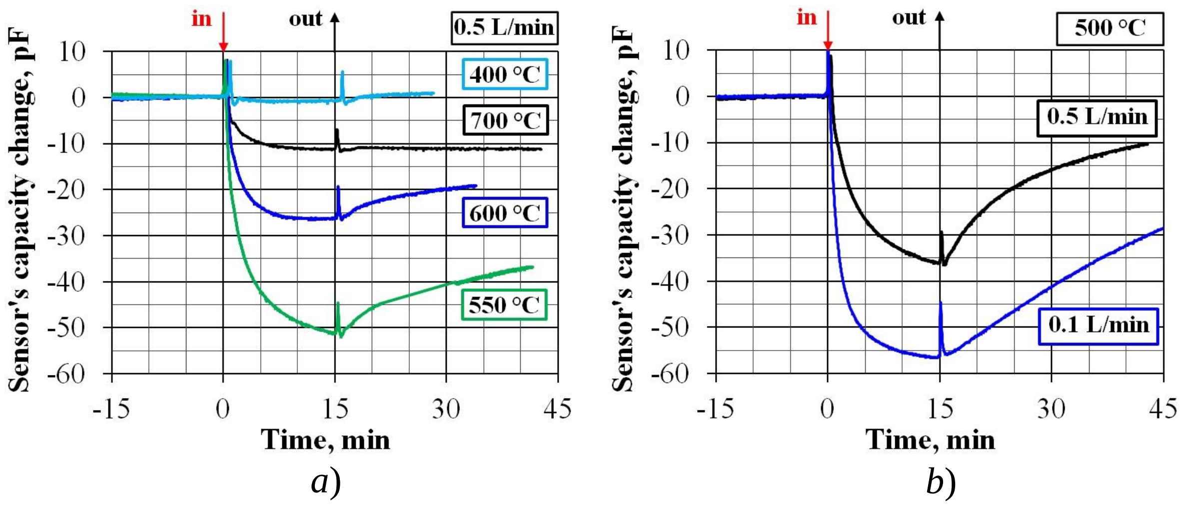


Fig. 5. (a) MIS sensor responses to nitro compound vapor pyrolysis products with a concentration of about 3.5 ng/cm^3 (380 ppb; the initial mass of nitro compound in the sample is at least 1 mg; evaporation area 5 ± 1 cm^2) depending on the pyrolysis chamber heating temperature. Sampling flow 0.5 L/min. (b) Influence of the sampling flow on the sensor response at a fixed pyrolysis chamber's heating temperature of 500°C (under the same nitro compound vapor concentration about 3.5 ng/cm^3).

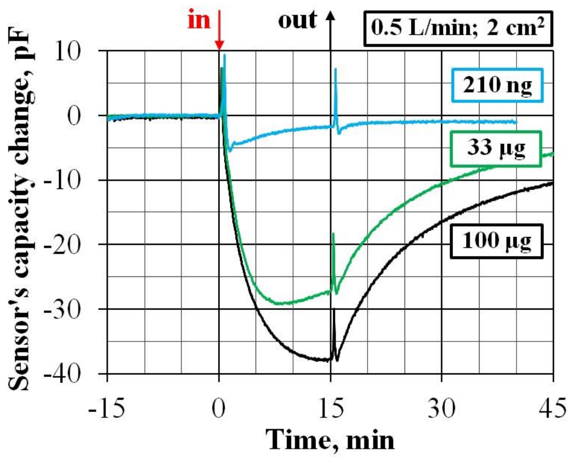
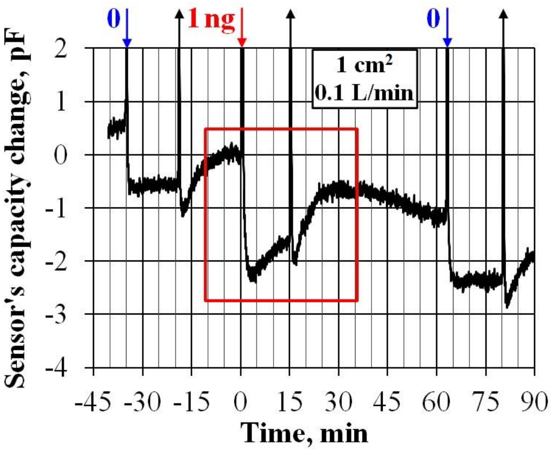


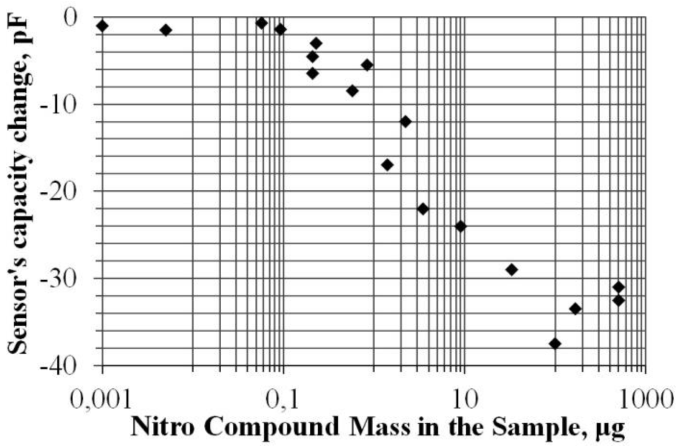
Fig. 6. An illustration of the decrease in the nitro compound vapor concentration during the experiment due to the small initial mass of the nitro compound in the sample (less than 100 µg at an evaporation area of 2 cm^2) and a significant reduction in the evaporation area during 15 min of the sample heating in the evaporator. The pyrolysis chamber's heating temperature is 500°C.

As can be seen from Fig. 5, the MIS sensor's sensitivity to nitro compound vapor appears when the sample is exposed to a temperature of 400°C in the pyrolysis chamber. As the temperature rises (up to approximately 550°C), the response increases, and then (from 550 to 700°C) decreases, while the responses' time parameters increase, which indicates a change in the reaction mechanism and, as a result, pyrolysis products. An increase in the vapor's exposure detention under heating due to a decrease in the sampling flow (Fig. 5, *b*) also affects the pyrolysis mode. Thus, using the MIS sensor, it was possible to experimentally confirm the data of quantum chemical calculations [27] and establish the maximum sensor's response when a nitro compound vapor sample is exposed to a 500 – 550°C temperature for a 1 s average duration.

In further experiments to determine the MIS sensors' sensitivity threshold to the nitro compound vapor's pyrolysis products, the values of the pyrolysis chamber heating temperature of 500°C and the sampling flow of 0.5 L/min were taken as the optimal, at which the sensor response for 15 min to the nitro compound concentration 380 ppb amounted to 36 pF. According to the graduation in Fig. 2, *b*, this response value corresponds to a concentration of 460 ppb NO_2 in the products of nitro compound pyrolysis, which correlates with the error of the experimental technique and indicates the nitroarene molecules' pyrolysis process by the radical cleavage mechanism of the C–N bond with the separation of one NO_2 group [27]. However, as the nitro compound mass in the samples decreased, their productivity fell directly during the experiment due to the evaporation area's instability (Fig. 6). Therefore, to record the sensor response to low nitro compound vapor's concentrations, including 1 ng (Fig. 7, *a*), the sample evaporation area was reduced first to 2 cm^2, and then to 1 cm^2, while the sampling flow was also reduced to 0.1 L/min. For the experiment's purity, each measurement for 1 ng of nitroarene detection was preceded by a series of measurements with empty foil, which was subsequently used as a substrate for the sample (Fig. 7, *a*).



a)



b)

Fig. 7. (*a*) MIS sensor's response to a 1 ng nitro compound sample (the beginning moment of the concentration exposure is indicated by the red down arrow). The zero next to the blue down arrow indicates an empty foil measurement. The black arrows up indicate the end moments of the concentration exposure. (*b*) Experimental data on the dependence of the MIS sensors' response of the nitro compound mass in the sample with an evaporation area from 1 to 6 cm^2 and sampling flow from 0.1 to 0.5 L/min.

Summary experimental data on the dependence of the MIS sensors' response of the nitro compound mass in the sample are shown in Fig. 7, *b*.

Assuming that 1 ng of nitro compound evaporated completely in 3 min (Fig. 7, *a*), we can estimate the concentration of nitroarene vapor as 1 ng/(3 min×0.1 L/min) = 3.3 ng/L, what means 3.3×10^{-12} g/cm^3. However, reducing the flow to 0.1 L/min could increase the response due to the nitro compound vapor thermal decomposition with the formation of one or more NO_2 molecules (Fig. 5, *b*). According to the graduation in Fig. 2, *b*, the limit of NO_2 concentration detection (LOD) for the MIS sensor is at the level of 2 – 3 ppb, which, in terms of nitro compound vapor, is 10^{-11}

g/cm^3. Therefore, it is possible to estimate the nitro compound vapor LOD for the MIS sensor in this work from 10^{-11} to 10^{-12} g/cm^3.

It is clear that in order to maintain a high level of MIS sensors' sensitivity to nitro compound vapor at the stage of a commercial product, a margin of sensitivity is required and, as a result, a search for ways to improve the technology for manufacturing gas-sensitive MIS structures. The beginning of this path was laid in [19, 20], where the results of a sensitivity comparison of MIS sensors with films of various materials (obtained by different physical-chemical methods) under a Pd electrode at ppb-concentration of NO_2 and ppm-concentration of H_2 are presented. The effect of a significant increase in the MIS sensors' sensitivity to NO_2 is also described there when an SnO_2 thin layer, obtained by reactive magnetron sputtering, is introduced into the Pd-SiO_2-Si structure. To be able to estimate the increase in the sensitivity level to NO_2 in Fig. 8 shows the response of MIS sensor with the Pd-SnO_2-SiO_2-Si structure at a concentration of 110 ppb. As can be seen, the change in the sensor's electrical capacitance is maximum at a bias voltage of minus (2.2 ± 0.7) V and is 210 ± 10 pF, which is an order of magnitude higher compared to the similar response of MIS sensors with the Pd-SiO_2-Si structure (see Fig. 2, *b*).

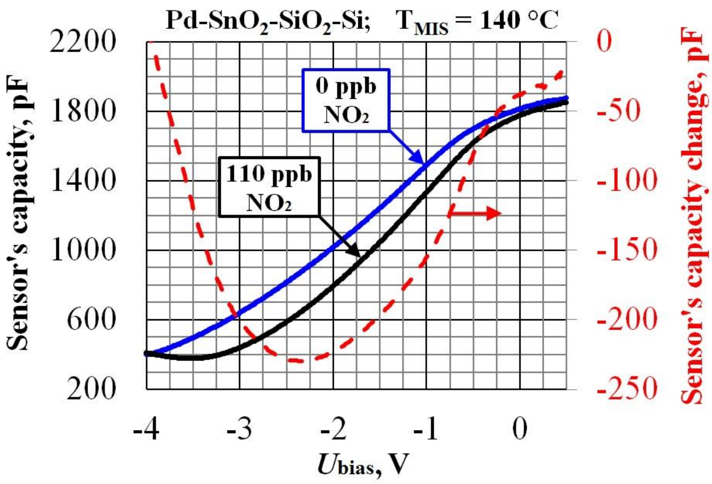


Fig. 8. Shift in the CVC of the MIS sensor with the Pd-SnO_2-SiO_2-Si structure under the act of 110 ppb NO_2. The blue solid line is the CVC of the sensor in an atmosphere of the clean dry air, the black line is the CVC in an environment of 110 ppb NO_2 in the air. The red dotted line is the magnitude of the change in electric capacitance under the influence of gas depending on the bias voltage applied to the electrodes of the MIS structure.

It was shown in [19, 23] that such an increase in the sensitivity to NO_2 due to the improvement of the technology for manufacturing capacitive MIS structures for gas sensitive sensors based on them makes it possible to improve the LOD parameters of NO_2 (and, consequently, the LOD of nitro-containing gases) by at least five times. In particular, due to this, the results of this work have received practical implementation in the design and creation of the first of its kind prototype detector of nitro-containing substances based on the MIS sensor [23].

CONCLUSION

Various temperature and time modes of high-energy nitro compound vapor pyrolysis in the gas phase have been studied. Optimal modes have been established for using the pyrolysis method in determining low concentrations of nitro-containing gases using sensors based on MIS capacitors.

It has been established that the MIS sensor's sensitivity to nitro compound vapor appears when a gaseous sample is exposed to a temperature of 400°C with an average of 1 s. The MIS sensor's response to nitro compound vapor is maximized when a gaseous sample is exposed to a temperature of 500 – 550°C with an average exposure time 1 s.

The limit of detection for nitro compound mass and vapor concentration in the air by MIS sensors with the Pd-SiO_2-Si structure were established: 1 ng and $10^{-11} – 10^{-12}$ g/cm^3, respectively, which can be further improved due to the effect of increasing (on the order) of the MIS sensor's sensitivity to NO_2 through the introduction into the Pd-SiO_2-Si structure of the SnO_2 layer, obtained by reactive magnetron sputtering.

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CONFLICT OF INTERESTS:

The authors declare no conflict of interests.

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