High temperature semiconductor sensor for the detection of fluorine

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Abstract

A chemical semiconductor sensor based on a silicon carbide substrate was investigated for the high temperature measurements of fluorine up to 350°C. The use of the structure SiC:SiO2:LaF3:Pt at room temperature leads to results comparable to the silicon based sensor. The influence of the temperature on the sensor response time was smaller than expected but the increased desorption rate and a high signal to noise ratio improved the detection limit. An impulse method using the initial slope of the response curve was shown to be advantageous. © 1998 Elsevier Science S.A. All rights reserved.

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1. Introduction

Fluorine is used for several industrial processes, for example in the production of polymers or the preparation of nuclear fuels. However, the gas is toxic even at low concentrations. Therefore, there is a great demand for sensors for this gas and for alarm systems controlling the environment.

Electrochemical cells for the detection of fluorine are produced by several companies (e.g. [1]), but they all have the liquid electrolyte as the main disadvantage. Murin et al. [2] proposed the use of a single crystal of LaF3 coated with a platinum film to get an all solid state 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 the gas electrode and of the reversible back side contact. These problems were partially solved by using pellets of solid electrolyte sintered at high temperature and high isotropic pressure and application of an amperometric measurement scheme (e.g. [3]), but the solid state fluorine sensors have not been commercialized.

The use of a metal insulator semiconductor (MIS) structure for the fluorine gas sensor promises an improvement of the properties of the sensing structure because the electrochemical component of the sensor and a microelectronic preamplifier are two parts of the same device. Its application also permits the use of all-microelectronic technology for sensor production.

We presented an early type of an semiconductor based fluorine sensor using a Si/LaF3/Pt structure at the Fifth International Meeting on Chemical Sensors [4]. At the Sixth Meeting [5] the optimization of the chemically active layers LaF3 and Pt was reported. At the Orlando ACS Meeting 1996 [6] the influence of preconditioning the sensor and the sensor mechanism were discussed. A drawback of the sensor was the dependence of the response rate on the gas concentration. This dependence leads to a slow response at small concentrations. Operation of the sensor at higher temperatures should lead to a considerably faster response.

The application of silicon based field effect devices is restricted to temperatures below 220°C. Due to the band gap of 3 eV for silicon carbide, it is possible to operate the sensor at temperatures higher than 600°C. This paper will show the advantages of the sensor based on silicon carbide as the semiconductor material instead
of silicon. Kinetic investigations lead to special conditions for the sensor application.

2. Experimental

The 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.

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 argon atmosphere in a way leading to a three phase boundary LaF₃/Pt/gas formation. A scheme of the sensor used in our experiments is given in Fig. 1a.

The capacitance (c) of the samples was measured using a Hewlett-Packard 4284A type LCR meter. High frequency capacitance voltage (V) measurements result in C–V curves of the type presented in Fig. 2. The change of gas concentration leads to a shift of these curves on the voltage axis. For the determination of the shift in voltage we used the constant capacitance method [7]. For some measurements the change of capacitance at constant voltage was recorded because this is the more direct device output signal. In this last case using the steepness of the C–V curve this change in capacitance can be recalculated to a change of voltage at the interface Pt/LaF₃. The photocurrent measurements were carried out using a Stafford Research Systems SR830 DSP lock-in amplifier.

Two special cells were designed for the high temperature measurement of the silicon carbide samples. In the first cell the samples were heated by a ceramic heater from the back side. The heater was covered by a metallic plate 1 mm thick. This plate fixed the sample and assured the back side contact of the sensor. Using this device gas sensitivities between room temperature and 400°C could be measured. Another 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 a temperature of 350°C in the fluorine containing atmosphere.

The gas sensitivity was measured under gas flow conditions. Commercial mixtures of 100 or 10 ppm of fluorine in synthetic air were mixed with synthetic air using computer-driven mass flow controllers to obtain different concentrations of fluorine in the range 0.03–100 ppm. Maximum gas flow velocity was 0.5 l min⁻¹.

3. Results and discussion

For sensor characterization, C–V as well as photocurrent–voltage curves were used. Photocurrent measurements were tested with the aim of achieving lateral resolution in further experiments. As expected, no difference between the two characterization methods was found for the determination of sensitivities and sensor kinetics.

Typical C–V curves are shown in Fig. 2. They were measured at 10 kHz and an AC voltage amplitude equal to 10 mV. The investigation of temperature dependence of the sensor behaviour showed changes in the capacitance of the structure SiC/SiO₂/LaF₃/Pt. This can be explained considering the properties of the ionic conductor LaF₃. The electrical properties of the sensor structure can be described by the simplified equivalent circuit given in Fig. 1b.

The thin layer of LaF₃ is described by a capacitance and a parallel resistance representing the ionic conduc-
Fig. 3. Fluorine sensitivity of the silicon carbide sensor at room temperature. Baseline concentration is 9 ppm; sensitivity of the structure is 34 mV per decade.

Sensitivity caused by the mobile fluoride ions. At low temperatures the mobility and the concentration of mobile fluoride ions were small, and the accumulation capacitance was dominated by the capacitance of the LaF$_3$ since the thickness of the SiO$_2$ is only 28 nm. With increasing temperature, the conductivity in the ionic conducting layer increased by several orders of magnitude as shown using impedance spectroscopy [8]. Hence, the impedance of the LaF$_3$ layer was now dominated by the resistance while its capacitance became negligible. Instead, the thin SiO$_2$ layer determined the accumulation capacitance of the structure at high temperatures. The capacitance found in the accumulation region is in good agreement with the value calculated for the SiO$_2$ layer.

The substitution of the semiconductor substrate silicon used in previous experiments by the wide gap material silicon carbide should not change the sensor properties because the reaction determining the potential takes place at the three phase boundary LaF$_3$/Pt/gas. This means that the voltage drop at the interface Pt/LaF$_3$ changes with a change in gas concentration. The sensor operation in constant capacitance mode results in a constant surface potential of the semiconductor and a constant voltage drop for the SiC/SiO$_2$/LaF$_3$ subsystem (for theory of $C-V$ measurements see [9–11]). Therefore, the constant capacitance method causes a change of gate voltage which compensates the change of the voltage drop at the LaF$_3$/Pt interface. Ultimately, the silicon carbide is just an in situ amplifier as is well known for silicon based devices. The comparison of sensitivity measurements for silicon carbide based sensors with the silicon sensors did not in fact show any considerable changes at room temperature.

The room temperature gas sensitivity of the silicon carbide based sensor is presented in Fig. 3. The concentration dependence of the equilibrium sensor signal showed a linear dependence with a slope (sensor sensitivity) of $33 \pm 2$ mV per decade of fluorine concentration on the logarithmic scale. This corresponds to the two electron electrochemical process taking place on the three phase boundary LaF$_3$/Pt/gas:

$$F_2 + 2e^- \rightarrow 2F^-$$

(1)

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

$$E = E_0 + \frac{RT}{zF} \ln([F_2])$$

(2)

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

The theoretical value of the slope $RT/zF$ should be $29 \pm 1$ mV per decade depending on the precise value of room temperature. Our sensor shows a somewhat larger sensitivity which could be due to the HF impurity in the fluorine gas caused by the reaction of fluorine with traces of water in synthetic air.

At elevated operational temperatures two versions of sensor behaviour are possible. If the sensing mechanism remains the same as at room temperature (Eq. (1)), this process should be accelerated and the response time should obey the Arrhenius law. In this case we should observe the same two electron process but at a higher rate. Another possible behaviour is a change of the reaction mechanism. This change not only leads to a change in the sensor response rate, but also to a change of the sensor sensitivity.

It was surprising that the sensor response rate is hardly affected by temperature even up to 350°C. Fig. 4 presents the influence of the temperature on the response rate of the MIS structure gas sensor. The influence of temperature on the sensitivity of the gas sensor was much greater. The concentration dependence of the sensor signal is shown in the Fig. 5.
The sensitivity of the sensor at 330°C was $135 \pm 10$ mV per decade. This value is a little higher than the theoretical sensitivity for a one electron electrode process at this temperature (120 mV per decade). The high sensitivity of the sensor may be due to dissociation of molecular fluorine, which was possible because of the low bond energy of the fluorine molecule (about 37 kcal mol$^{-1}$). This value makes the temperature of 330°C sufficient for the partial dissociation of F$_2$.

$$F_2 + \text{surface} \rightarrow 2F$$ (3)

Dissociation near 100% would lead to the one electron process on the gas electrode and to the sensor sensitivity close to 120 mV per decade.

The equilibrium constant for this reaction is $K = 1.1 \times 10^{25} \times \exp(-18920/T)$. This value was measured in fluorine flow conditions with the use of an EPR spectrometer as an atom detector (V.F. Sinianski, V.N. Bezmelnitsyn, A.A. Vasiliev, private communication). The concentration of atoms calculated using this constant is 14% of the initial 1 ppm concentration of molecular fluorine in air at 330°C. This is not sufficient to explain the sensor sensitivity of about 135 mV per decade.

The rate of the sensor reaction to the stepwise change of fluorine concentration is only slightly affected by the increase of the temperature. It increases by a factor of between 2 and 3 when the temperature is changed from room temperature to 300°C.

To improve the determination of low concentrations of fluorine an impulse scheme, which was developed earlier for hydrogen determination [12], was applied. In this scheme the sensing element was permanently exposed to a constant reference fluorine concentration. This assured stability of the sensor properties and particularly of the flat band voltage of the MIS structure.

The concentration to be measured was supplied for a short time and the time derivative of the sensor signal measured.

An example of this curve measured at room temperature is presented in Fig. 6. The reference concentration should be chosen close to the level most important for the measurement. As reference, a fluorine concentration of 0.3 ppm was chosen. This value is the official tolerable level of fluorine in air for industrial conditions in Russia (in Germany this level is 0.1 ppm). Fig. 6 demonstrates the possibility that two orders of magnitude of fluorine concentration can be measured by the ‘initial slope’ method. These measurements were done at room temperature.

The slopes of the initial parts of the peaks, calculated from the results of Fig. 6, are presented in Fig. 7. The plot presented in Fig. 7 shows the dependence close to linear between the initial slope of the sensor signal and
the fluorine concentration. This dependence differs from the Nernst dependence of the equilibrium sensor signal on the gas concentration (Fig. 3). This linear dependence could be described with the following model.

We assume that the fluorine adsorption is a rate determining reaction and that the low fluorine concentration allows the use of a Henry adsorption equation to describe this process. In this case we can write Eq. (4) and Eq. (5) for the room temperature and no dissociation of fluorine as follows:

\[(F_2)_{\text{ads}} \leftrightarrow (F_2)_{\text{gas}}\]  
\[\frac{d(F_2)_{\text{ads}}}{dt} = -k_1(F_2)_{\text{ads}} + k_2(F_2)\]  

where \([F_2]_{\text{ads}}\) is the current concentration of adsorbed molecules, \([F_2]_{\text{gas}}\) is the fluorine concentration in gas, and \(k_1\) and \(k_2\) are the desorption and adsorption rate constants, respectively.

In the equilibrium state I (before the fluorine concentration step), the concentration of adsorbed molecules can be estimated using the Henry approximation:

\[[F_2]_{\text{ads}} I = \frac{k_2}{k_1} \times [F_2]_I\]  

Just after the concentration step (state II) the surface concentration changes more slowly than the gas phase fluorine concentration:

\[\Delta[F_2]_{\text{ads}}/\Delta t = -k_1[F_2]_{\text{ads}} I + k_2[F_2]_I\]  

where \([F_2]_{\text{ads}} I\) is the concentration of adsorbed molecules before the concentration step (state I), \([F_2]_I\) is the fluorine concentration after the concentration step (state II). Substituting Eq. (6) into Eq. (7) we get:

\[\Delta[F_2]_{\text{ads}}/\Delta t = k_2([F_2]_I - [F_2]_I)\]  

If the adsorption is a rate determining process, the sensor signal \(V\) follows the current concentration of adsorbed fluorine molecules, and for its derivative we can write Eq. (9) as follows:

\[dV/dt = (RT/zF) \times d(ln[F_2]_{\text{ads}})/dt\]  
\[\approx (RT/zF) \times (1/[F_2]_{\text{ads}} I) \times (\Delta[F_2]_{\text{ads}}/\Delta t)\]  

and substituting Eq. (8) into Eq. (9) we get:

\[dV/dt \approx \Delta[F_2]_{\text{ads}}/\Delta t = k_2([F_2]_I - [F_2]_I)\]  

Therefore the points in the plot presented in Fig. 7 should lie on the same straight line at concentrations above and below 0.3 ppm (the reference level). The points are in fact very close to the same straight line. The difference between the slopes of two lines in Fig. 7 demonstrates the precision of our approximation. The low detection level for this measurement set is less than 0.03 ppm. It was difficult to achieve lower fluorine concentrations because the uncertainty in the fluorine concentration becomes too large.

The high temperature measurement significantly improved the signal to noise ratio (an example of the initial slope measurement at 330°C is given in Fig. 8) due to the change in \(C-V\) curve shown in Fig. 2. These data are compared with the room temperature measurement in Fig. 9; a significant increase of the sensitivity of the sensor at 330°C is seen.

High temperature measurements of the initial slope can decrease the total time of the concentration measurement. This is due to both a small acceleration of the processes on the surface and to the improvement of the signal to noise ratio. The minimum time for the measurement of the fluorine concentration by this method is now about 100 s, consisting of 10 s for the initial slope measurement and 90 s recovery time.
4. Conclusions

The properties of the silicon carbide based sensor structure SiC/SiO2/LaF3/Pt were investigated for the high temperature (up to 350°C) measurements of fluorine concentrations. It was shown that the use of this structure at room temperature leads to results comparable to the silicon based sensor. The influence of the temperature on the sensor response time was smaller than expected. Nevertheless, the increased desorption rate and a high signal to noise ratio improved the detection limit of the sensor. An impulse method using the initial slope of the response curve was shown to be advantageous. It permits the fluorine gas concentration to be measured down to 0.03 ppm with a repetition frequency of about 1 measurement per minute.

The model including the physical adsorption of fluorine on the sensor surface rate determining process was suggested for the description of the sensor behaviour.

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References