Mechanistic investigation on an all solid state fluorine sensor

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Abstract

A semiconductor field effect structure Si/SiO2/Si3N4/LaF3/Pt can be used for the detection of fluorine in air. Depending on the preparation, two different sensor types were investigated having advantages at low or high fluorine concentrations, respectively. Combining these sensors concentrations between 0.01 and 1000 ppm can be detected. The mechanism of the sensor was shown to be an electrochemical charge transfer at the three-phase boundary LaF3/Pt/gas. Differences in the mechanism of the two sensor types are due to partial fluorination of the platinum at concentrations higher than 10 ppm. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Fluorine is well known to be a very reactive and toxic gas. Nevertheless, it is used in several industrial processes, chemical laboratories and even in gas mixtures for eximer lasers in a large number of physical experiments. The maximum concentration allowed in air is very low, e.g. 0.1 ppm in Germany. Therefore, there is a requirement for sensors detecting fluorine in air at low concentrations but also at higher concentrations near to an unfounded outlet of the gas.

Electrochemical cells using liquid electrolyte have been used for fluorine detection [1]. These sensors have the disadvantages in production and stability known for all the electrodes using liquid electrolyte.

Several all solid state sensors have been developed using the field effect in the semiconductor material silicon [2]. The sensor device most near to standard processes of the semiconductor industries is the metal insulator semiconductor field effect transistor (MISFET).

For the detection of fluorine gas, Murin [3] used a single crystal of the ion conductor LaF3 covered with Pt on both sides. This is leading to an all solid state electrochemical cell. We suggested for modifying an oxygen sensor [4] using a MIS structure Si/SiO2/Si3N4/LaF3/Pt for the detection of fluorine [5]. The early sensor samples did show a strong variation in sensitivity leading to the need of further optimization. Special preparation methods did result in two different sensor types (called I and II) having advantages at high- or low-concentrations, respectively [6]. The substitution of the semiconductor substrate silicon by the large band gap material silicon carbide provided the possibility of fluorine detection from room temperature up to 350°C [7].

It was the aim of this paper to investigate the sensor response mechanism of the two fluorine sensor types and to explain the differences in the behavior of the two similar devices.
2. Experimental

For sensor preparation, n-silicon substrates were used. SiO$_2$ (76 nm) and Si$_3$N$_4$ (80 nm) insulator layers were produced by industrial standard technologies. A LaF$_3$ layer (240 nm) was deposited on top of the Si$_3$N$_4$ by thermal vapor deposition. A platinum gate electrode was produced by a sputtering technique in an argon plasma in a way providing a three-phase boundary LaF$_3$/Pt/gas. The typical thickness of this layer was 30 nm, but it was varied for some experiments. The resulting structure was Si/SiO$_2$/Si$_3$N$_4$/LaF$_3$/Pt.

A storage of the sensor in 1000 or 10 ppm of fluorine for 24 h did lead to sensors called type I or II, respectively.

High frequency capacitance–voltage (CV) measurements were used for the field effect sensor characterization. A change in gas concentration causes a shift of the capacitance–voltage curve on the voltage axis. This voltage shift corresponds to the change of electrical potential difference at the sensitive interface LaF$_3$/Pt. Gas concentrations were adjusted by computer controlled dilution of industrial prepared fluorine gas. The typical thickness of this layer was 30 nm, but it was varied for some experiments. The resulting structure was Si/SiO$_2$/Si$_3$N$_4$/LaF$_3$/Pt.

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X-ray photoelectron spectroscopy (XPS)-surface analysis was carried out with a PHI 595 at the Freienius Institute, Dresden, Germany.

3. Results and discussion

3.1. Determination of sensor parameters

Our early investigations on Si/SiO$_2$/Si$_3$N$_4$/LaF$_3$/Pt-sensor structures [5] did show sensitivity to fluorine but a bad reproducibility of sensor behavior (sensitivities varying between 60 and 200 mV/dec). The reproducibility was much improved using the two different preparation procedures described in the experimental part, but it leads to important differences in the sensitivity and dynamic behavior between these two variants. The sensitivity for the two sensor types under investigation is shown in Fig. 1. A linear dependence of the electrical potential difference on the logarithm of fluorine concentration was found for both sensor types for increasing as well as decreasing concentrations. This corresponds to the Nernst equation (Eq. (1))

\[
\Delta E = E_2 - E_1 = \frac{RT}{nF} \ln(c_2) - \frac{RT}{nF} \ln(c_1) = \frac{RT}{nF} \ln\left(\frac{c_2}{c_1}\right)
\]

with \(\Delta E\) = change in the electrical potential difference \(E\) caused by a change in fluorine concentration from \(c_1\) to \(c_2\).

The linear range extends to four orders of magnitude for each sensor type and for a combination of the sensors a measuring range of six orders of magnitude is available. For the type I sensor, the response to fluorine resulted in a shift of electrical potential difference equal to 116 mV for a change in concentration by a factor of ten. On the other hand for the type II sensor, the sensitivity was determined to be 29.0 mV/dec. The statistical error was determined to be 2.3 mV/dec \((n = 132)\) for the type I sensor and 0.6 mV/dec \((n = 22)\) for type II. For the second, this appears to be a typical statistical error while for the type I sensor a distribution of sensitivities between 50 and 185 mV/dec was found.

A nearly Gaussian distribution did lead to a high number of sensors showing sensitivities very near to 116 mV/dec. This distribution of sensitivities might be a first argument for a complex sensor mechanism of type I samples including for example a mixed potential. A formal calculation of the number of electrons exchanged according to Eq. (1) leads to \(z = 0.5\) and \(z = 2\) for type I and II, respectively. The very unusual value of \(z = 0.5\) will be discussed later.

The dynamic response of both sensor types could only be described by empirical equations. For the type I sensor, it was shown in [9] that the best fit of the potential/time-curves was found using Eq. (2) suggested by Müller [8] for the fluoride ion sensitive electrode.

\[
\Delta E = \frac{t}{a + bt} = \Delta E_0 \frac{t}{a_1 + t}
\]

Eq. (3) suggested by Rechnitz and Kugler [10] can be used to describe the response of type II sensors. The experimental data and the fit according to Eq. (3) are given in Fig. 2 for a fast change in fluorine concentration from 0.5 to 3 ppm.

\[
\Delta E = \Delta E_0 \log\left(\frac{c_2}{c_1}\right)(1 - \exp(-k\sqrt{t}))
\]

Because of the empirical character of the response equations, the more simple determination of a response
time $t_{50}$ (time for half of the potential change after a fast change of concentration) was used for further investigations. The influence of the fluorine concentration on the dynamic behavior is given in Fig. 3. It might be interesting to mention that the change in response rate found here is in contrast to the results for an oxygen sensor using the same active layers LaF$_3$ and Pt [4]. For the oxygen sensor, the response time was independent on concentration.

The double logarithmic representation in Fig. 3 gives a linear response for both sensors. Therefore, the influence of concentration can be described by Eq. (4):

$$t_{50} = k c^{A}$$

where the values for the exponent $A$ are $-0.508 \pm 0.022$ and $-0.521 \pm 0.023$ for type I and II, respectively. Besides the fact that the influence of concentration is the same it is obvious that the response of type II sensors is faster by a factor equal to 30.

The values determined for exponent $A$ are both very near to 0.5 and might be understood as a square route relation. This type of influence of concentration on the response time was found by Johansson and Norberg [11] for the glass electrode. They used the Butler–Volmer equation to describe the dynamic behavior of the pH-electrode. Using some simplifications they found Eq. (5)

$$\Delta E = \Delta E_0 \log\left(\frac{c_2}{c_1}\right) \left(1 - \exp(-kt)\right)$$

with

$$k = \text{const} \sqrt{c_2}$$

Eq. (5) does not give a very good fit of our response curves but there are simplifications in the calculation of Eq. (5) and the gas sensor system might be even more complicated than an ion exchange at solid/electrolyte interfaces. Nevertheless, the good correlation of the influence of concentration on sensor behavior between experiment and an equation derived from the fundamental equation of electrochemistry gives an reasonable argument for the electrochemical character of the sensor response mechanism.

The influence of fluorine concentration on the sensor response rate is the reason that for both sensors it is not reasonable to give a limit of detection which is caused by thermodynamics. Type I sensors can be used down to 0.1 ppm but because of the slow response rate in the range below 10 ppm, the type II sensor is much faster and preferable for low concentrations. The type II sensor was used down to 6 ppb.

Impedance measurements using a LaF$_3$-single crystal/Pt model system [9] did give a fluorine concentration dependent exchange resistance. The equivalent circuit used for the description of impedance spectra exhibits a capacitance (or more exactly a constant phase element) in parallel to the concentration dependent resistance equal to 9.8 $\mu$F/cm$^2$. This is a value very near to typical data for electrochemical double layers. Therefore, the frequency dependent investigations give strong arguments for an electrochemical character of the sensor response mechanism. Furthermore, the results of the impedance measurements were used to calculate the sensor response time. Even with the very simple assumption

$$\tau = RC$$

a very good approximation of the response time found for the polycrystalline semiconductor sensor was found.
In another experiment, the platinum was replaced by a thin layer of gold. Here fluorine sensitivity was found comparable to the system using Pt. Therefore, it is shown that there is no need of a specific catalytic activity of the platinum. It should be noted that for the oxygen sensor using the same thin layer structure even more metals were successfully applied (e.g. Al) [4]. For the fluorine sensor these experiments were restricted because of the instability of thin metal films in fluorine gas atmosphere.

Typically sensors using solid electrolytes (SE) have a symmetrical structure Me/SE/Me with the need of a reference gas at constant concentration on the reference part [13]. Some others are using multi-layer systems providing thermodynamically determined equilibria between the ion conducting solid electrolyte and the electronic conduction in the metal [14]. It is an advantage of the semiconductor based sensors that because of the signal amplification (in the silicon) in a nanometer scale distance to the signal generation at the LaF3:Pt interface there is no need for a reversible reference contact [15,16]. The stability of the capacitive contact Si3N4:LaF3 was already shown for a sensor for the detection of fluoride ions in solutions. Therefore, for the gas sensor described here, there is no need for a reference gas making its application much more simple.

3.3. Variation of Pt layer thickness

To improve the knowledge about the sensor mechanism, the thickness of the platinum layer was varied. The results are given in Figs. 4 and 5. An influence of the metal electrode thickness on the sensor response dynamics is not very surprising but the influence on the sensitivity shown in Fig. 5 was not aspected. For the type I sensor response time and sensitivity are independent on the Pt layer thickness in the thickness range up to 50 nm. Therefore, there is no diffusion part in determining the sensor response rate. For a thickness higher than 100 nm only slow and instable sensor response was found. This might be due to the fact that for higher thicknesses, the fluorine cannot reach the three-phase boundary LaF3:Pt anymore.

For the type I sensor the response rate is depending on the Pt layer thickness. The exponent $m$ was determined to be 0.57. Assuming a diffusion process to be rate determining, this exponent should have a value equal to two. Therefore, a simple diffusion model cannot be an explanation for the dynamic behavior found. It is more reasonable to discuss the change in response rate in a context with the dependence of sensitivity on the metal layer thickness found for the type I sensor.
In the concentration range 1–10 ppm both sensor types are successfully applied. Therefore, fast concentration changes between these two values were investigated. Sensors with Pt layer thicknesses of 10, 30 and 80 nm were compared. Fig. 6 gives the response after seven different treatments following each other. On the left for virginal sensors a certain initial drift and the typical type II behavior — fast response and small sensitivity — was observed for the three different thicknesses under investigation. After a treatment at 100-ppm fluorine, the sensors having the thicker Pt layer did not change their behavior while the sensor prepared with a 10-nm Pt layer gave an increase in sensitivity and a decrease in response rate. An increase in the time of treatment and especially in the fluorine concentration led to the same observation for the other sensors. Finally, all the sensors have a behavior near to the type I characteristics when treated for hours in 1000 ppm of fluorine.

A pronounced difference between the two sensor types investigated is the value of the flat band voltage. This characteristic point of the capacitance/voltage curve is typically used to determine the shift in electrical potential difference, which gives the sensitivity. The value of the flat band voltage is depending on the electrical potential difference at the sensitive layers LaF₃/Pt but also on the silicon, the insulator and the interface between these layers. Therefore, some variation of flat band voltage from sensor to sensor is usual. Nevertheless, the shift in voltage for each sensor is clearly defined. Typically a difference in flat band voltage between the two sensor types was found to be about 500 mV at 10 ppm of fluorine. In Fig. 7 this shift in electrical potential difference is shown for the same conditions as in Fig. 6. The faster shift of the 10-nm sample to the new stationary behavior is clearly seen. After a long time treatment all the sensors are coming to nearly the same value of stationary electrical potential difference. In Fig. 8 the change of sensitivity is given for the same experiment. The change in sensitivity is faster for thin layer of Pt as already seen but the sensitivity remains different depending on Pt layer thickness. This was proven to be true even for much longer time of treatment at 1000 ppm.

3.5. Surface analysis

The reason for changes in sensor behavior after contact to high concentrations of fluorine (100–1000 ppm) were investigated using XPS. A fluorination of the platinum was considered as the hypothetical reaction. To avoid speculative results, samples without LaF₃ layer were prepared making sure that fluorine found could only be from PtF₄. Even knowing that some of the platinum fluorides are not very stable in vacuum, it was possible to detect fluorine at the surface.
The XPS spectrum found is given in Fig. 9. A detailed investigation of the Pt4f7/2 signal (Fig. 10) showed a peak at a binding energy $E_B = 76.6$ eV. This is a large shift as typical for fluoride. A clear conclusion, which of the platinum fluorides is on the surface, was not possible because of the absence of a reference material. A comparison with the results Salyn et al. [17] who investigated K$_2$PtF$_6$ gave an argument for PtF$_6$, but it cannot be clearly distinguished from PtF$_4$ or others. Auger electron spectroscopy (AES) was used for the investigation of Pt fluorination in [9]. Here the presence of fluoride was proven even after sputtering 30 nm of Pt. Additional arguments for the fluorination of the Pt at our conditions were found by X-ray investigations, atomic force microscopy (AFM) and quartz micro balance (QMB)[18]. A decision between the different fluorides was not possible again.

4. Conclusion

The sensor mechanism should be discussed starting with the simpler one of type II. Arguments for an electrochemical charge transfer across an interface have been given from the sensitivity, the concentration dependence of response kinetics and the independence on Pt layer thickness. The number of charge carriers exchanged was determined to be equal to two. The substantial role of the fluoride ion conducting material LaF$_3$ leads to the conclusion that in the end F$^-$ ions should be exchanged at the three-phase boundary LaF$_3$/Pt/gas. In a first step fluorine adsorbed at the Pt will be ionized:

$$\text{F}_2 + 2e^- \leftrightarrow 2\text{F}^-$$

(9)

The stabilization of the of the ion by a transfer to vacancies in the LaF$_3$

$$2\text{F}^- \leftrightarrow 2\text{F}^-_{\text{LaF}_3}$$

(10)

is the process leading to charge separation and the final reason for a change in the electrical potential difference according to the Nernst equation

$$\Delta E = \frac{RT}{2F} \ln \left( \frac{c_{F^-(2)}}{c_{F^-(1)}} \right)$$

(11)

with $c_{F^-(1)}$ denoting concentration of fluorine before change of gas and $c_{F^-(2)}$ standing for concentration of fluorine after change of gas.

The sensitivity of 29 mV/dec at room temperature calculated for this mechanism is in accordance with the experimental results.

For the type I sensor the situation is much more complex. The sensitivity found for the standard Pt layer
thickness of 30 nm was equal to 116 mV. A formal application of the Nernst equation would lead to half an electron or ion exchanged which is not a reasonable value. Next the sensitivity was found to be depending on Pt layer thickness. On the other hand, the kinetic data and especially the impedance investigations are strong arguments for an electrochemical charge transfer mechanism. The investigation on the influence of high fluorine concentrations on the Pt film did show a fluorination for the type I sensor. A final result in which fluoride was formed on the surface was not achieved but the formation of PtF\textsubscript{6} will be assumed in the following.

The first step of the sensor response reaction could be the shift of the PtF\textsubscript{6} formation equilibrium:

\[ \text{Pt} + 3\text{F}_2 \leftrightarrow \text{PtF}_6 \]  \hspace{1cm} (12)

Next dissociation can be assumed

\[ \text{PtF}_6 \leftrightarrow \text{PtF}_5^+ + \text{F}_\text{Pt}^- \]  \hspace{1cm} (13)

The resulting fluoride ion can be transferred into the LaF\textsubscript{3} as discussed above leading to the electrical potential difference generation

\[ \text{F}_\text{Pt}^- \leftrightarrow \text{F}^+ \text{LaF}_3 \]  \hspace{1cm} (14)

This results in a Nernst equation as given in Eq. (15)

\[ \Delta E = \frac{RT}{F} \ln \left( \frac{\text{c}_{\text{F}(2)}}{\text{c}_{\text{F}(1)}} \right) = \frac{3RT}{F} \ln \left( \frac{\text{c}_{\text{F}(2)}}{\text{c}_{\text{F}(1)}} \right) \]  \hspace{1cm} (15)

The sensitivity calculated for this mechanism is equal to 174 mV/dec. An extrapolation of the thickness dependence of sensitivity as shown in Fig. 5 down to values near 1 nm gives such sensitivities. For the higher thicknesses normally used the behavior is more complicated again. A superposition of response according to Eqs. (12)–(14) and to the mechanism according to type II reaction can explain this behavior. For very thin Pt layers they are fluorinated to a high degree leading to the high sensitivity for sensor response based on Eqs. (12)–(14). For more thick layers, the degree of fluorination is lower (only surface fluorinated) and therefore a superposition with reactions according to Eqs. (9) and (10) will occur. This is not a typical mixed potential where different agents are leading to different reactions. For our situation it is more reasonable to understand the behavior as a parallel reaction of two mechanisms for the same molecule to be detected. For a given thickness of the platinum layer a stable sensitivity will be achieved even when the sensor response is not determined by simple thermodynamics. The dependence of the response time on the Pt layer thickness found for type I sensors can be understood to be caused by these parallel reactions.

The sensor properties presented above result in two different application conditions for the sensor types. For concentrations higher than 10 ppm, the type I sensors can be used. For smaller concentrations, it is still working but because of the slow response of this sensor, type II sensors are preferable. Type II sensors can be used down to 10 ppb but for high concentrations (> 100 ppm) it becomes unstable because of a slow fluorination of the surface. Therefore, it should be used for concentrations smaller than 10 ppm only. If necessary, the combination of the two sensors in a sensor system gives the possibility of fluorine detection in the large range between 0.01 and 1000 ppm.

References