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Discrimination and Quantification of Volatile Organic Compounds in the ppb-Range with Gas Sensitive SiC-Field Effect Transistors

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Abstract

Gas sensitive FETs based on SiC have been studied for the discrimination and quantification of hazardous volatile organic compounds (VOCs) in the low ppb range. The sensor performance was increased by temperature cycled operation (TCO) and data evaluation based on multivariate statistics, here Linear Discriminant Analysis (LDA). Discrimination of formaldehyde, naphthalene and benzene with varying concentrations in the ppb range is demonstrated. In addition, it is shown that naphthalene can be quantified in the relevant concentration range independent of the relative humidity and against a high ethanol background. Hence, gas sensitive SiC-FETs are suitable sensors for determining indoor air quality.

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Keywords: Indoor Air Quality; trace level; temperature modulation; pattern recognition; Linear Discriminant Analysis

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1. Introduction

Quality of indoor air is strongly affected by volatile organic compounds (VOCs) which pose a serious health risk even at very low concentrations (usually in the low ppb range). Lack of fresh air can lead to sick building syndrome (SBS) with symptoms like acute discomfort, headache and difficulties in concentrating [1]. Some VOCs like benzene are carcinogenic, their concentration should thus be as low as possible. Since people spend most of their time indoors (approx. 80-85 %) there is an increasing need for automated energy-efficient ventilation systems which are not only based on the CO_2 level but also take the VOC concentration into account. Different organizations, e.g. the World Health Organization (WHO) [2], and research projects, e.g. INDEX [3], have studied the impact of VOCs on humans and have suggested priority lists and guideline values. Target VOCs of high relevance are benzene (guideline value 1.5 ppb), naphthalene (guideline value 5.6 ppb) and formaldehyde (guideline value 80 ppb).

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Gas sensitive field effect transistors based on silicon and, later, also on silicon carbide (SiC-FETs) have been studied and improved for many years [4]. By using catalytically active gate materials like platinum or iridium excellent gas-sensitivity is achieved for SiC-FETs. The sensitivity of the sensor depends mainly on the gate material and its structure, the underlying insulator as well as the operating temperature.

The sensing principle of SiC-FETs is based on the formation of a polarized layer at the metal-insulator interface or a change in metal work function of the transistor. For porous gates, gas molecules approaching the surface can either dissociate on the catalyst after adsorption or can directly interact with the insulator. In oxygen containing atmospheres the sensing mechanism can partly be explained by spill-over effects of dissociated hydrogen and / or adsorbed oxygen which influence the electric field in the underlying oxide. A more comprehensive explanation of the sensing principles can be found in [5].

Selectivity of the SiC-FETs can be improved by dynamic operation, e.g. temperature cycled- (TCO) and/or gate bias cycled operation (GBCO) [6], [7]. Recently, it we have reported that gas sensitive field effect transistors based on silicon carbide are highly sensitive to VOC [8].

In this work not only detection and discrimination of VOC is presented, but also quantification of single VOCs.

2. Experimental Setup and Signal Processing

For all measurements, depletion type SiC-FETs with porous gate metals either 25 nm platinum or 30 nm iridium were used [9]. The SiC chip was glued on a ceramic heater (Heraeus) together with a Pt-100 temperature sensor. The FET was operated in a constant current mode (I_D = const.) and the resulting voltage drop, V_{DS}, was recorded as the sensor signal. A simple temperature cycle consisting of three temperature plateaus (for Pt-gate: 180 °C, 200 °C, 220 °C and for Ir-gate 250 °C, 300 °C, 350 °C) with a duration of 15 s each, was used (see also [8]). Naphthalene, benzene and formaldehyde were chosen as target VOCs; in addition, ethanol was tested as interference at concentrations up to 1 ppm and the background humidity was also varied. A new gas mixing system based on permeation ovens and gas pre-dilution was used for all measurements [10].

Measurement data has been normalized cycle-wise by setting the cycle mean to one in order to reduce the influence of sensor drift. Gas significant features, like mean values and slopes, describing the shape of the sensor response have been extracted in seven different parts of each cycle. Based on these features, pattern recognition, like Linear Discriminant Analysis (LDA) has been performed for discrimination and quantification of VOCs. The results have been validated by leave-one-out-cross validation (LOOCV) with a Mahalanobis distance classifier.

3. Results and Discussion

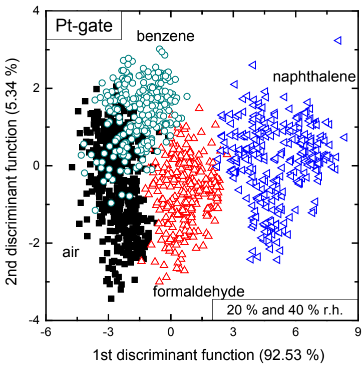
3.1. Discrimination of Volatile Organic Compounds

Discrimination of the three selected VOCs independent of the relative humidity level is possible as shown in Fig. 1a. Each group holds three different concentrations at two different humidity levels (20 % and 40 % r.h.). Although the scatter is quite high, leave-one-out-cross validation leads to an overall correct classification rate of almost 89 %. Benzene (2.5, 3.5, 4.5 ppb) is difficult to detect and the corresponding group show significant overlap with the air group resulting in a validation rate of only 80 %. For naphthalene and formaldehyde validation rates of 99 % and 95 % respectively can be reached.

A much better separation of the gases can be achieved when only one humidity level is taken into account. However, for real applications it is important to use as much information as possible for the training in order to make the discrimination robust.

3.2. Quantification of Naphthalene in Air

After identification of a target VOC, quantification is required as basis for determining the ventilation strategy. Fig. 2a shows a 2D-LDA scatter plot and the corresponding histogram for the first discriminant function (DF1) which basically represents all the discriminatory information (>99 %). A clear separation of the different concentration groups, again independent of the relative humidity level, was found. In Fig. 2b the LDA was only



(a)

Leave-one-out-cross validation

group	correctly classified
overall	88.62 %
air (20 % + 40 % r.h.)	83.23 %
naphthalene	99.23 %
formaldehyde	95.19 %
benzene	79.92 %

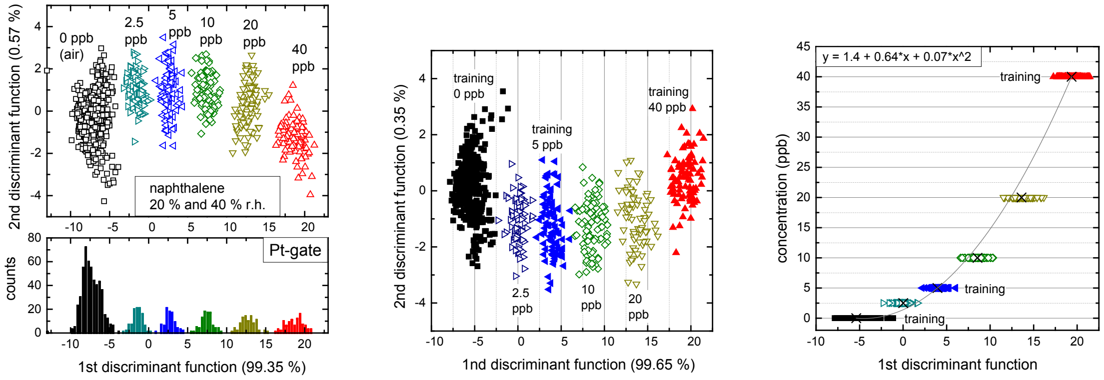
(b)

Fig. 1 (a) Discrimination of benzene (2.5, 3.5 and 4.5 ppb), naphthalene (10, 20 and 40 ppb), formaldehyde (50, 75, 100 ppb) and carrier gas with combined relative humidity levels (20 % and 40% r.h.), and (b) result of leave-one-out cross validation (LOOCV).

trained with three concentrations (0, 5, 40 ppb, marked by solid symbols). The LDA coefficients obtained from the training were then used to project "unknown" data points in the same plot (2.5, 10, 20 ppb, marked by open symbols). It can be observed that the "unknown" data (new groups) fits to the "LDA model" obtained from the training procedure. In order to allow quantification, centroids of the training group are plotted versus their DF1 values and then fitted using a second order polynomial (cf. Fig. 2c). The "unknown" groups (open symbols) are again projected into the same plot. They are located close to the fit-curve so that a prediction of unknown concentrations using the given equation is possible. In principle, the uncertainty of the quantification is represented by the scatter of the groups along DF1 together with the distance of the centroids to the fit-curve.

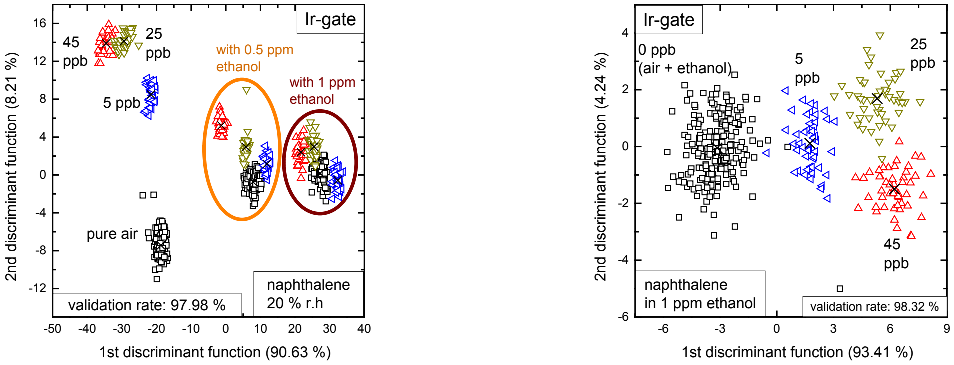
3.3. Quantification of Naphthalene in Ethanol

Not only quantification of naphthalene in air is possible but also discrimination in different ethanol atmospheres. In Fig. 3a a 2D-LDA scatter plot of an Ir-gate FET is given which shows discrimination of three different naphthalene concentrations (5, 25, 45 ppb) in three different ethanol atmospheres (0, 500, 1000 ppb) at 20 % r.h.. It can be observed that naphthalene groups with the same ethanol background form clusters in the LDA plot, thus the algorithm basically separates different ethanol backgrounds, and show that ethanol has a strong influence. With increasing ethanol concentration the naphthalene groups overlap more making a direct quantification of naphthalene almost impossible. Therefore a hierarchical strategy (multi-step LDA) could be used similar to [11]. In a first step



(a) (b) (c)

Fig. 2 (a) Quantification of naphthalene independent of the humidity level. Each group contains data at 20 % and 40 % r.h., (b) projection of unknown naphthalene concentrations (open symbols), and (c) prediction of unknown concentrations.



(a) (b)

Fig. 3 (a) Discrimination of different naphthalene concentrations in 20 % r.h. and with additional 0.5 ppm and 1 ppm ethanol, and (b) quantification of naphthalene in 1 ppm ethanol.

the background (here: ethanol) needs to be determined and based on this decision a second LDA is used to quantify the naphthalene concentration. Fig. 3b shows a quantification of naphthalene in an atmosphere of 1 ppm ethanol at 20 % r.h.. The scatter is slightly higher and the groups are not aligned along DF1 as it was in Fig. 2a, however, determination of the approximate concentration is still possible.

4. Conclusion and Outlook

In this work, discrimination of three different VOCs independent of the relative humidity level is demonstrated with gas sensitive FETs run in TCO. The suggested approach facilitates quantification of naphthalene independent of relative humidity level as well as in a high ethanol atmosphere.

Thus, SiC-FETs are promising candidates for IAQ applications. Future work will address optimization of the sensitive layers as well as the TCO.

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