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SiC-FET sensors for selective and quantitative detection of VOCs down to ppb level

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Abstract

With the increased interest in development of cheap, simple means for indoor air quality monitoring, and specifically in relation to certain well-known pollutant substances with adverse health effects even at very low concentrations, such as different Volatile Organic Compounds (VOCs), this contribution aims at providing an overview of the development status of the silicon carbide field effect transistor (SiC FET) based sensor platform for ppb level detection of VOCs. Optimizing the transducer design, the gas-sensitive material(s) composition, structure and processing, its mode of operation - applying temperature cycled operation in conjunction with multivariate data evaluation - and long-term performance it has been possible to demonstrate promising results regarding the sensor technology's ability to achieve both single-digit ppb sensitivity towards e.g. naphthalene as well as selective detection of individual substances in a mixture of different VOCs.

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Keywords: indoor air quality monitoring; field effect transistor gas sensors; silicon carbide; pulsed laser deposition; temperature cycled operation

1. Introduction

Modern-day people spend increasingly more of their time in indoor environments, both at home and in work related contexts. Following this trend it has become more and more apparent that people to a higher degree than ever before are exposed to different kinds of air pollutants which are generated or accumulated in the indoor environment.

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With the rapid development of new materials which are introduced in a wide range of home and office products, from new insulation materials to chemicals such as softeners added to plastic food containers, concerns about the indoor air quality is just expected to increase. According to a study published 2013 by the EU project *HealthVent*, the number of annual healthy life-years being lost as a result of indoor air pollution within EU alone is estimated to two millions [1]. The Environmental Protection Agency (EPA) in USA has also ranked impaired indoor air quality as one of the five most important contemporary health risks [2]. Currently this area also suffers from a lack of detailed information on both the presence and the effects of many of the substances which potentially could be found in the indoor air on personal health. In addition to a general appellation from WHO to relevant organizations to work for the development of methods regarding evaluation of indoor air quality [3], a number of EU-initiated research programs in the area as well as the statement from EPA in 2005 that ”the development of improved personal monitors that are less cumbersome for users to wear and that can accurately sample for a broader range of chemicals is needed” [2], confirms the importance of research into and development of cheap, low-power, distributed/portable/ wearable sensors and sensor systems for continuous monitoring of the indoor air quality. This contribution therefore treats the current development status of the silicon carbide (SiC) field effect transistor (FET) based sensor platform in connection to this application and field of research.

1.1. FET based gas sensors – basic design and transduction principles

The basic design of SiC FET gas sensors is displayed in Fig. 1(a). By applying as gate contact in traditional MOSFETs (Metal Oxide Semiconductor Field Effect Transistor) a material (commonly a catalytic metal) which interacts with one or more gaseous substances such that the gate to substrate electric field is modulated, FET based gas sensors can be fabricated. When, for example, exposing a Pt gate MOSFET structure to hydrogen, atomic hydrogen is generated through dissociative adsorption on the catalytic metal surface. Free hydrogen atoms subsequently diffuse through the thin Pt film and adsorb on top of oxygen atoms in the surface of the oxide, see Fig. 1(b). The resulting hydroxide groups give rise to a change in polarization of the metal/oxide interface, affecting the gate-to-semiconductor electric field. Two more principles by which this electric field can be modulated are through the adsorption on the oxide surface of ions, e.g. oxygen anions (Fig. 1(b)), and a change in the gate metal work function. The change in gate-to-semiconductor electric field in turn modulates the number of charge carriers in the top part of the semiconductor and thus the I_D/V_{DS}-characteristics of the device (Fig. 1(c)). Either the change in drain current upon gas exposure when supplying a constant drain voltage or vice versa is taken as the sensor output [4].

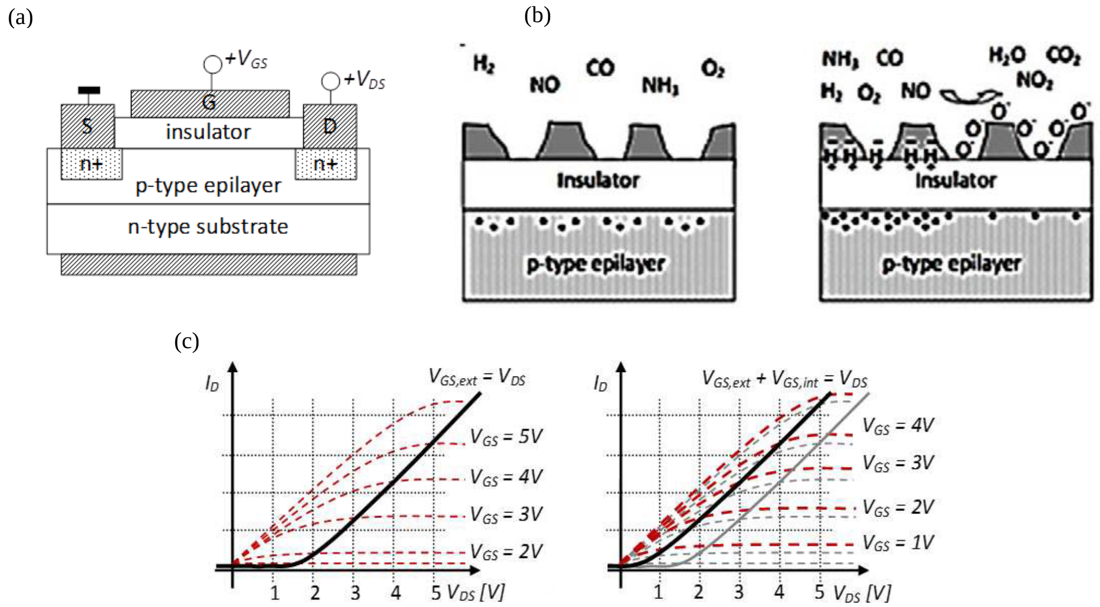

Fig. 1 displays in (a) the basic cross-sectional design of a field effect transistor based gas sensor and in (b) and (c) the change in the number of mobile charge carriers in the top part of the semiconductor upon gas exposure and the resulting change in I/V characteristics, respectively.

1.2. SiC-FET based gas sensors in relation to the field of air quality monitoring

Transistor based transducers are potentially well suited for the development of small, cheap and deployable sensors for environmental monitoring, both as stationary and personal (wearable) monitors, mainly due to easy mass production, cheap and simple driver and read-out electronics, easy integration into sensor systems, and the possibility for realizing very low standby power consumption (with the possible realization of battery and/or energy harvesting powered sensors). Furthermore, realizing FET gas sensors in SiC provides good possibilities to selectively detect a wider range of gaseous substances with a single (or a few) sensor elements due to the ability to apply a wide range of operation temperatures in conjunction with smart data evaluation, as will be further treated below.

2. Basic transducer development

In order to be applicable for indoor air quality monitoring, good sensitivity to even single-digit ppb concentrations of certain substances is required for the sensor technology. This applies just as much to the basic transducer (the transistor device) itself as the gas sensitive materials and the sensor operation. By, e.g., studying the influence on the general sensitivity to different gaseous substances of different design parameters it has been concluded that almost a factor of two in general sensitivity can be gained by optimizing the thickness of the gate dielectrics without jeopardizing long-term performance (see Fig. 2). Through the application of a high-k material as at least part of the gate dielectrics the general sensitivity can be improved even a bit further. On the topic of long-term reliability, which is of utmost importance since even the slightest instabilities have a large effect on the possibility to reliably quantify small concentrations, detailed studies have shown that device designs allowing smaller field strengths between the different device terminals provide better long-term performance.

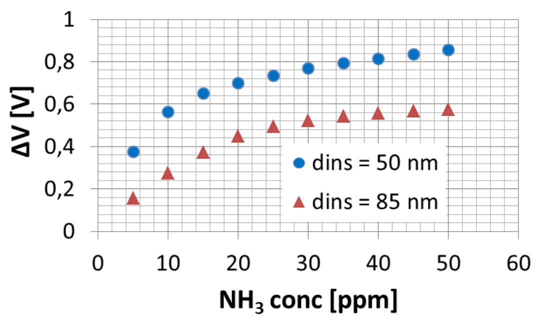

Fig. 2 displays the increase in sensor response (sensor voltage signal change, ΔV) upon a decrease in gate insulator thickness (dins), as exemplified by the exposure of the sensor devices to different concentrations of ammonia

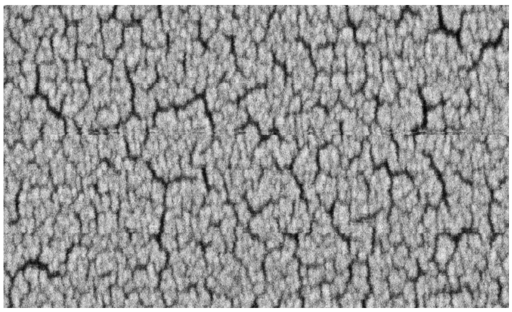

Fig. 3 displays an example of a nanostructured thin-film of Ir applied as gate contact in a SiC-FET gas sensor device, in this particular example deposited by DC magnetron sputtering

3. Gas-sensitive materials and their processing

Using nanostructured gate materials, such as Pt and Ir, with large surface area (see Fig. 3) ensures high catalytic activity, which in turn provides high sensitivity to gaseous substances undergoing reactions such as dissociative adsorption on the surface of the gate contact. In relation to the basic transduction mechanisms of the FET sensor platform this is especially important for the detection of hydrogen-containing species such as various VOCs. Through the development of Pulsed Laser Deposition (PLD) processes [5] for some gas-sensitive materials it has proven possible to gain better control over the film nanostructure, additionally with improved size distribution of the nanograins and better film reproducibility. Generally, pulsed laser deposition also provides better film adhesion and so better long-term stability which, as mentioned above, also has a positive effect on the sensitivity over time (signal to noise ratio). Employing pulsed laser deposition also of oxide materials, applied as the top surface of the FET gate insulator stack, it has been shown possible to process really thin, good quality gate dielectric films/surfaces of some different materials, e.g. WO_3, to tune the selectivity of the FET sensor devices. Influencing the reactions of adsorbing substances at the three-phase boundaries between the metal, oxide, and the gas-phase as well as the adsorption on the insulator surface as such it has been shown that the employment of different insulator materials improves the possibility to separate and quantify different VOCs.

In combining the optimized SiC FET transducer with a nanostructured thin-film iridium-gate, sensor devices highly sensitive to naphthalene (see Figure 4) have for instance been demonstrated. This kind of sensor device also exhibits a detection limit below 0.5 ppb over the whole range from dry air up to 60 % relative humidity (r.h.) [6].

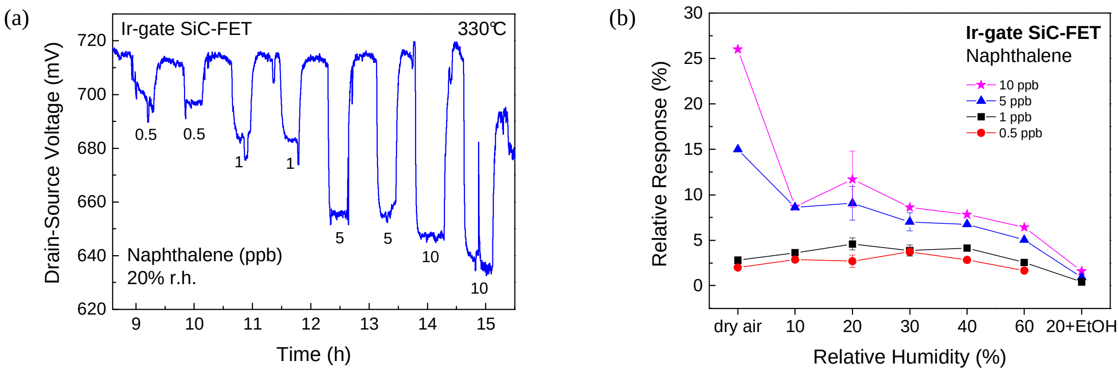

Fig 4 (a) Sensor response to ultra-low concentrations of naphthalene from 0.5 to 10 ppb; (b) Relative response to naphthalene as a function of the relative humidity. The figure shows also the effect of 0.5 ppm ethanol (EtOH), introduced as interfering gas, to the sensor response.

4. Mode of operation

As touched upon in the introduction, the possibility to operate the sensor devices over a wide range of temperatures also opens up for exploring a multitude of reactions different substances undergo at different temperatures, and which influences the sensor signal. Utilizing that different substances undergo these reactions at different temperatures, it has been shown possible to selectively detect and even to some extent quantify different VOCs, such as formaldehyde, in a gas mixture containing also other VOCs through temperature cycled operation and multivariate data evaluation procedures applied to the resulting signals from just one sensor element [7]. The application of temperature cycled operation for each of a combined selection of sensor elements, with different gas-sensitive gate and insulator materials, thus provide improved possibilities for detection of individual VOCs.

Acknowledgements

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References

[1] http://www.env-health.org/news/latest-news/article/indoor-air-quality-launch-of-eu, 2016-07-21
[2] U.S. EPA report 402-B-05-001, March 2005
[3] WHO report "The right to healthy indoor air", EUR/00/5020494, The Netherlands, 2000, http://www.euro.who.int/__data/assets/pdf_file/0019/117316/E69828.pdf, 2016-07-21
[4] M. Andersson, R. Pearce, A. Lloyd Spetz, New generation SiC based field effect transistor gas sensors, Sensors and Actuators B 179 (2013), 95-106.

[5] J.Huotari, J. Lappalainen, J. Puustinen, T. Baur, C. Alépée, T. Haapalainen, S. Komulainen, J. Pylvänäinen, and A. Lloyd Spetz, Pulsed Laser Deposition of Metal Oxide Nanoparticles, Agglomerates, and Nanotrees for Chemical Sensors, Procedia Engineering 120 (2015), 1158-1161.
[6] D. Puglisi, J. Eriksson, C. Bur, A. Schuetze, A. Lloyd Spetz, and M. Andersson, Catalytic metal-gate field effect transistors based on SiC for indoor air quality control, J. Sens. Sens. Syst. 4 (2015) 1-8.
[7] M. Bastuck, D. Puglisi, J. Huotari, T. Sauerwald, J. Lappalainen, A. Lloyd Spetz, M. Andersson, and A. Schütze, Exploring the selectivity of WO_3 with Iridium catalyst in an ethanol/naphthalene mixture using multivariate statistics, Thin Solid Films, submitted