Super-sensitivity of an all solid-state fluorine sensor: mechanistic investigations

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Abstract

The super ionic conductor LaF₃ is the essential part of an n-Si–SiO₂/Si₃N₄/LaF₃/Pt sensor structure for the detection of fluorine in air. The semiconductor sensor, which is based on the field effect in the silicon substrate, was fabricated using thin film technology. The sensitivity depended on the Pt layer thickness resulting in a value of 116 mV/dec for 30 nm Pt films. The results of impedance spectroscopy showed the electrochemical ion exchange at the three-phase boundary LaF₃/Pt/gas to be the rate-determining step of the sensing process. A fluoride ion is introduced into the ionic conductor LaF₃. The interaction of Pt with fluorine gas at concentrations of 1000 ppm was investigated using Auger electron spectroscopy and a quartz crystal microbalance. It was shown that a nanometer-scale thin film of PtF₆ was formed. The formation of this film was the reason for the extremely high sensitivity. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The determination of fluorine is very important for environmental monitoring. The lowest tolerable level is for example 0.1 ppm in Germany [1]. It is difficult to detect such low concentrations with sufficient precision.

Currently, electrochemical cells are used for the detection of fluorine. These sensors have the typical disadvantages in production and application known for all cells using a liquid electrolyte.

Recently, we developed a semiconductor sensor for the detection of fluorine. A field effect structure n-Si–SiO₂/Si₃N₄/LaF₃/Pt was shown to be sensitive to fluorine [2]. The ionic conductor LaF₃ used in this thin layer structure was prepared without any doping of the layer. A disadvantage of these first developments was a lack in reproducibility of the sensitivity (49–200 mV/log(p(F₂))). Based on a pre-treatment with small concentrations of fluorine in air, a stable sensor was found with a sensitivity of 29 mV/dec [3]. The mechanism of this type of sensor can be easily described using Nernst’s law. Another
stable sensor was received with a special pre-treatment of the sensor in 1000 ppm of fluorine. After this pre-treatment a stable sensitivity was found between 0.1 and 1000 ppm of 115–120 mV/dec [4]. This super-sensitivity is difficult to describe by a simple electrochemical reaction. Therefore, it was the aim of this paper to investigate the mechanism of this sensor type in more detail.

2. Experimental

The semiconductor substrates used were n-Si with an isolator of 76 nm SiO₂ and 80 nm Si₃N₄ on the top. 240 nm of the ionic conductor LaF₃ were deposited on these substrates using thermal vapour deposition. Platinum gate contacts were produced by sputtering in an argon plasma. A schematic of the sensor is given in Fig. 1.

The sensors were characterised at different concentrations of fluorine in synthetic air by high-frequency capacitance–voltage measurements with a computer controlled measuring and gas mixing system. The C(V) curve is shifting on the voltage axis with different concentrations of fluorine [2].

The thickness of the platinum film was varied, and the kinetics and the sensitivity of the samples were measured. Impedance spectroscopy was used to study the kinetics of the sensor. Single crystals of LaF₃ were coated with platinum on one side. The backside of the crystal was exposed to an electrolyte solution containing 1 M NaCl and 0.1 M NaF. A Zahner Imd 5 impedance spectrometer was used to carry out the impedance measurements. To study the fluorination of the platinum, we used samples based on n-Si/SiO₂/Si₃N₄/Pt with a 50-nm platinum gate. These samples were fluorinated for 24 h in 1000 ppm fluorine. These samples were investigated by the Fresenius Institute in Dresden using Auger electron spectroscopy (AES). To detect the mass of fluorinated platinum a quartz crystal microbalance (QCM) was used. The quartz was coated with 50 nm of platinum. The change of mass of the platinum was investigated during fluorination in 1000 ppm of fluorine.

3. Results

3.1. Sensor data and influence of the Pt layer thickness

The sensor parameters of the n-Si/SiO₂/Si₃N₄/LaF₃/Pt structure were mainly investigated using samples prepared with a Pt layer thickness of 30 nm. For this standard condition the sensitivity to fluorine in air was determined to be 116 mV/dec. The influence of the Pt-layer thickness found in our experiments will be discussed later on. Selectivity investigations including a variation of the oxygen and hydrogen fluoride concentration and the humidity at a constant fluorine concentration of 10 ppm did not show any influence of these gases. Furthermore, the sensitivity to fluorine was not depending on the concentration of these gases.

The drift behaviour of the sensor was not optimized until now. Some sensors did show a drift of more than 1 mV/h. For 20% of the sensors this value was already 0.5±0.1 mV/h. This may be due to reasons from the semiconductor/insulator structure or due to the electrochemical process. Drift minimisation will be a task for further technological development.

A mathematical description of the dynamic response of the sensor to fast changes in the fluorine concentration was attempted with several equations [5]. The only appropriate description was found using an empirical equation given by Müller [6] (Fig. 2).

\[ \Delta E(t) = \Delta E_0 \log \left( \frac{c_2}{c_1} \right) \frac{1}{1 + at} \]  

(1)
Fig. 2. Sensor response for a concentration change from 44 to 100 ppm (measured points) compared to the fit according Eq. (1) (solid line).

Fig. 3. Dependence of the response time $t_{50}$ for change of gas concentration from 100 to 44 ppm on the thickness of the platinum layer (dots and line fit); dotted line, function expected for diffusion.

where $\Delta E$ is sensitivity; $a$ is a time constant; $c_1$ is concentration of gas before change of concentration; $c_2$ is concentration of gas after change of concentration.

It might be noteworthy that Eq. (1) is known to be valid for the fluoride ion selective electrode [7] based on a LaF$_3$ single crystal. For this ion selective electrode, it is the exchange reaction of the fluoride ion between the ionic conductor LaF$_3$ and an aqueous electrolyte which is rate determining.

The response rate of the fluorine sensor was found to be concentration dependent. We found the response rate not depending on the ratio of the concentrations ($c_1$ and $c_2$) but only from the final concentration ($c_2$). This means that the response rate is slower for a concentration change from a high to a low concentration compared to the opposite change. But if the final concentration is equal the response times are equal within the error of measurement.

An empirical analysis given in [3] leads to a formal description of the response time by Eq. (2)

$$t_{50} = k c_2^m$$

where $k$ is a constant for individual sample and a value of $m$ equal to $-0.51$ (see also Fig. 6). Again this value is very near to the analogous value for the fluoride ion selective electrode which was determined to be $m = -0.55$ [8].

Fig. 3 shows the response time $t_{50}$ (50% of the signal after change of gas) for a change in the gas concentration from 100 to 44 ppm as a function of the thickness of the platinum film. The response time increases with an increase in the Pt layer thickness. However, the relationship between the response time and the thickness of the platinum layer does not indicate a diffusion controlled kinetics. For diffusion controlled kinetics the gradient of the curve should be 2 on a double logarithmic scale, but the gradient found is much smaller.

In contrast to the dynamic response the sensitivity was not expected to depend on the metal layer thickness. Nevertheless, the results given in Fig. 4 show a strong decrease of sensitivity with the increase of Pt layer thickness. In our earlier experiments [4] we found the need for stabilising the sensitivity by a treatment in 1000 ppm of fluorine. To exclude an influence of changes of sensor behaviour with time, long time treatments up to 72 h were carried out. It was shown that the dependence of sensitivity on metal thickness is the same for different length of treatment in fluorine.

The components of the thin layer structure were varied to improve the knowledge about the role of the ionic conductor and the metal layer. A replacement of LaF$_3$ by other fluoride ion conducting materials such as BaF$_2$ resulted also in a fluorine sensitive structure. In contrast to this a substitution
Fig. 4. Dependence of sensitivity on thickness of the platinum layer with a change of gas concentration from 100 to 44 ppm.

Fig. 5. Bode diagram of a measurement at a single crystal of LaF$_3$ covered by a 5-nm platinum contact in different concentrations of fluorine: (---) 100 ppm, (---) 10 ppm, (- - -) 1 ppm.

Fig. 6. Equivalent circuit for the impedance measurement of Fig. 5.

by an insulator as Si$_3$N$_4$ did not give any fluorine sensitivity. Hence, a reaction at the platinum alone does not give a change in potential as it is known for work function sensors [9], and the fluoride ionic conductor is an essential part of the fluorine sensor. In another experiment, the platinum was replaced by a thin layer of gold. Here a fluorine sensitivity was found comparable to that of sensor structures using Pt, i.e., the sensitivity to fluorine is not caused by the specific catalytic activity of the platinum.

3.2. Impedance spectroscopy

Impedance spectroscopy on a structure n-Si/SiO$_2$/Si$_3$N$_4$/LaF$_3$/Pt resulted in spectra mainly dominated by the insulator layers. Therefore, for the investigation of the sensor mechanism a single crystal of LaF$_3$ in contact to a Pt layer prepared in the same way as for the semiconductor structure was investigated. The sensitivity data of this single crystal-based sensor were comparable to the semiconductor sensor. Hence, results of impedance measurements at the single crystal should be transferable to the thin film structure.

Fig. 5 shows an example of spectra of a single crystal of LaF$_3$ at different concentrations of fluorine. It was possible to describe the measurements by the equivalent circuit given in Fig. 6. Elements 1 and 2 have been shown to represent the interface LaF$_3$/Pt as it is suggested in [10]. The elements 3 and 4 are representing a space charge region in the LaF$_3$. The element number 5 is the bulk resistance of the LaF$_3$. The fitted values of the elements according to this model are presented in Table 1. Element 1 (resistance) depends on the concentration of fluorine, while the other elements are independent from the concentration. It is possible to estimate the thickness of the interface LaF$_3$/Pt and the space charge region by using elements 3 and 4. A dielectric constant of 12 was used as an approximation for LaF$_3$. Thicknesses of about 1 nm for the phase boundary LaF$_3$/Pt and about 26 nm for the space charge region were calculated. These
values are in good agreement with values typically known for double layers [11] and space charge regions [12].

Fig. 7 shows the dependence of element number 1 on the concentration in double logarithmic scale compared to the change of the $t_{50}$ time of the semiconductor sensors. The concentration dependence found for element 1 in combination with an atomic scale interface thickness are arguments to classify it as an electrochemical exchange resistance. For the exchange resistance 1 we obtained a slope of $-0.467$ which is similar to the slope of the response time. This is a further argument, that an electrochemical reaction takes place as the sensing process.

Using the values of the exchange resistance and the capacitance of the phase boundary LaF$_3$/Pt (CPE) the kinetics of the sensor response can be calculated using a simplified model of charging a capacitance:

$$t_{50} = RC \cdot \ln 2$$  \hspace{1cm} (3)

with $R$ the exchange resistance 1 and $C$ the capacitance from CPE 2.

The calculated response time $t_{50}$ from the model was compared with the measured $t_{50}$ time of a standard sensor. For a change of the gas concentration from 100 to 44 ppm the statistical mean value of the $t_{50}$ times is about 28 s. With the help of the line fit in Fig. 7 the $t_{50}$ time for a gas concentration of 44 ppm was calculated, resulting in a $t_{50}$ time of 14 s. Taking into account that the element we found is not really a capacitance but a CPE and impedance measurements were carried out at single crystals while response times were determined for polycrystalline layers on the semiconductor structures, the agreement of the values is surprisingly good. Nevertheless, Eq. (3) can not be used for the description of the whole response curve (Fig. 2). Therefore, the total response process is more complicated.

### 3.3. Interaction of platinum with fluorine

The dependence of the sensitivity on the thickness of the Pt layer leads to the idea, that the platinum might be fluorinated. To verify a fluorination of platinum AES measurements have been done after 24 h of exposure to 1000 ppm of fluorine. A fluorination of platinum is shown in Fig. 8. Furthermore, an in situ plasma-etching was used to achieve a deep profile of the sensor. Even at a depth of 30 nm fluorine was found (2 min of sputter time) (Fig. 9). A clear decision which one of the platinum fluorides is formed on the surface was not possible.

QCM measurements were used for additional investigation of the interaction of Pt with F$_2$ at a concentration of 1000 ppm. The result is given in Fig. 10. The mass of the platinum film is increasing in the first 90 min of contact with the gas. For longer times a decrease of mass was observed. The thickness of the fluorinated layer was estimated to be 1.4 nm. The decrease in mass can be understood as a desorption of a fluorination product. This is an argument for the formation of PtF$_6$ at the surface.
Fig. 10. QCM measurement of the interaction of a 30-nm Pt film with 1000 ppm of fluorine.

because it is the only platinum fluoride, which has a low boiling point (69.1°C) [13].

4. Discussion

The sensitivity of the fluorine sensor depends on the logarithm of the fluorine concentration. This is a first argument for an electrochemical mechanism of potential formation as described by the Nernst equation:

$$\Delta E = \frac{RT}{nF} \ln \left( \frac{c_2}{c_1} \right)$$

with $\Delta E$, total potential shift; $R$, gas constant; $T$, temperature; $F$, Faraday constant; $n$, number of exchanged electrons per molecule.

The dynamic behaviour of the sensor gives additional reasons to assume a charge transfer at the LaF$_3$/Pt interface to be the rate determining process. The results of impedance spectroscopy are a clear evidence for an electrochemical charge transfer process. On the other hand, the very high sensitivity would formally lead to a number of electrons exchanged smaller than one. Therefore, the formation of PtF$_6$ at the surface can be assumed to be the first step of the reaction:

$$\text{Pt} + 3\text{F}_2 \leftrightarrow \text{PtF}_6$$

Next dissociation can be assumed:

$$\text{PtF}_6 \leftrightarrow \text{PtF}_5^+ + \text{F}_p$$

(The unstable PtF$_5^+$ can react to other products at the surface not to be discussed here.)

The fluoride ion can then be exchanged between the Pt and the fluoride ion conductor LaF$_3$:

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

This is leading to a potential shift corresponding to Nernst’s law:
\[ \Delta E = \frac{RT}{F} \ln \left( \frac{c_3}{c_1} \right) \]  

(8)

It follows that:

\[ \Delta E = \frac{3RT}{F} \ln \left( \frac{c_3}{c_1} \right) \]  

(9)

This mechanism would correspond to a sensitivity of about 174 mV/dec.

In Fig. 4 the effect of the platinum layer thickness on the sensitivity was shown. An extrapolation of the curve to a thickness of 1 nm leads to sensitivities close to 174 mV/dec. The thickness of the fluorinated layer determined by QCM (1.4 nm) is leading to the conclusion that a sensitivity of 174 mV/dec will only be found if the Pt is fluorinated to a very high degree.

In Ref. [3] the same sensor with a different pre-treatment (at low concentrations of fluorine) was presented. This sensor type showed a sensitivity of 29 mV/dec. A simple mechanism based on the exchange of two electrons was shown to be reasonable. Therefore, for sensors treated at high concentrations and prepared with the standard Pt thickness of 30 nm, both mechanisms will be in competition. For a variation of metal layer thickness this would lead to sensitivities between 29 and 174 mV/dec. For thinner platinum layers the sensitivity is higher because a larger percentage of the platinum is fluorinated than for thicker platinum.

References

[1] EG-Sicherheitsdatenblatt für Fluor (15.11.95).