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Chemical Sensor Systems for Emission control from Combustions

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Abstract:
Environmental and health concern has increased the importance to monitor and control emissions from combustion processes like toxic gases and particulate matter. The SiC-FET technology offers versatile and powerful sensors for gas detection also in combination with combustion of particles. Emission control has been demonstrated e.g. for small and medium sized power plants and diesel exhausts. The potential danger of nanoparticles makes such detectors interesting not only for detection of concentration and size of particles but also detection of the content of particles. The SiC-FET technology lends itself for smart sensing and smart data evaluation, which largely improves the information from such a sensor system. Here we report progress on the sensor technology itself, the application of a sensor system as an alarm for ammonia emission and preliminary results of particle detection.

Key words: SiC, FET, gas sensor, particle detector, alarm, data evaluation.

Introduction

Fuel combustion generates heat and power but also pollution like nitrogen oxide gases and particles. EPA (Environmental Protection Agency, USA) restrictions for e.g. heavy duty diesel trucks are now down to almost zero emission levels, followed by a large part of the world. Technological solutions to lower the emissions have therefore been developed, such as combustion with recirculation of exhaust gases, the use of urea injection to reduce nitrogen oxide gases and particulate filters. Similarly important is the control methods for the dangerous emissions. Sensors e.g. for oxygen and nitrogen oxide monitoring in diesel exhausts are commercially available and still an active research field [1, 2]. A number of particulate sensors are available which detect particles according to size and mass or volume concentration, improvements are reported in articles as well as the use of such equipments [3, 4]. Here we report on the SiC-FET sensor technology progress, their demonstration as ammonia sensors, discuss the improvement through use of smart sensing and show preliminary results for detection especially of particle content.

SiC-FET sensor platform

A new generation Metal Insulator Semi-conductor Field Effect Transistor (MISFET) devices based on 4H-SiC, see Fig. 1, has been designed and processed to be used as sensors e.g. for flue gas monitoring and other high temperature applications [5]. Catalytic metals such as Pt and Ir are typically deposited as gas sensitive gate materials.

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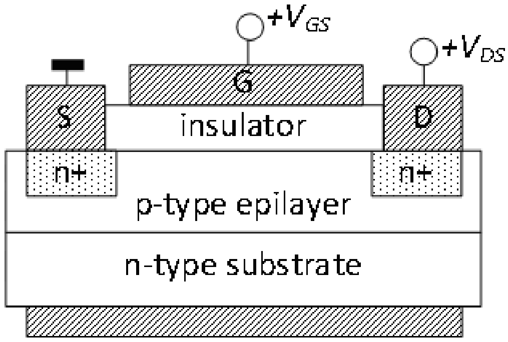

Fig. 1. Cross-sectional view of a MISFET transducer platform for gas sensors.

The I/V-characteristics during exposure to various concentrations of hydrogen, ammonia and carbonaceous substances at 150-300°C has been obtained, see Fig. 2. The long-term stability of devices with discontinuous metal films upon exposure to certain gas mixtures at elevated temperatures (> 350°C) has in earlier generations of field effect sensors been poorer as compared to devices with dense, homogeneous gate contacts. The long-term stability of the new MISFET transducer was found to be substantially better than earlier generations, with only a 10% loss of signal over a full four weeks and an overall baseline drift of less than 4% (where most of the drift occurred the first few hours, most probably due to annealing of contacts). This should be compared to a 70% loss of signal and approximately 15% baseline drift exhibited by the earlier generation under the same conditions.

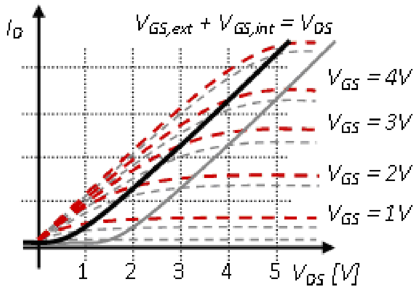

Fig.2. Typical I/V characteristics of a MISFET transducer device in absence (grey dashed line) and presence (red dashed line) of a gas which can introduce an internal voltage drop at the gate metal/ insulator interface and thereby shift the I/V-curve.

SiC-FET as an ammonia alarm

Due to their increased sensitivity to species other than hydrogen, e.g. NH_3, CO and NO, SiC-FET devices with thin, discontinuous gate metals have been utilized for several high temperature applications, such as determination of ammonia concentration in diesel for use in ammonia slip monitoring e.g. for control of SCR/SNCR exhaust systems [6] or emissions monitoring and control of biomass fuelled domestic heating systems [7]. Figure 3 displays that this transducer platform is able to detect ammonia with high sensitivity and at an alarm level of 15-20ppm ammonia in typical flue gases with very little interference from other flue gas substances.

Recently it was demonstrated that largely improved information is possible from the SiC-FETs through smart sensing e.g. by operation in temperature or bias cycled mode and applying smart data evaluation [8, Bur et al, this conference proceeding].

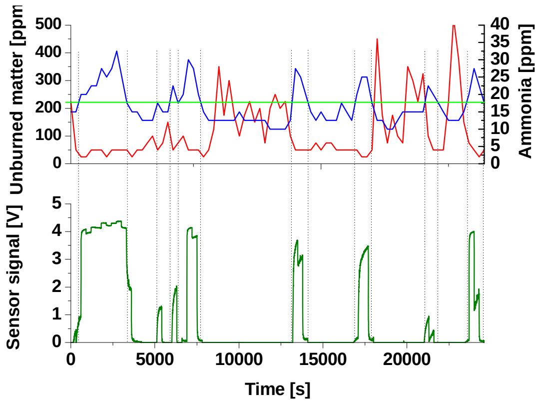

Fig. 3. The upper panel displays flue gas emissions of unburned matter (red (lower curve during first 0-8000 s)) and ammonia slip (blue) whereas the lower panel shows the corresponding sensor signal set to an alarm level of 15-20ppm ammonia.

Particle detection

Nanotechnology has revolutionized the material science area and provided e.g. new sensitive, selective and stable materials for sensors. However, depending on size, shape, content and concentration, particles may also be harmful to our health, since the small size makes possible for particles to enter the human body through lung tissue as well as through the skin. Both content and shape seem to be especially important parameters, which influences the toxic effect of the particles. Particle detectors for size and concentration are already in the market as mentioned earlier, while a particle detector, which detects the content of particles is under development.

Impedance spectroscopy applied between interdigital electrodes, IDEs, has the potential to reveal particle size and to some extent content of particles [9]. Here impedance spectroscopy was used to characterize different kinds of particles, particles from a steel plant and carbon nanotubes.

IDEs on sapphire of Ti 30nm / Pt 300 nm with 10 µm or 20 µm gaps between the fingers [10] were used for collection of particles from the inside environment of a steel plant. The collected particles were characterized by SEM and impedance spectroscopy together with carbon nanotubes, CNTs, for comparison. The particles from the steel plant and CNTs were mixed in cyclopentanol. The concentration of CNT's in solution was either 0.089 mg/ml or 0.0089 mg/ml. The concentration of the steel plant particles in solution were 0.18 mg/ml and 4 mg/ml. The different solutions were deposited on top of the electrodes and then dried in air.

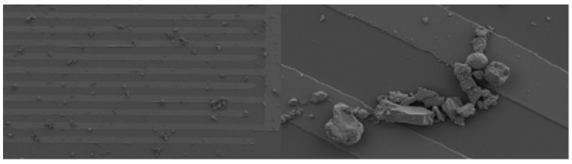

Fig. 4. Particles from the steel plant on top of 20 µm IDE structure

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) studies confirmed that the particles from the steel plant consisted mostly of ferrous-oxides. Figure 4 shows the SEM image of ferrous-oxide particles on top of IDE with 20 µm gap.

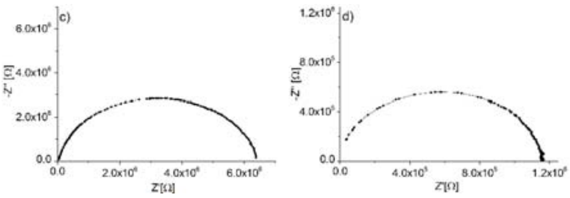

Fig. 5. Impedance spectra of steel plant particles (to the left) and CNT (to the right).

Impedance spectra of the samples were measured over the frequency range 200Hz - 1MHz by a probe station connected to Agilent 4284A LCR-meter. From the results it could be seen that the spectra varied according to particle concentration and composition. In Fig. 5 the complex impedance spectra of different measurements are shown. Both the steel plant particles and CNT's had a semicircle shaped capacitive impedance spectrum. The fitting of the measurement data to equivalent circuitry may provide further information.

One idea is to heat the particles and to detect desorbed species and combustion products. Figure 6 shows a preliminary result from heating of fly ash samples collected at a coal fired power plant in Germany. The ash samples contain ammonia originating from the SCR system in the power plant. The fly ash sample was heated with a linear heating ramp up to approx. 800°C. A SiC-FET sensor was used to detect desorbing specie as well as combustion products by transporting the headspace of the heated ash to the sensor with a small gas flow (50 ml/ min). The response of the sensor to repeated heating of one ash sample, see Fig. 6, is most likely due to emitted ammonia molecules from the fly ash.

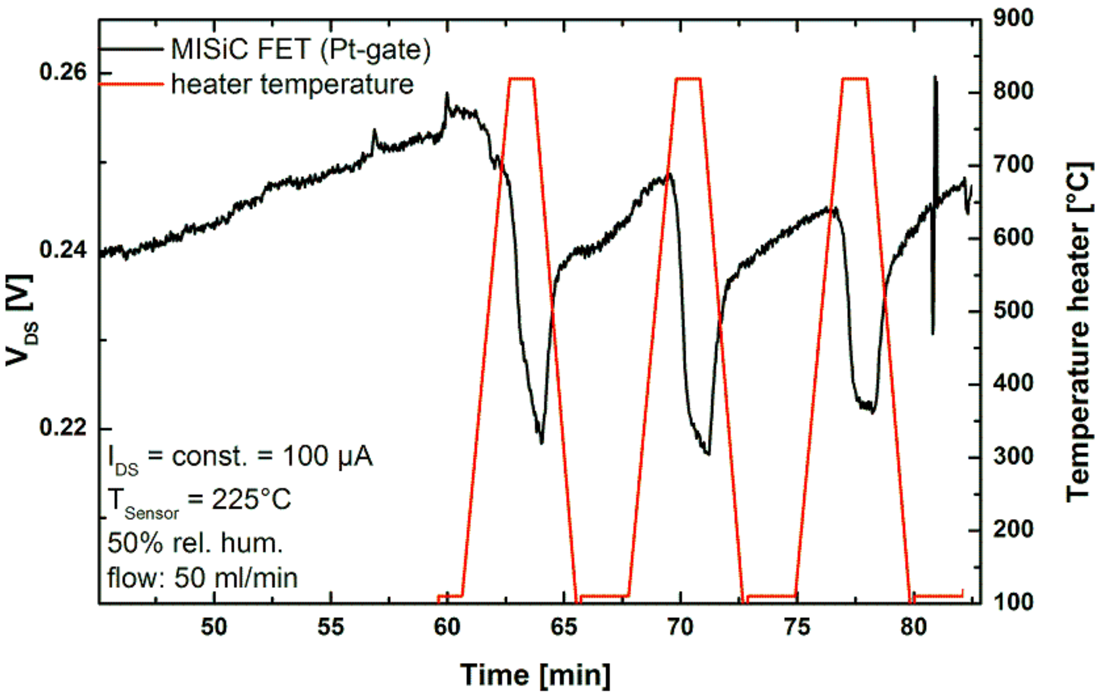

Fig. 6. First experimental results for detection of ammonia containing fly ash particles. The particles are heated repeatedly up to approx. 800°C and emissions are detected by SiC-FET devices.

Conclusions

Combustion of fuel like diesel or biofuels generates important energy but also emissions of toxic gases and particulate matter. A new layout has improved the stability and selectivity of silicon carbide based FET gas sensors. The application of these sensors as an alarm for ammonia gas has been demonstrated. Preliminary results from detection of content of particles are presented. Impedance spectroscopy of collected particles from a steel plant and carbon nanotubes may potentially reveal size and content of particles. The heating of fly ash from a power plant generated ammonia which was detected by a SiC FET gas sensor. The power plant facilitates urea injection for removal of nitrogen oxide gases, which is the origin of the ammonia in the fly ash.

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