Semiconductor sensors for the detection of fluorocarbons, fluorine and hydrogen fluoride

W. Moritz\textsuperscript{a,*}, L. Bartholomäus\textsuperscript{a}, U. Roth\textsuperscript{a}, V. Filippov\textsuperscript{b}, A. Vasiliev\textsuperscript{b}, A. Terentjev\textsuperscript{b}

\textsuperscript{a}Humboldt-University, Berlin, Institute of Physical Chemistry, Berlin, Germany  
\textsuperscript{b}RRC Kurchatov Institute, Moscow, Russian Federation

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Abstract

The sensitivity of metal–insulator–semiconductor structure gas sensors based on silicon or silicon carbide to different fluorine-containing gases was studied in the temperature range 20–530 °C. Silicon based gas sensors could be used for the determination of fluorine and hydrogen fluoride at room temperature. The sensitivity to fluorine is 28.0 \pm 0.5 mV/lg(p(F\textsubscript{2})), the sensitivity to HF is 44.4 \pm 1.6 mV/(p(HF)), and the detection is about 10 ppb in both instances. High temperature silicon carbide sensors can be applied for the determination of fluorine and fluorocarbons (CF\textsubscript{3}CH\textsubscript{2}F, CF\textsubscript{3}CCl\textsubscript{3}, CF\textsubscript{3}CH\textsubscript{2}Cl, CHClF\textsubscript{2}, CCl\textsubscript{2}F\textsubscript{2}, CCl\textsubscript{3}F) up to 530 °C. The sensor signal for fluorocarbon concentration measurements demonstrates a Nernstian concentration dependence. The detection limit for these gases is ca. 10 ppm. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The determination of fluorine pollution is a very important problem. This is due to the large use of technologies where fluorine arises as a result of production of important products. For example the gaseous fluoride pollution from aluminium, glass and plastics factories could influence ecology of whole regions. The lowest tolerable level is stated differently by the industrial laws of different countries and lies between 0.05 and 0.5 ppm for F\textsubscript{2}.

Some fluorohydrocarbons are known to cause critical changes in the ozone concentration in the atmosphere. Consequently, substitutes have been developed as for example R134a. Therefore, there is a great demand for sensors for these gases and alarm systems controlling the environment.

For the detection of fluorine, electrochemical cells are produced by several companies [1]. They all have a liquid electrolyte as their main disadvantage.

Murin et al. [2] have proposed to use a single crystal of LaF\textsubscript{3} covered with a platinum film to develop a potentiometric device for the determination of fluorine. Drawbacks of this sensor are the high price of the single crystal and the formation and stability of a reversible rear contact.

Sensors for the detection of fluorocarbons were developed using metal-oxide-semiconductor type materials as V–Mo–Al\textsubscript{2}O\textsubscript{3}/ZnO [3] or sulphur-doped SnO\textsubscript{2} [4]. Several fluorocarbons such as CF\textsubscript{3}CH\textsubscript{2}F or CCl\textsubscript{2}FCCIF\textsubscript{2} have been measured at 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.

The operational principles of metal/insulator/semiconductor (MIS) chemical sensors including the ion-selective effect transistors (ISFETs) and GasFETs have been described elsewhere (e.g. [5,6]). Recently we reported the first results on the detection of fluorine, hydrogen fluoride and fluorocarbons using such a semiconductor structure having a thin layer system LaF3/Pt as the sensitive top layers [7–12]. In our experiments we used this sensitive system deposited on two different semiconductor/insulator substrates to get a field-effect type sensor. Because of the low band gap of the silicon-based devices, their application is restricted to temperatures <200°C. Sensors with silicon carbide used as the substrate have been shown to work from room temperature up to 530°C in our experiments. For this type of sensor capacitance/voltage (CV) curves are improved by increasing the temperature [9,10] making its application preferable at temperatures >200°C. For the detection of fluorine two different sensor behaviours were found depending on the preparation of the sensor. Each state was advantageous for certain concentration ranges (smaller or greater than 10 ppm) [13]. In this paper we will concentrate on the sensor for the lower concentration range.

In the present paper investigations of the sensitivity of the semiconductor sensor to fluorine, hydrogen fluoride and fluorocarbons (CF3CH2F, CF3CCl3, CF3CH2Cl, CHClF2, CCl2F2 and CCl3F) will be presented. The temperature dependence of sensor behaviour and the dynamics of sensor response will be reported.

2. Experimental

The SiC semiconductor substrates (Joffe-Institute, St. Petersburg) used were 6H-SiC chips (3×3 mm²) with an epitaxial layer of SiC (n-type, carrier concentration (0.5−8)×10¹⁶ cm⁻³). A SiO₂ insulating layer (28 nm thick) was grown by thermal oxidation. Si-based structures were prepared using an n-type wafer with a carrier concentration of 5×10¹⁴ cm⁻³.

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 three phase boundary (LaF₃/Pt/gas) formation. A scheme of the SiC-based sensor used in our experiments is given in Fig. 1.

The capacitance of the samples was measured using a Hewlett-Packard 4284A type LCR meter. A computer controlled system for the determination of a flat band voltage was used.

The measuring cell was designed specially for high temperature measurements of the kinetics of gas sensing processes. The nickel cell had an aluminium oxide insulator and a free volume of less than 0.2 cm³ and was heated by an external heater. The rear and top side contacts were made of platinum and graphite, respectively. This cell assured low noise measurements of the capacitance of the sensor up to 530°C in a fluorine-containing atmosphere.

The gas sensitivity was measured under gas flow conditions. 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 5–10,000 ppm. Maximum gas flow velocity was 0.51 min⁻¹.

3. Results and discussion

3.1. Sensitivity to fluorine

It was shown that the sensors using the different semiconductor materials (Si and SiC) but with an
identical preparation of the sensitive thin layer system LaF$_3$/Pt give no difference in sensor response. This confirms that the potential determining reaction takes place, at the LaF$_3$/Pt interface and is not influenced by the semiconductor substrate. A typical result of sensor behaviour at room temperature is given in Fig. 2. There is a fast and stable response in the range near to the maximum tolerable level of fluorine, which is 0.1 ppm in Germany. For very small gas concentrations the influence of fluorine concentration on the response rate becomes important. In Fig. 3 the response time $t_{50}$ (the time necessary for 50% potential change after a change in concentration) is shown for various concentrations. The influence of the concentration on the response time can be described by the equation:

$$t_{50} = k \cdot p_{F_2}^n,$$

(1)

where $t_{50}$ is the time necessary to reach half of the final sensor signal, and $p_{F_2}$ is the fluorine pressure. The experimental value of $n$ was determined to be $-0.52 \pm 0.02$.

The slow response of the sensor at low fluorine concentrations is the reason for the limit of detection to be about 10 ppb.

The sensitivity was found to be of the Nernstian type with a slope of $28.0 \pm 0.5$ mV/\text{lg}(p_{F_2}) at room temperature, as shown in Fig. 4. This is in accordance with a formal exchange of two electrons in the surface electrochemical reaction.

Temperature dependent measurements of fluorine detection using the two different semiconductor materials in the range from room temperature up to 400°C yield a sensitivity to fluorine over the whole temperature range. An example for the sensitivity at 330°C is given in Fig. 4. At this temperature the slope of the Nernst equation was $135 \pm 3$ mV/\text{lg}(p_{F_2}). This corresponds to a value of electrons exchanged near to unity. The influence of temperature on the dynamic behaviour of the fluorine sensor was surprisingly small. The response rate was only increased by a factor of 2 or 3 when increasing the temperature from room temperature up to 300°C. These results lead to the conclusion that the sensor response mechanisms did change somewhat with temperature. But beside the
possibility of sensor application at high temperature the conclusion is that there is no advantage of heating the sensor to high temperatures. Therefore, there was no need for extended investigations of fluorine sensitivity of the MIS structure in the high temperature range.

The mechanism of operation of the fluorine sensor at room temperature can be explained by the properties of the fluoride ion-conducting material LaF$_3$ which was shown to be able to rapidly exchange fluoride ions across a phase boundary [14,15]. The behaviour of the fluorine gas sensor corresponds to a two electron electrochemical process taking place on the three phase boundary LaF$_3$/platinum/gas:

$$\text{F}_2 + 2e^- \rightarrow 2\text{F}^- \quad (2)$$

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

$$E = E_0 + \frac{RT}{zF} \ln ([\text{F}_2]), \quad (3)$$

where $R$ is the gas constant, $T$ the temperature, $F$ the Faraday number, and $z$ the number of electrons (ions) transferred in the reaction ($z = 2$ in reaction (2)). The stabilisation of the fluoride ion and the charge separation between the two solid phases is due to the insertion of the ion into vacancies in the LaF$_3$ lattice.

3.2. Sensitivity to hydrogen fluoride

In contrast to fluorine detection a fast and stable response to hydrogen fluoride was found only for temperatures $<100^\circ C$ as shown in Fig. 5 for a temperature of $23^\circ C$. At higher temperatures (about $200^\circ C$) a change of gas concentration leads only to small and unstable shifts in voltage.

For temperatures $>350^\circ C$ a specific behaviour, important for the understanding of 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. 6). The voltage remains at the value specific for pure synthetic air or there is a shift equal to $<3 \text{ mV}$ but with a sign opposite to the direction expected for HF. If the concentration reaches a certain critical value, the voltage is shifted after a certain delay time by several tens of mV (see Fig. 6). After this “pre-treatment” procedure a sensitivity to low concentrations was found.

This behaviour can be explained by considering the surface chemistry of LaF$_3$. Using X-ray photoelectron spectroscopy (XPS), oxygen was shown [16,17] to be present in the surface. The oxygen content increased with temperature. Therefore, the delay and the shift in signal can be considered to be an activation process.

![Fig. 5. Sensitivity of the Si based MIS sensor to hydrogen fluoride.](image-url)
due to an exchange of oxygen with fluoride. The concentration dependencies for high and low temperatures are given in Fig. 7. Sensitivities were determined to be $44.4 \pm 1.6 \text{ mV/} \lg (p(\text{HF}))$ at $23^\circ \text{C}$ and ca. $84.4 \pm 0.8 \text{ mV/} \lg (p(\text{HF}))$ at $370^\circ \text{C}$. For both temperatures a linear dependence of the potential on the logarithm of gas concentrations was found. But for Eq. (3) no integral value of $z$ was found, which indicates a complex sensor mechanism.

3.3. Sensitivity to fluorocarbons

Measurements using different fluorocarbons at room temperature did not lead to any sensitivity. Near

![Fig. 6](image1.png)

Fig. 6. Conditioning of the SiC-based MIS sensor at $390^\circ \text{C}$ in hydrogen fluoride. The HF concentrations are written on the top of the graph.

![Fig. 7](image2.png)

Fig. 7. Hydrogen fluoride sensitivity of the SiC-based sensor at $23^\circ \text{C}$.
to 200°C we found some signals but stability and reproducibility was poor. Therefore, investigations of sensitivity to fluorocarbons have been possible only in the higher temperature range using the silicon carbide-based sensor structures. For the range 200–330°C a complex behaviour with potential shifts in different directions was found, as is described elsewhere [18]. Further increase of temperature resulted in stable detection of all fluorocarbons included in the measuring program. The sensitivity for different fluorocarbons (CF₃CH₂F, CF₃CCl₃, CF₃CH₂Cl, CHClF₂, CCl₂F₂ and CCl₃F) was investigated. A typical sensor response to different concentrations of a fluorocarbon in synthetic air is given in Fig. 8. The graph represents the sensor behaviour for the first contact with CF₃CCl₃ without any treatment for stabilisation. In comparison to Fig. 6 there was no initial shift or sensor activation process observed. A comparable behaviour was found for all gases investigated.

The potential shift (equivalent to the change in bias voltage) was in the same direction as it was found for fluorine and hydrogen fluoride. A linear dependence of the potential shift on the logarithm of gas concentration was found to be similar to the fluorine and HF response of the sensor. In Fig. 9 this is illustrated for two different temperatures for CCl₃F sensitivity measurement. The sensitivities are very different for the various fluorocarbons investigated as is summarised in Table 1. (There is no value for CCl₂F₂ because there was a slow response and therefore no equilibrium value was achieved for this gas in the temperature range investigated). The formal application of the Nernst equation did lead to numbers of electrons exchanged between 2 and 5 depending on the gas and the temperature of the experiment. These values are not very reasonable and further investigation is necessary to get improved knowledge for explanation of sensitivities.

The kinetics of sensor response has been investigated depending on gas concentration and sensor Table 1

<table>
<thead>
<tr>
<th>Fluorocarbon</th>
<th>Temperature (°C)</th>
<th>Sensitivity (mV/dec)</th>
<th>α</th>
<th>ΔE_{act} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₁₁(FCl₂F)</td>
<td>458</td>
<td>79</td>
<td>0.51</td>
<td>1</td>
</tr>
<tr>
<td>F₁₁₄(CF₃CH₂F)</td>
<td>450</td>
<td>62</td>
<td>0.79</td>
<td>1.6</td>
</tr>
<tr>
<td>F₂₂ (CHClF₂)</td>
<td>458</td>
<td>29</td>
<td>0.64</td>
<td>0.8</td>
</tr>
<tr>
<td>F₁₃₃ (CF₃CH₂Cl)</td>
<td>451</td>
<td>28</td>
<td>0.75</td>
<td>0.4</td>
</tr>
<tr>
<td>F₁₂ (CCl₃F₂)</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>1.3</td>
</tr>
<tr>
<td>F₁₁₃(CF₃CCl₃)</td>
<td>450</td>
<td>51</td>
<td>1.2</td>
<td>1.1</td>
</tr>
</tbody>
</table>
temperature. The dynamic behaviour was characterised in these experiments using the initial slope $r$ of the potential/time curve after a change in gas concentration:

$$r = \left( \frac{dU}{dr} \right)_{t=0} = k \cdot c_{FC}^0.$$  

The strong influence of the concentration on the dynamic behaviour is shown for different temperatures using CF$_3$CCl$_3$ as an example (Fig. 10). The exponent $\alpha$ (Eq. (4)) resulting from the linear fit of the double logarithmic graph is given in brackets. It gives a nearly linear dependence of the response rate on the concentration for CF$_3$CCl$_3$. For the other gases the
corresponding exponents $\alpha$ are given in Table 1. In contrast to fluorine the response rate for the detection of fluorocarbons is strongly influenced by temperature. The activation energy calculated from the temperature dependence of response rate is also given in Table 1.

The limit of detection at 500°C was shown to be about 10 ppm. The strong influence of gas concentration and the temperature on the response rate led to the conclusion that the limit of detection can be much improved by a further increase in temperature.

The substantial role of LaF$_3$ in the sensing mechanism was shown in an experiment using a similar field-effect sensor SiC/epi-SiC/SiO$_2$/Pt (without a LaF$_3$ layer). This structure did not give the response to fluorocarbons shown with the SiC/epi-SiC/SiO$_2$/LaF$_3$/Pt-structure.

For the discussion of the mechanism of detection of fluorocarbons it is very important that a fluoride ion can be introduced to a defect (ion vacancy) in the LaF$_3$. We have proved the existence of a three phase boundary LaF$_3$/Pt/gas for the structures under investigation [16,17]. Therefore, the fluorine atom of the fluorocarbon can have a strong interaction with the LaF$_3$ and an electron transfer from the platinum to the molecule is possible at the same time or in consecutive steps. The principle is illustrated in Fig. 11.

4. Conclusions

We have shown that a field effect semiconductor sensor using LaF$_3$ and Pt as the chemically sensitive components can be realised leading to a structure Si/SiO$_2$/Si$_3$N$_4$/LaF$_3$/Pt or SiC/epi-SiC/SiO$_2$/LaF$_3$/Pt. Sensitivity to fluorine, hydrogen fluoride and various fluorocarbons in synthetic air was demonstrated. If selectivity between these gases is required for special applications sensors operated at 25°C, 190°C and 500°C can be combined leading to a system were at least one of the sensors is insensitive, as described above.

Acknowledgements

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References


