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Novel rGO-based Gas Sensor Platform for Low-Power Gas Sensing Applications †

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Abstract: In this paper we report on novel gas sensors platform using standard MEMS micromachining technology and the rGO (reduced Graphene Oxide) material as concept to increase the sensing surface with the goal to increase the sensitivity and reduce the power consumption. A standard IDE (Au Interdigital Electrodes) platform has been used as substrate. On top of the IDE elecrodes a thin rGO-layer with 3D arrangement has been deposited using the Electrophoretic Deposition (EPD) technique. This increases the sensor surface significantly. To fabricate the novel 3D arranged Graphene biosensor, the reduced Graphene Oxide - Polyethylene Glycol - Amine (rGO-PEG-NH_2) was suspended in Isopropyl alcohol. The ζ-potential of the in-solution Graphene flakes was optimized adding $MgCl_2 \cdot 6H_2O$ and enhanced to +46 mV. A high performance ultrasonic mixer is used to crumple and disperse the rGO-PEG-NH_2 flakes within the solvent. The layer thickness can be tuned by using deposition time and current. The deposited rGO material has been functionalized by using sensing MOX nanomaterials like SnO_2, CuO, ZnO. First results show very promising behavior of the new platform – acetone, CO and CO_2 have been detected even at room temperature.

Keywords: Gas sensing; rGO-based; MOX

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1. Introduction

Chemoresistive gas sensors based on semiconducting metal oxides (MOX) have been successful realized and fabricated for many years. They are used in many applications, such as automotive, indoor air quality and smart phones. They offer many advantages in compare to other gas sensing principles. They are inexpensive, simple, cheap, stable and can be very sensitive. There is continuous effort to improve the performance of these sensors. All MOX gas sensors used deposited sensing layer over insulating substrate provided with electrodes and heaters. First sensors have used thick film on alumina subtrates or on alumina tubes. Such sensors are still successful on the market. Such gas sensors typically are exhibiting a power consumption of 0.2 to 1 W [1]. Silicon micromachining technology offers some important advantages such as high volume production and small feature size. Typically a thermally insulated heating elements suspended on a dialectric membrane such SiN, SiO or SiC is realized. Au or Pt electrodes are patterned on top of the membrane. This concept helps to reduce the power consumtion. With this concept MOX gas sensors with lower power (< 200 mW) have been realized.

2. Sensor Concept and Sensor Fabrication

Typical MOX-based MEMS gas sensor is using a planar concept as shown in figure 1. The thin membrane can be realized by using bulk micro machining. The working principle of such MOX gas sensors relies on the change in conductance of the thin gas sensitive MOX layer (n or p type) when exposure to reducing or oxidizing gas at a certain temperature. The IDC electrodes and micro heaters are realized by using standard Au or Pt sputter and etching techniques. The gas sensitive MOX layer is realized by reactive sputter technique or drop casting on top of the IDC electrodes. Such concept has many advantages such simple, compact, cheap and suitability for mass production.

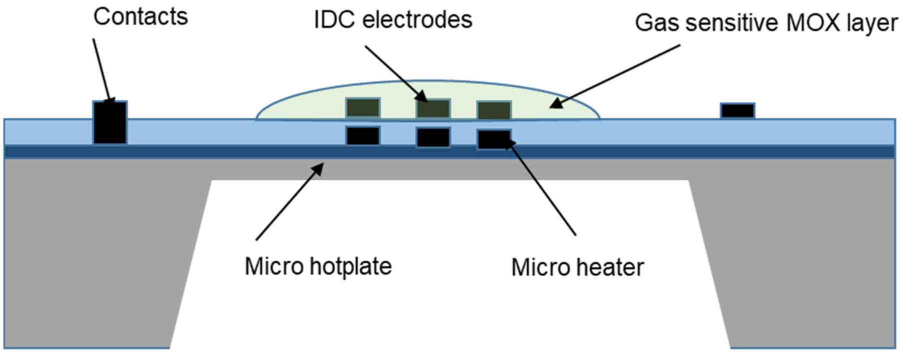


Figure 1. Typical concept for MEMS MOX gas sensors in bulk micromachining. Micro heaters and electrodes are realized on an insulated suspended mechanical structure such SiO, SiN, or SiC.

The heater is needed in order to lower the resistivity of the gas sensitivity layer and to improve the kinetics of the chemical reactions between sensing material and gases [1]. The heater is embedded in sandwich in a thin dielectric membrane to improve thermal insulation and to reduce the power consumption, which is typically in the order of a few tens of milliwatts. At temperatures between 150°C-400°C oxygen from atmosphere is adsorbed on the surface of the MOX layer by trapping the electrons from the bulk. This has the effect of increasing the resistance of the sensor in the case of n-type MOX is used, or decreasing the resistance in the case of p-type material. The pre-adsorbed oxygen or the MOX is reacting with the target gas in the atmosphere and determines the resistance change. Although the working principle is simple, the sensing process is very complex and depending on many factors such as surface reaction, porosity of the layer (total sensing area), temperature, charge transfer process and so on. Compact layers have normally low relative resistance change or low sensitivity. Gases can penetrate better in porous layers, which increase the surface for chemical reaction between sensing material and gas species. It’s the reason for their higher sensitivity. Different porous morphologies have been published in last years [2-13] using nanowires, nanosheets, nano particles etc.

In this paper we report on novel gas sensors platform using standard MEMS micromachining technology and the rGO material as concept to increase the sensing surface with the goal to increase the sensitivity and reduce the power consumption. A standard IDE (Au Interdigital Electrodes) platform has been used as substrate. On top of the IDE electrodes a thin rGO-layer with 3D arrangement has been deposited using the Electrophoretic Deposition (EPD) technique. The EPD is an advanced technique, which allows to deposit suspended particles on a target, using an electrical field. This technique has many advantages such as less contamination and better uniformity in compare to other transfer techniques like stamping, drop casting or spin-on. The transfer of graphene material is still the most critical step in sensor fabrication using this type of carbon nanomaterial [15]. The rGO particles are charged up and so can be moved in the fluid toward the chip surface. The particle velocity in determined by the applied field and the particle potential (ζ-potential). Knowing the potential of the suspended rGO particle is essential to operate an EDP for deposition of particles. EDP deposition leads to a 3D arrangement of the rGO particles on the chip surface. This increases the sensor surface significantly. The figure 2 shows schematically the 3D arrangement of the rGO flakes in compare to a planar one. The overall sensor concept can be seen in figure 3.

To fabricate the novel 3D arranged Graphene biosensor, the reduced Graphene Oxide (from company Sixth Element) - Polyethylene Glycol - Amine (rGO-PEG-NH_2) was suspended in Isopropyl alcohol. This reduced Graphene Oxide has nearly the same properties as CVD grown Graphene. The ζ-potential of the in-solution Graphene flakes was optimized adding $MgCl_2 \cdot 6H_2O$ and enhanced to +46 mV. An ultrasonic homogenizer (Hielscher, model UP200St) was used to shatter agglomerates of the rGO-PEG-NH_2 raw material to microscopic particles well-dispersed within the solvent. The solution has been filtered to define the flakes size for deposition. The layer thickness can be tuned by using deposition time and current. In this work a uniform layer of 2μm thickness is used.

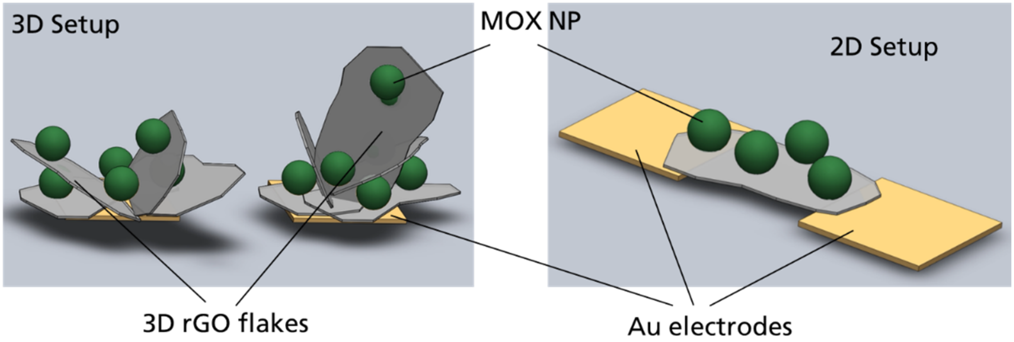


Figure 2. 3D arrangement of rGO flakes in order to increase the sensing area between sensing material and gas species. Left – planar arrangement. Gold – IDC electrodes, grey – rGO and green – MOX nano particles.

Metal oxides (MOX) are widely used for gas sensing in thin film. But they have poor gas selectivity and need relatively high operating temperatures in order to react with gases. But thanks to the combined efforts of synthesis procedures, analytical instruments and robust fabrication techniques there are vast of new gas sensing nanomaterials available [14]. The sensing MOX material (nanoparticles WO_3, CuO, SnO_2, ZnO) has been successfully functionalized. Comprehensive overview of MOX nanomaterials can be obtained in [14].

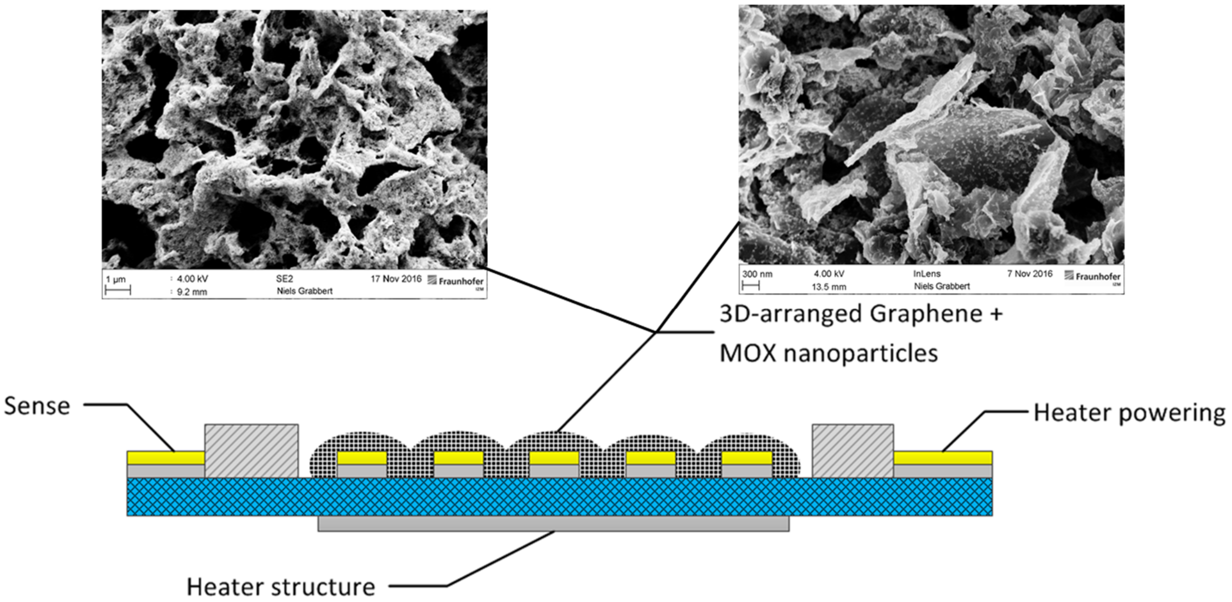


Figure 3. Concept used in this work with metal oxide nano particle decorated 3D arranged Graphene scaffold as innovative gas sensor approach. The 3D arranged rGO scaffold has been deposited on top of IDC electrodes by using electrophoretic method. This 3D arrangement has enlarged sensor surface in compare to the planar concept in standard MOX MEMS gas sensor described above. Left top the arrangement of the rGO-flakes (scale 1µm), and right top enlargement (scale 300nm) of rGO flakes with MOX NP on top.

3. Results

First results show very promising behavior of the new platform. The technology processes are stable and could be up scaled for mass production of low-cost gas sensors. The rGO material is a low-cost nanomaterial from Sixth Element and has been produced using Hummer method. Figure 4 shows the surfaces of the gas sensor platform before and after the EDP deposition process.

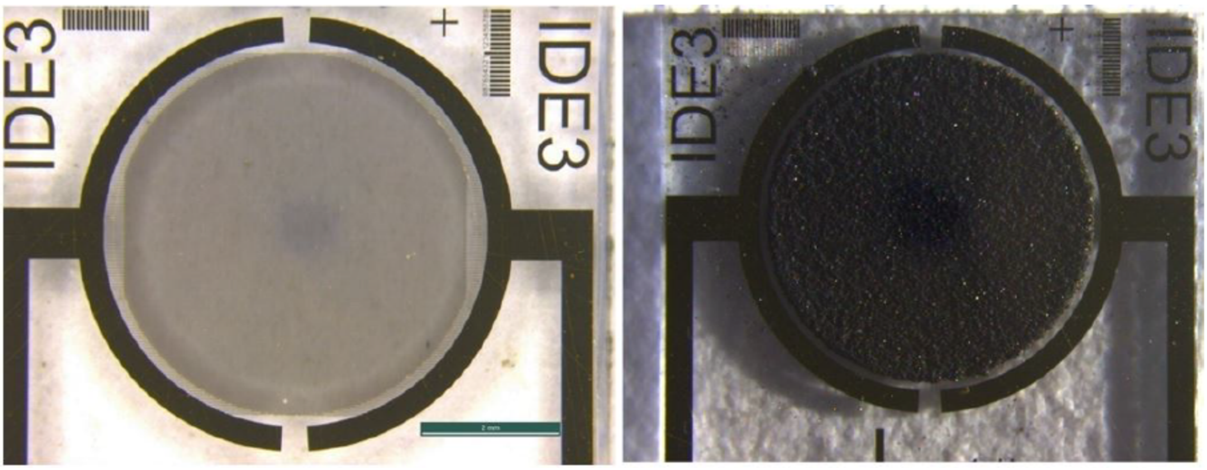
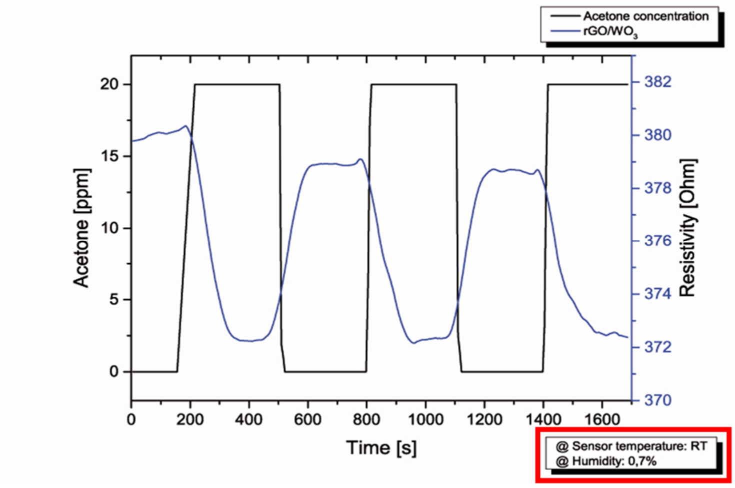


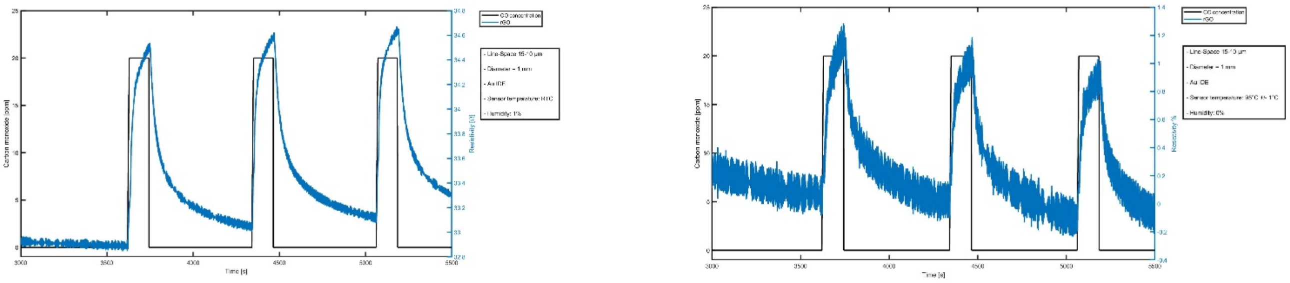
Figure 4. Chip before rGO deposition (**left**) and after EDP deposition process (**right**). Sensor diameter is 1mm.

The platform has been used to gases. For example – acetone, CO and CO_2 could be detected even at room temperature. The figures below show some sensor data of detection of acetone and CO at room temperature. In case of CO it could be seen, that the presence of humidity has very high influence on the sensor signal. The figure 6 shows the sensor signal with CO gas at RT and at 95°C. The resistance decreases at high temperature.



- Very early results
- Without any optimizations
- Room temperature
- Low ppm range
- Norm. response 2%

Figure 5. Detection of acetone with the sensor platform rGO functionalized with WO_3 MOX nanoparticles at room temperature as example.



(**a**) (**b**)

Figure 6. Detection of CO using rGO platform at RT (**left**) and 95 °C (**right**).

4. Conclusions

A novel platform using rGO and functionalized using MOX NP for gas sensing applications is presented in this paper. For deposition of uniform rGO layer EDP method has been used. This deposition method has some advantages in depositing of nanomaterials in compare to other technique. It leads also to 3D arrangement of rGO. The EDP deposition process could be scaled up for mass production. The idea of using rGO flakes and EDP deposition technique is to increase the sensing surface with the goal to realize low-power low-cost and high sensitive gas sensors in future. The platform is sensitive for gas detection already at RT. It needs further excessive investigation in future in term of reaction and charge transport in the material system, the enlargement effect of sensing surface, the temperature dependency, the role of humidity and long-term stability.

5. Patents

FhG IZM team has pending patent related to the rGO deposition method for use in bio detection.

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Conflicts of Interest: Authors declare no conflict of interest.

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