Hydrocarbon and Fluorocarbon Monitoring by MIS Sensors Using an Ni Catalytic Thermodestructor

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Abstract—An increase in the number of gases detectable by sensors based on Pd–SiO₂–Si (MIS) and Pt–LaF₃–Si₃N₄–SiO₂–Si (MEIS) structures was achieved by the application of an external catalyst element (CE). It was shown that as a result of the decomposition of hydrocarbon and fluorocarbon molecules on a Ni coil (CE), the products detectable by metal-insulator-semiconductor (MIS) and metal-electrolyte-insulator-semiconductor (MEIS) sensors are formed. The simultaneous catalytic oxidation of hydrocarbons and their thermal decomposition result in an optimum CE temperature of about 1050 K for propane. The kinetics of the thermal decomposition of gases on Ni were investigated. The activation energy of the reaction for C₃H₈ and the enthalpy in the case of CF₃I were estimated.

Index Terms—Fluorocarbons, hydrocarbons, metal-insulator-semiconductor (MIS) and metal-electrolyte-insulator-semiconductor (MEIS) sensors, thermal decomposition.

I. INTRODUCTION

Gas sensors based on metal-insulator-semiconductors (MISs) and structures with an additional undergate layer of solid electrolyte LaF₃ [metal-electrolyte-insulator-semiconductor (MEIS)] have high sensitivity to hydrogen, fluorine, and hydrogen fluoride. An extension of the number of detectable gases can be achieved by means of a considerable increase in sensor working temperature. Application of wide-bandgap semiconductor silicon carbide (SiC) instead of silicon gives the possibility of increasing the working temperature of the sensor to ~1000 K. This leads to the registration of hydrocarbons by MIS sensors [1] and chlorofluorocarbons (Freon) by sensors with LaF₃ layers [2].

Unfortunately, a high working temperature results in a decrease in sensor lifetime, which is due to oxidation of the ohmic contact. Application of an external catalyst element (CE) gives the possibility of avoiding sensor degradation at high temperature. The high-temperature catalytic decomposition of gas molecules leads to gaseous products, which can be detected by sensors working at the usual temperature [3].

The possibility of using Ni as a material for the external thermodestructor was investigated in this paper. The high catalytic activity of nickel and its stable operation in fluorine-containing atmosphere are the reasons for our interest on this metal [4].

II. EXPERIMENT

Sensors based on Pt–LaF₃–Si₃N₄–SiO₂–Si (MEIS) and Pd–SiO₂–Si (MIS) structures were used. The Pt–LaF₃–Si₃N₄–SiO₂–Si structures were prepared using an n–Si/SiO₂ (20 nm)/Si₃N₄ (80 nm) wafer with a donor concentration of 2.5 · 10¹⁴ cm⁻³. A backside ohmic aluminum contact was fabricated by vacuum evaporation of metal. LaF₃ (150 nm) layers were deposited on the insulator by thermal evaporation in a high-vacuum system. DC cathode sputtering in argon plasma through a metal shadow mask was used to deposit the Pt gate with an area of 3 mm². The thickness of the Pt gate of the structures was increased up to 400 nm to avoid the influence of the dipole moment of the polar molecules [5], [6], which can be generated during the reaction thermal decomposition.

The aging of the MEIS sensors, which work at room temperature, was observed. A method using a short heating pulse [7] was developed to maintain stable sensor response for a long time. The energy necessary for this sensor activation is only 10⁻³ J per day.

The Pd–SiO₂–Si-based sensors were manufactured as hybrid circuits. A gas-sensitive element (MIS capacitor) and temperature sensor (a silicon diode) were installed on a thin insulator wafer with resistive heater. The thermal sensor was used in the feedback circuit of the electronic controller. This controller stabilized the preset temperature of the gas-sensitive structure in a temperature range of 300–460 K with an accuracy of 0.2 K. Palladium gates (about 100 nm thick and 0.3 mm² in area) were formed by thermal laser-beam evaporation (laser ablation). The MIS sensor aging was not observed in all experiments (more than some hundreds of measurements).

The sensors were characterized by the high-frequency capacitance–voltage method using a Hewlett Packard 4284A type LCR meter. A computer-controlled system for the determination of the bias voltage shift at constant capacitance was used. The stationary value of bias voltage shift ΔU and the initial rate of bias voltage shift dΔU/dt were used as a sensor signal correlated with gas concentration.

Gas mixtures of Freon, fluorine, propane, or hydrogen in synthetic dry air were used in this paper. The gas was diluted with synthetic air using computer-operated mass-flow controllers to obtain desirable concentrations. The gas mixture passed first through the reactor (a quartz tube with a diameter of 0.4 cm
whose volume was equal to about 1.2 cm$^3$) with a CE (Ni wire coil) and then through a measurement cell with the sensors. The reactor and the measurement cell were connected by a 20-cm-long Teflon tube. An increase in tube length of up to 100 cm did not influence the sensor response and only led to increasing the “transport” time. The temperature of the thermodestructor was controlled by the measurement of the Ni coil resistance. The gas flow in the range of 1–6 cm$^3$/s was stabilized by a mass-flow-controller-based installation.

III. RESULTS AND DISCUSSION

A. Thermal Decomposition of Freons on a Ni Destructor

The following fluorochlorocarbons with and without hydrogen were investigated: CF$_3$–CH$_2$Cl (F133), CF$_3$–CH$_2$F (F134) and CF$_3$–CCl (F113). It can be assumed that hydrogen, fluorine, and hydrogen fluoride will be the products of the thermal decomposition of these gases [8]. The sensors based on the MEIS structure can detect H$_2$ [9], F$_2$ and HF [10] at room temperature. The sensor signal for hydrogen is opposite in sign to that for fluorine and hydrogen fluoride. Furthermore, the sensitivity to HF and F$_2$ is different. This could be used for preliminary conclusions about decomposition products. More complete information about the products of the Freon thermal decomposition on Ni can be obtained from mass-spectrometer measurements, but it is beyond the scope of this paper.

The MEIS sensor response curves for 5000-ppm F134 in air that passed through the reactor at different temperatures of the Ni thermodestructor are shown on Fig. 1. For all the Freons used in the experiments, both with and without hydrogen, positive values of the sensor response ($\Delta U > 0$) were observed. It means that the main products of the Freon decomposition reaction on Ni that cause the sensor signal are fluorine or hydrogen fluoride.

More detailed experiments were carried out with F133 and F113. The bias voltage shifts $\Delta U$ of the MEIS sensor, which depend on the Ni destructor temperature, for a concentration of these two gases of equal to 1000 ppm in air are presented in Fig. 2.

The sensitivity of the MEIS sensors to F$_2$ was measured in this paper and was about 120 mV/dec of the fluorine
concentration. The sensitivity to hydrogen fluoride is only 55 mV/dec [10]. The comparison of these sensitivity data leads to the conclusion that fluorine is the main product of decomposition. For F133, one molecule of F$_2$ is produced from Freon. There is no explanation for the high value of sensitivity for F113 of 280 mV/dec. The detailed investigation of the thermodecomposition of Freon will be done in future.

The sensor signal of $\Delta U = 150$ mV was observed at a concentration of 20-ppm fluorine in air. Thus, the partial pressure of the active component (calculated for F$_2$) corresponds to 2% of the Freon pressure in the middle range of the Ni temperature.

For the practical application of the external CE in the measuring sensor systems, the estimation of the value of the thermodecomposition reaction time necessary for the formation of detectable concentration of the product is important. The sensor signal as a function of the reaction time ($t = \text{reactor volume/gas flow rate}$) is shown in Fig. 4 for F113 and F133.

In the case of F133, an increase in the reaction time did lead to an increase in the sensor signal. Taking into account that the change of the sensor signal is proportional to the logarithm of the concentrations, it easy to show that for F133, dependence between the concentration of the detected components and the reaction time is linear. Decreasing the sensor signal from 150 mV at a reaction time of 0.63 s to 70 mV at a reaction time of 0.16 s is a result of decreasing the concentration by a factor of 3.9 ($\log C_1/C_2 = (150 - 70)/136$). This value is very close to the ratio of the reaction times. For F133, the conditions are leading to dynamic control.

In contrast to this, for F113, the equilibrium of the thermodecomposition reaction was observed, as proven by the nearly constant values in Fig. 4. The enthalpy $\Delta H$ of this reaction was estimated using the van Hoff equation, i.e.,

$$\frac{d \ln K}{d(1/T)} = -\frac{\Delta H}{R}$$

where $K$ is the equilibrium constant.

Because of only 2% decomposition, the Freon concentration can be regarded as constant, and the change in $K$ is proportional to the change in fluorine concentration. From the Nernst equation, $\ln(\dot{C})$ is $\Delta U$ divided by the sensitivity. The sensor signal $\Delta U$ versus the inverse Ni temperature is shown in Fig. 5. The value of the reaction enthalpy calculated from this dependence was equal to 40 ± 2 kJ/mol.

**B. Thermal Decomposition of Propane on Ni Destructor**

The interaction of propane C$_3$H$_8$ with a metal catalyst in the presence of oxygen leads to the decomposition and oxidation of hydrocarbon.

The oxidation results in the formation of water and carbon dioxide. The sensitivity of the MIS sensor to water vapor is rather small [11] and completely absent to carbon dioxide.

As a result of a competition between the decomposition and oxidation processes of propane, the optimum temperature of the CE, at which the concentration of products registered by a sensor is maximum, is observed. To estimate the working range of the CE temperature and for calibration of the MIS sensor, the influence of the Ni destructor temperature on the initial rate of the bias voltage shift $d\Delta U/dt$ under the action of 200-ppm hydrogen in air was analyzed (Fig. 6). The intensive hydrogen oxidation with an activation energy of about 18 kJ/mol starts at a CE temperature that is higher than 900 K.
The Pd–SiO$_2$–Si sensor signals $\Delta U$ and $d\Delta U/dt$ versus the CE temperature for 2000-ppm propane in air after passing through the reactor are shown in Fig. 7. The maximum sensor signal corresponding to 200 ppm of hydrogen in air is observed at a CE temperature of about 1050 K. The working temperature of the sensor was 403 K.

To determine the main product of the propane decomposition on Ni, the sensor signal as a function of working temperature of the gas-sensitive structure was investigated. The value of the activation energy $\Delta E_{\text{act}}$ was determined from

$$
\frac{d\Delta U}{dt} = \text{const} \cdot \exp \left( -\frac{\Delta E_{\text{act}}}{kT} \right).
$$

For hydrogen interaction with the Pd–SiO$_2$–Si sensor, the activation energy is in the range of 0.25–0.3 eV [12]. The estimation of the value of $\Delta E_{\text{act}}$ from the temperature dependence $d\Delta U/dt$ plotted in the Arrhenius coordinate for the product of the thermodecomposition of 2000-ppm propane in air at a CE temperature of 1000 K gives the value of 0.3 eV (Fig. 8). The typical values of the activation energy of the dissociation for different bonds of hydrocarbons are in the range of 350–460 kJ/mol [14].

The value of the reaction time for the formation of a detectable concentration of the thermodecomposition products is rather low. It gives the possibility of using the method of impulse CE heating. The result of the experiment with 2000-ppm propane is shown in Fig. 10. There is no sensor signal at a Ni destructor temperature of about 873 K. An impulse increase in a CE temperature of up to 993 K leads to the appearance of the MIS sensor response. The duration of the temperature impulse in the experiment was 20 s. The bias voltage shift $\Delta U$ did not reach the stationary value, but the concentration could be estimated from the initial rate of the bias voltage shift $d\Delta U/dt$. Practically, the pulse duration could be decreased in time, as is evident from the experiment. The next impulse of the
temperature after signal relaxation (about 60 s) gives the same sensor signal. The application of the impulse-heating method allows elimination of the influence of gas tubes and decrease in power consumption.

IV. CONCLUSION

The properties of Ni as a material for the external catalytic element were investigated. It was demonstrated that the MEIS and MIS sensors at their usual working temperature could detect the products of the thermodecomposition of Freon and propane, respectively. The nature of the reactions, which occur on the surface of the Ni catalyst, was investigated. It was shown that the kinetics of Freon thermodecomposition on Ni CE depends on the structure of the Freon molecule. The reaction of propane oxidation on Ni at a CE temperature of more than 1050 K caused the decrease in detectable product concentration. It is the reason for the maximum in the temperature dependence of the MIS sensor signal. The application of the CE impulse-heating method was demonstrated for propane thermodecomposition.

Pure gases were used in the experiments, and no changing of the Ni properties was observed. However, for practical application (ambient atmospheric air) of the Ni thermodestructor, poisoning of the catalyst could occur. It imposes certain restrictions on the opportunities of the considered method and on possible fields of application of sensors with catalytically active gates.

REFERENCES