Field-effect sensor for the selective detection of fluorocarbons

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Abstract

A chemical semiconductor sensor for the temperature range up to 400°C was developed using silicon carbide with an epitaxial layer of SiC as the substrate. Thin layers of LaF\textsubscript{3} and Pt were deposited on the semiconductor/insulator structure to form a three-phase boundary with the gas under investigation. The sensor was shown to be sensitive to fluorine, hydrogen fluoride and different fluorocarbons. The influence of the operation temperature on the sensor response signal was investigated in the range from room temperature up to 400°C. For the fluorocarbons CF\textsubscript{3}CH\textsubscript{2}F, CF\textsubscript{3}CCl\textsubscript{3}, CHClF\textsubscript{2}, CF\textsubscript{3}CH\textsubscript{2}Cl and CCl\textsubscript{3}F a selective detection was achieved at temperatures near to 400°C. The substantial role of the fluoride ion conducting material LaF\textsubscript{3} for the sensor detection principle was proven. A mechanism including the chemisorption of the fluorocarbon at the Pt surface and an insertion of fluorine into LaF\textsubscript{3} was discussed.

Keywords: Sensor; Selective detection; Fluorocarbons

1. Introduction

Chlorofluorocarbons have been implicated in atmospheric ozone depletion. Although they are no longer used in industrialised countries there is some production in developing countries. Furthermore, large amounts of chlorofluorocarbons are still in use and their waste treatment has to be developed. For control of these processes and other applications, where it is important to know the gas concentration, chemical sensors may be advantageous. These sensors should be selective for fluorine containing compounds. In addition, it may be useful to have the possibility of detection of the fluorohydrocarbons which are the alternative compounds to chlorofluorocarbons.

Sensors for the detection of fluorocarbons were developed using the metal–oxide-semiconductor type materials as V–Mo–Al\textsubscript{2}O\textsubscript{3}/ZnO [1] or sulphur doped SnO\textsubscript{2} [2]. Several fluorocarbons such as CF\textsubscript{3}CH\textsubscript{2}F or CCl\textsubscript{3}FCCl\textsubscript{3}F have been measured at a temperature of 400°C at concentrations down to 5 ppm. It is a disadvantage of these types of sensors that there is also sensitivity to other hydrocarbons and no selectivity to fluorine containing compounds. This effect can be improved only slightly by the addition of sulphur. Moreover, it is necessary to point out that reproducible measurements with sensors based on metal–oxide semiconductors require the presence of constant oxygen concentration in investigated gases mixtures. This can considerably restrict the field of application of these kind of sensors.

Recently, we developed a field-effect semiconductor sensor for the detection of fluorine and hydrogen fluoride in atmospheric air as well as in inert gases [3,4]. This sensor is a metal/insulator-semiconductor (MIS) device and has a structure Si/SiO\textsubscript{2}/Si\textsubscript{3}N\textsubscript{4}/LaF\textsubscript{3}/Pt. The active components of this sensor are the LaF\textsubscript{3} layer and the Pt gate electrode forming a three-phase boundary with the gas under investigation. Already at an initial stage of sensor development it was successfully proved that such a sensor can be used for the detection of fluorocarbons. That is a signal was found for 1,1,1,2-tetrafluoroethane at a temperature of 180°C [5].

Subsequent investigations showed that this temperature is too low for a stable sensor response and also for the detection of other fluorocarbons. Unfortunately, the silicon-based semiconductor field-effect sensors can be used only up to a temperature of about 200°C because of the small band gap of Si. Therefore, we developed a high temperature gas sensor based on the large band gap semiconductor silicon carbide (SiC) using the same sensitive layers (LaF\textsubscript{3} and Pt). It was demonstrated that at room temperature these sensors have

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sensing properties comparable to the silicon-based devices [6–8]. Using the SiC-based sensors it was shown that fluorine can be detected in the temperature range from room temperature up to 400°C. A very small change was observed in response kinetics with variation of the working temperature [7].

The operation principles which are common for all MIS chemical semiconductor sensors including the ISFET and GasFET are described already elsewhere (e.g. [9,10]). Therefore, we will give here only a brief description of the working principle of this device.

A scheme of the sensor structure and of the electrical potential distribution across this multilayer device is given in Fig. 1. The sensor consists of two components which are to be discussed. The first component contains the chemically sensitive layers and interfaces (potential difference $V_1$) and the second is the semiconductor part (potential difference $V_2$) which is a directly attached electronic amplifier of the sensor output signal. The specific interaction of one of the gas constituents with the sensitive layers (here LaF$_3$ and Pt) leads to concentration-dependent potential differences at the LaF$_3$/Pt interface ($V'_1$ or $V''_1$ for two different concentrations) that are comparable to the behaviour of ion selective electrodes.

On the other hand, the semiconductor/insulator structure has a voltage-dependent capacitance because of a change in the band bending in the semiconductor surface region. A typical capacitance/voltage (CV)-curve is shown in the inset of Fig. 2. Since the potential difference at the LaF$_3$/Pt interface is a part of the total voltage ($V$) applied to the sensor, the CV-curves are shifted along the voltage axis due to a concentration change by a value equal to the voltage difference $\Delta V=V'_1-V''_1$. If the capacitance $C_0$ of the MIS structure is fixed by an external electronic device, the potential changes can be detected from the steep part of CV-curves as this condition ($C_0=\text{const}$) means that the voltage drop in the semiconductor part ($V_2$) is constant. Hence the shift in externally applied voltage necessary to maintain a constant capacitance $C_0$ is equal but opposite in sign to $\Delta V$ caused by the sensing electrochemical reaction at the interface.

It was the aim of this work to investigate if the sensor based on electrochemical reactions at the three phase boundary LaF$_3$/Pt/gas can be used for the selective detection of fluorine containing molecules. Selectivity is required here for a group of compounds (fluorocarbons) compared to other molecules without a fluorine atom. The high mobility of fluoride ions in the LaF$_3$ even at room temperature and the insertion of fluoride ions into the LaF$_3$ from HF or F$_2$ are encouraging factors for expecting such selectivity.

2. Experimental

The semiconductor substrates (Joffe-Institute, St.-Petersburg) used in the present work were 6H-SiC chips
(3x3 mm²) with an epitaxial layer of SiC (n-type, carrier concentration (0.5x10¹⁶–8x10¹⁶ cm⁻³). A SiO₂ insulating layer (28 nm thick) was grown by thermal oxidation.

These samples were coated with a LaF₃ layer (240 nm) using a high vacuum evaporation technique. Platinum gate contacts (thickness 30 nm) were produced by sputtering in an argon atmosphere in a way leading to the formation of a three-phase boundary LaF₃/Pt/gas.

The capacitance of the samples was measured 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 measuring cell, containing the investigated structure, was designed specially for high-temperature measurements of the kinetics of gas sensing processes. The nickel cell had an aluminium oxide insulator and was heated by an external oven. The free volume of the cell was less than 0.2 cm³. The rear and top side contacts of the sensor (sample) holder were made of platinum and graphite, respectively. This cell assured low noise measurements of the capacitance of the sensor up to a temperature of 400°C even in fluorine containing atmosphere.

The gas sensitivity was measured under gas flow conditions. Pre-prepared mixtures of 10 000 ppm of fluorocarbons in synthetic air were mixed with synthetic air using computer driven mass flow controllers to obtain different concentrations of fluorocarbons in the range 200–10 000 ppm. Maximum gas flow velocity was 0.25 l/min.

3. Results and discussion

In Fig. 2 it is demonstrated that for our structure based on the large band gap silicon carbide semiconductor, CV-curves with a sufficient steepness can be obtained at high temperatures. For temperatures below 160°C the steepness of the CV-curves is smaller. This temperature dependence is due to the increase in ion conductivity in the LaF₃ layer as discussed in detail in [6].

The utilisation of the fluoride ion conducting material LaF₃ in contact with the platinum layer leads to a specific sensitivity to gases containing fluorine or hydrogen fluoride. For fluorine we found a good sensitivity at room temperature and temperatures up to 400°C. At room temperature a fast response and a sensitivity of 29 mV/lg p(F₂) was determined.

This sensitivity corresponds to the two electron electrochemical process taking place on the three phase boundary LaF₃/Pt/gas:

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

and the concentration dependence of the potential is given by the Nernst equation:

\[ E = E_0 + \frac{RT}{zF} \ln([\text{F}_2]) \tag{2} \]

where \( R \) is the gas constant, \( T \) the temperature, \( F \) the Faraday number, and \( z \) is the number of electrons transferred in the reaction, \( z=2 \) in reaction (1).

The results of the measurements at 330°C are given in Fig. 3. The possibility of fluorine detection is clearly shown even when the response rate is not very high. In the inset of Fig. 3 sensitivity is shown to be 132 mV/lg p(F₂) for this temperature.

In contrast to these results a fast and stable response to hydrogen fluoride was found only for temperatures smaller than 100°C as shown in Fig. 4 for a temperature of 23°C. At higher temperatures (about 200°C) a change of

![Fig. 3. F₂ sensitivity of a SiC based gas sensor at 330°C. (concentration in ppm in the upper part).](image-url)
gas concentration leads only to small and unstable shifts in voltage.

For temperatures higher than 350°C a specific behaviour, important for the understanding of the fluorocarbon detection, was found. As long as HF concentrations smaller than 2–3 ppm are introduced to the measuring cell with the sensor, practically no sensitivity was found (left part of Fig. 5). The voltage remains at the value specific for pure synthetic air or there is a shift equal to less than 3 mV but with a sign opposite to the direction expected for HF. If concentration reaches a certain critical value, the voltage is shifted after a certain delay time by several tens of mV (see Fig. 5). After this “pre-treatment” procedure a sensitivity for low concentrations was found.

This behaviour can be explained considering the surface chemistry of LaF₃. Using XPS, oxygen was shown [11] to be present in the surface. The oxygen content increases with temperature. Therefore, the delay and shift in signal can be considered to be an activation process due to an exchange of oxygen by fluoride. The concentration dependencies for high and low temperatures are given in Fig. 6. Sensitivities were determined to be 42 mV/lg p(HF) at 23°C and 85 mV/lg p(HF) at 370°C.

The sensitivity of the semiconductor sensor to fluorocarbons was investigated in mixtures of the gases under investigation with synthetic air. Gas concentrations were adjusted between 0 and 10000 ppm for CF₃CH₂F, CF₃CCl₃, CHClF₂, CF₂CH₂Cl and CCl₃F. Representative results are given in Figs. 7 and 8 for the detection of 1,1,1,2-tetrafluoroethane and 1,1,1-trichlorotrifluoroethane at temperature of 373°C and 390°C, respectively. For both gases no sensitivity was found at room temperature. In the temperature range 370–400°C the response is fast enough to get stable potentials within minutes. The direction of potential shift with increasing concentration coincides with the direction specific for increasing HF concentration. No initial shift in potential was observed as it was for HF.

The investigation of the temperature dependence of the sensor response to fluorocarbons did show a more complex behaviour for the temperature range 200–330°C. In
Fig. 9(a) and (b) the results for the same change in concentration are compared for 260°C and 310°C, respectively. For both temperatures a change in potential was found but it is opposite in sign for the 260°C experiment compared to higher temperatures. For some other gases the “normal” sensitivity was found already at the lower temperature as is shown in Fig. 10 for CF<sub>3</sub>CCl<sub>3</sub>. In order to obtain more detailed information on this behaviour, CH<sub>4</sub> and CCl<sub>4</sub> were included in the measurement program. Results for CH<sub>4</sub> are shown in Fig. 11. There is a sensitivity similar to Fig. 9(a) for the lower temperature and only a small swing followed by a signal going to zero at the higher temperature. Comparable results were found for CCl<sub>4</sub>. Therefore, the low-temperature behaviour has to be explained by a mechanism different to that at temperatures near to 400°C. In the temperature range near to 400°C only fluorine containing molecules were detected. At temperatures lower than 330°C there is no detection of a release of fluorine species and no detection selective for fluorine containing molecules.

It is known that field effect transistor (FET) gas sensors with palladium and platinum gate are extremely sensitive to a change in hydrogen concentration [12]. Furthermore, the MIS-structures (FET is one of the variants of MIS structures) with LaF<sub>3</sub> layer, used in our experiment, are sensitive to oxygen in some conditions, as was shown earlier [13]. Therefore, a non-specific detection caused by consumption of oxygen or catalytic decomposition leading to superficial hydrogen formation can occur at low temperature. In some experiments, in the temperature range 250–320°C, we observed in the first moment after supplying fluorocarbon concentration a shift of the potential in negative direction (specific for hydrogen detection or decrease of oxygen
concentration) and then, within 3 or 5 min, the voltage shift became positive as it is typical for selective reaction of fluorine containing compounds. This tendency is shown to a very small degree already in Fig. 9(a). Therefore, for temperatures below 330 °C there is a superposition of two mechanisms making this temperature range not suitable for a selective detection of fluorine containing molecules.

A comparison of the sensitivity of the sensor to different concentrations of different fluorocarbon gases is given in Fig. 12. In contrast to HF, the sensitivity was found to be much smaller (e.g. only 14 mV/lg \( p(\text{CHClF}_2) \)).

The influence of temperature on the sensitivity for different gases is shown in Fig. 13. An improvement in sensitivity was found for all the gases for increasing temperatures. For one of the gases (\( \text{CF}_3\text{CH}_2\text{Cl} \)) sensitivity is in the opposite direction for the whole temperature range investigated. We suppose that a temperature slightly higher than 400 °C will be necessary here to reach positive values of potential, as for other fluorinated compounds. Investigations in this temperature range are in progress.

The temperature dependence of the sensor response shown in Fig. 13 can be used to distinguish between different fluorocarbons using the sensor at different temperatures. Measurements at several temperatures will lead to much more detailed “fingerprints” for each fluorocarbon. This kind of investigation can be easily done by applying a temperature gradient to the sensor chip and taking advantage of the possibility of photocurrent measurements for lateral resolution.

To prove the selectivity of detection of fluorocarbons in comparison to other molecules free of fluorine, \( \text{CH}_4 \) and \( \text{CCl}_4 \) were tested at a temperature of 380 °C using the sensor under investigation. Within the error of experiment there was no signal caused by 5000 ppm of these gases.

Furthermore, a similar field-effect sensor \( \text{SiC/epi–SiC/\( \text{SiO}_2/\text{Pt} \) (without \( \text{LaF}_3 \)-layer)} \) did not give any response to fluorocarbons, as shown with the \( \text{SiC/epi–SiC/\( \text{SiO}_2/\text{LaF}_3/\text{Pt} \)-structure} \). This is an argument for the determining role of the \( \text{LaF}_3 \) for the sensing mechanism. It is well known that \( \text{LaF}_3 \) is a superionic conductor for fluoride ions and the exchange of ions with aqueous solutions leads to a fluoride ion sensor. Furthermore, we have shown the possibility of the detection of fluoride and hydrogen fluoride using the same sensor as for fluorocarbons.

A detailed investigation of the sensing mechanism will be the subject of further investigations. A first concept for such a mechanism will be given below.

It is well known that at the temperatures used in our experiments isomerisation, dehydrohalogenation and dismutation of fluorocarbons on catalytic surfaces are observed [14,15]. An investigation of the catalytic activity of \( \text{LaF}_3 \) at 350 °C did not show any reaction and the nickel (used for the measuring cell) is also not a catalyst [16].

Nevertheless, we have to discuss in this paper a classical catalytic reaction on the reactor (cell) walls followed by a detection of reaction products. The sensor can detect gas phase molecular fluoride but this cannot be a product of decomposition of fluorocarbons. On the other hand, HF was shown to be an intermediate and final product of catalytic reactions of fluorocarbons pyrolysis and pyrohydrolysis [14,15]. Therefore, a mechanism of sensor response might be the catalytic decomposition of fluorocarbons on the reactor (cell) walls followed by the detection of the reaction product HF.

Arguments against this mechanism are:

1. As described earlier, when even low concentrations of hydrogen fluoride are detected by our MIS structure we observed a big initial potential shift (several tens of mV) in comparison with pure air. This potential shift corresponds, according to our point of view, to the removal of superficial oxygen from the lanthanum trifluoride film. In the case of fluorocarbons detection we did not observe this initial potential shift.
2. There is a very big difference in the sensitivities of our MIS structure to fluorocarbons and hydrogen fluoride. The HF sensitivity at 380°C is equal to about 85 mV/\text{lg(p(HF))}, but for most of fluorocarbons it is only about 14 mV/dec. Therefore, it is unlikely that this sensitivity could be explained by the decomposition of the fluorocarbons on the hot wall of the reactor followed by a detection of a decomposition product (HF).

As an alternative mechanism we can assume that for the fluorocarbons the decomposition and detection occur at the same point of the surface without HF as an intermediate product existing free in the gas phase. For this point of view we need not consider the thermodynamics of the species in the gaseous phase but have to assume that unstable species can be stabilised at the interface. It is very important for this mechanism that a fluoride ion can be introduced to a defect (ion vacancy) of LaF$_3$. We have proven the existence of a three-phase boundary LaF$_3$/Pt/gas for the structures under investigation [11]. Therefore, the fluoride atoms of the fluorocarbon may have a strong interaction with the LaF$_3$, with an electron transfer from the platinum to the fluorocarbon may have a strong interaction with the gas phase but have to assume that unstable species can be stabilised at the interface. It is very important for this mechanism that a fluoride ion can be introduced to a defect (ion vacancy) of LaF$_3$. We have proven the existence of a three-phase boundary LaF$_3$/Pt/gas for the structures under investigation [11]. Therefore, the fluoride atoms of the fluorocarbon may have a strong interaction with the LaF$_3$, with an electron transfer from the platinum to the molecule occurring at the same time or in consecutive steps.

4. Conclusion

We have shown that an MIS gas sensor having a structure SiC/epi–SiC/SiO$_2$/LaF$_3$/Pt can be used at temperatures up to 400°C for the measurement of F$_2$, HF and fluorocarbons. For temperatures near to 400°C a selective detection for molecules containing fluoride is achieved. The suggested sensitivity mechanism consists of direct interaction of chemisorbed fluorocarbons molecules with platinum gate material followed by insertion of the fluoride ion into the LaF$_3$ lattice. Measurements at elevated temperatures are in progress.

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References