Electrical characterization of graphene sensors

1st Patrik Staroň
Department of Physics
Brno University of Technology
Brno, Czech Republic
patrikstaron@vutbr.cz

***Abstract*—Graphene has shown to have great electrical, thermal and chemical properties. These qualities are suitable for construction of a chemical sensor with graphene as its sensing material. These graphene-based sensors are currently in the field of research and they are not yet viable for mass commercial application. Studies in graphene-based sensors span its very high sensitivity, selectivity, functionalization, manufacturability, stability and material configuration. We focus on the noise characterization in pristine graphene sensors, with different active channel size and layout of the electrodes. The topic of sensor characterization is difficult. Very often researchers omit the measurement setup and information about sample preparation. This article is focused on design of a sample, that is suitable for various graphene sensor experiments. We have come up with a successful design of highly configurable sample board with mounted graphene sensor, that are easy to work with. These samples are to be used for noise analysis of a graphene sensor, that is put in different gas environments.**

***Index Terms*—graphene, 2D sensor, measurement, sample preparation**

I. Introduction

Multiple industries, such as manufacturing, healthcare and automotive, have a need for reliable measurement of chemical composition in their environment. These environments include places where people work with dangerous substances and the environments need to comply with safety requirements, or areas with fire hazard or low air circulation. Measurement and detection of volatile substances in the air can be achieved only by gas sensing devices. This demand is one of the reasons why gas sensors are a topic of research up to this day.

As the research in material science progresses, there are new methods and options that can be tried, which promise advancement in design of a sensor with better properties and manufacturability [5].
While there are many commercial implementations of gas sensors, they have problems with accuracy, measurement precision, selectivity to certain molecule, cost and so on. [6].

Gas sensors are a subcategory of chemical sensors. While chemical sensor is meant to be used in generally any environment where detection of chemicals can be performed, gas sensors are meant to be placed in a gaseous environment, although a gas sensor can also to some extent work as a general chemical sensor [5] [7]. Further, the chemical (or gas) sensor can be classified as one based on 2D sensing material. These materials include graphene and its variants, phosphorene, transition metal dichalcogenides, hexagonal boron nitride, Molybdenum Disulfide and others.
The article focuses on graphene 2D chemical/gas sensor. Graphene is a material with spectacular properties. It has high carrier mobility [9] and thermal conductivity, has high mechanical strength [8] and provides various optical and geometrical advantages over all other materials.

This is a premise that lead to the research of how well this material can be used in detecting various gas molecules. It has been found, that graphene might be a suitable material to detect various gases at extreme resolution [10].

In reality, as it is a common case, graphene has problems not only with detection of certain gases, but also with interpreting the measured information from the sensor. As the resolution of the sensor goes up, the signal to noise ratio goes down.

The noise characteristics of graphene sensors is not well understood [11]. Making a sample which is easy to work with and is suitable for noise analysis is therefore very important. Some researchers provide some information about their experiment configuration, such as [12] or [13], little details are given regarding their sample mounting and configuration.
We are focusing on creating and testing a recipe for 2D sensor mounting which is documented in this paper, and later on this configuration will be used for sensor measurement and data analysis, mainly in spectral domain in a low-noise environment.

II. Sensor measurement

Generally there are multiple methods of data acquisition from sensors. Some sensors change their capacitance based on the gas concentration. Most of the sensors change their resistance. Theoretically, even optical state of the sensor and acoustic wave propagation differences can be used to detect gas on the sensing material. Most of the sensors contain electrodes that interface the sensing material and the electrodes provide means for measurement of the sensing material physical properties. These measurements may be more or less straight forward. Chemiresistive gas sensor measurement

is discussed in this chapter. Graphene sensors fall into this category and measurement of the sensors brings its own challenges. Especially with graphene sensors, which have potential to be very sensitive. Measurement can be performed using time and frequency domain. Time domain measurement is simple detection of resistance at particular time. Data processing is many times required to interpret the resistance as a concentration of particular gas. Frequency domain measurement consists of measuring the impedance of the sensing material at particular frequency and a range of frequencies is chosen. This can be beneficial, as some sensing materials have predictable resonance frequency and its shift is used to detect the concentration of the gas. Noise is a factor that influences the sensing performance too. Reaction process at the sensing material can be so slow, that the noise of the system may overtake and measurement can be compromised. This kind of noise is low-frequency noise (also known as 1/f noise). It is discussed in semiconductor based sensors but it may be also applicable to graphene sensors, as graphene provides its own source of noise. In research facilities, gas sensors are measured with devices such as 8753ES [1]. Network analyzer can measure resonant frequency by measuring resonator's return loss. Otherwise, resistance measurement with a good supply of current suffices. Sensors contain multiple sources of noise. Most dominant are two. Thermal noise and low-frequency noise. Thermal noise is present in all devices. In thermal sensors the thermal noise is caused by vibration of the atomic structures that produce current inconsistencies. This noise has spectral density

$$S = 4 \cdot k \cdot T \cdot R \tag{1}$$

where k is Boltzmann constant, T is temperature of the material in kelvin and R is the resistance of the material. This noise is constant at all measurement frequencies and this means it can be isolated. The other source of noise is the low-frequency noise and this noise is dominant at frequencies usually up to 100kHz [2]. The spectral density of this noise is roughly 1/f. This noise decreases with increasing frequency forming a knee called $f0$. At this knee the noise decreased to the point where it equals the thermal noise [2]. Another source of noise is noise from material inconsistencies. These inconsistencies come from metallic interfaces for example. Within graphene sensors, the grain boundaries contribute to noise. Grain boundary noise of graphene contributes to 1/f noise [3]. After the data from the sensor is acquired, the data can be post processed to increase the accuracy of the detected gas type and concentration. It is known that sensors tend to have long detection and recovery time and this poses problem when sensor is continuously measuring gas concentration. That is why advanced methods of gas sensor data processing have been developed, such as back propagation neural networks [4].

III. Measurement setup

We have several pristine graphene sensors available with geometry 1 and 2. These sensors are commercially available and many times require separation from a die and cleaning. These two steps are crucial for subsequent measurements with these sensors and they will be discussed later. The pattern used in the star electrode arrangement is called 'Hall Bar Geometry'. This electrode arrangement is done purposefully to enable the measurement of hall-effect [14]. However, the electrodes could be used for potential injection experiments. An ideal case would be to manufacture a silicon-based 3D structure with integrated analog amplifier, with graphene layer transferred directly onto the silicon oxide, with electrodes running several micrometers to the analog amplifier, that would be electrically well isolated and whose output would be available via bonding pads. This sensor must be connected to the amplifier via longer route and for good workability requires bonding onto a plate, which can be better worked with. The path should be low-noise and configurable at the same time.
To efficiently test these sensors, we came with a solution with the following recipe: A standard FR-4 board with 25µm of copper was pattern-etched using photolitography. Sodium-hydroxide with 30% hydrogen-peroxide was used for copper etching and sodium-carbonate was used for developing. This board was coated using ENIG process, which includes chemical plating of nickel onto copper (4.5µm) and chemical plating of gold onto nickel (0.05µ m). This is a 'soft' gold, while 'hard' gold is electroplated. Soft gold is cheaper to manufacture and there was a concern if the golden bonding wires would attach well onto 'soft' gold. Two-sensors bundle was cut off of a die and this bundle was cleaned and glued directly onto the PCB, using conductive silver-based polymer paste with baking time of 1.5h at 80°C. After the glue was set, the sensor was wedge-bonded by 25µ m Au wire. The bond onto the sensor pad was performed at 340kHz needle vibration during 230mS at 350mN force. This bonding was reproduced across all pads. The bonds onto the golden pad on the PCB were more difficult. The recipe is 440kHz during 320mS at 430mN force and the parameters vary based on the non-homogenity of the golden layer. Electroplated gold might be more homogenous. The Figures 4 and 5 show a visualization of the traces layout. To enable various configurations during testing, a matrix connection PCB was created, to enable a connection of any connector pin to any sensor pad. These structures enable to measure the two sensors at the same time. This setup is portable and the sensor is well-fixed onto the PCB. U.FL connectors were introduced for better HF-friendly path and easy connection and disconnection of the sensors. It has been proven to us that investing this little money and time into preparation of the samples using these connectors simplifies the work with the samples and is worth it. Connecting and disconnecting the sensors for measuring in a noise-reduced environment is therefore easy. The traces have been gold-plated to minimize changes of the material from the pads to the amplifier, although there is a concern that the inter-metallic phase of CU-NI-AU planar stack will contribute to the noise more, than a single hard side-by-side transition between AU and CU. This means that ultra-high sensitivity experiments may not be suitable with this solution.
Figure 1 requires three extra bonds to interconnect the con-

nectors to the sensors and this is better suited to measure the hall-effect. These boards can be mass-produced in a factory and the primary bottleneck is the bonding, which too could be automated.

Sensor is then connected to a circuit as shown in Figure 3, where chemiresistive properties can be measured. Current from a battery source is recommended, as batteries provide steady and very low-noise current. Voltage on the resistor is then amplified and measured in the spectral domain.

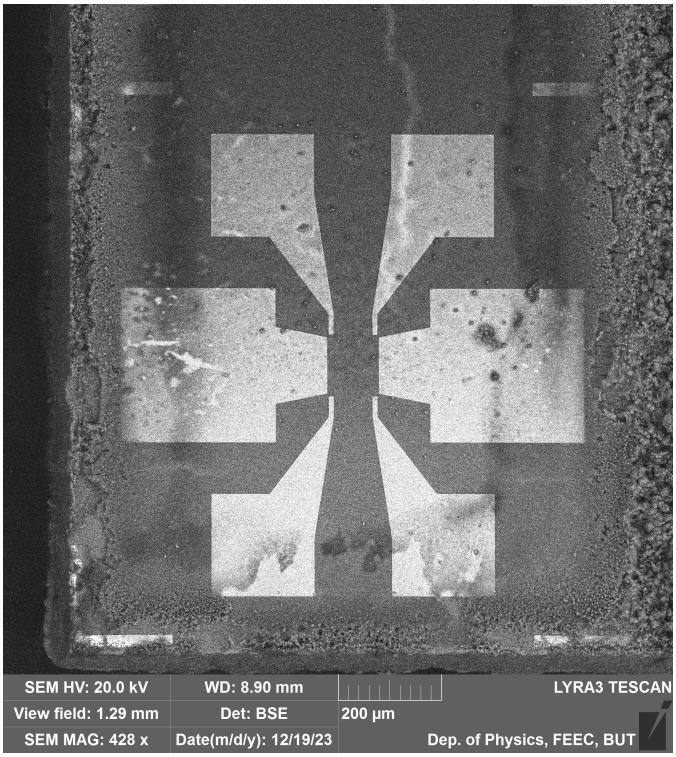

Fig. 1. Star electrode arrangement, acquired using scanning electron microscope.

IV. Cutting and cleaning

Sensor was cut using Laser-Dicer Oxford. Results after cutting are visible in the Figures 1 and 2. Whole sensor was coated by flake-like several microns thick deposition layer, which can be removed by acetone and incresed temperature. We used the following recipe that should theoretically clean the sensor: Preheat the sensor to 80°C and pour acetone directly on it. Then transfer the sensor to ultrasonic cleaner and clean the sensor for 5 minutes in acetone. While cleaning, the sensor cools down to room temperature. Then clean the sensor using isopropylalcohol to get rid of the dissolved molecules from the previous step. Also use an ultrasonic cleaner for 5 minutes at room temperature.

The result was that the graphene layer was indeed cleaned, but after raman spectroscopy, we observed defects of several microns in the graphene layer. Results are shown in the Figure 6.

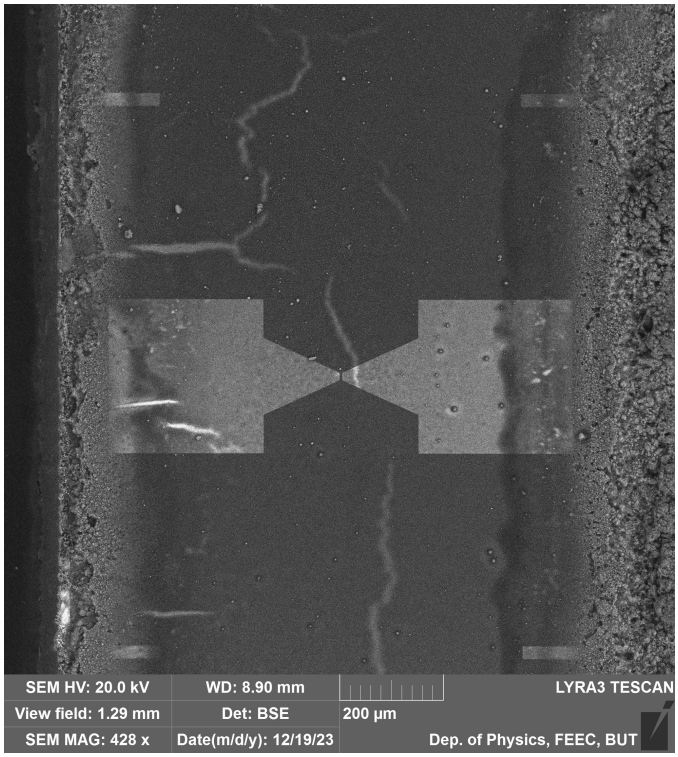

Fig. 2. Two-electrode arrangement, acquired using scanning electron microscope.

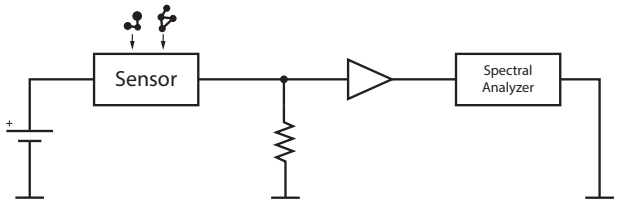

Fig. 3. Electrical diagram for mesuring the grapene sensor.

V. Conclusion

There is a great potential in graphene sensor technology. But making measurements on the graphene samples is not straightforward. We have proposed a solution on sensor preparation including its dicing and cleaning. Experiments with PCB substrate preparation, gold protection and sensor binding with U.FL sensor terminals were performed and proposed solution is portable and ready for various measurements. We have also proposed a noise measurement setup. Our results can be used for direct reproduction for reader's concrete application, and if the application is outside the usecase defined in this paper, the results and processes provided can be used for inspiration. The sample we have shown here will be used for noise analysis while changing the chemical environment around the sensor.

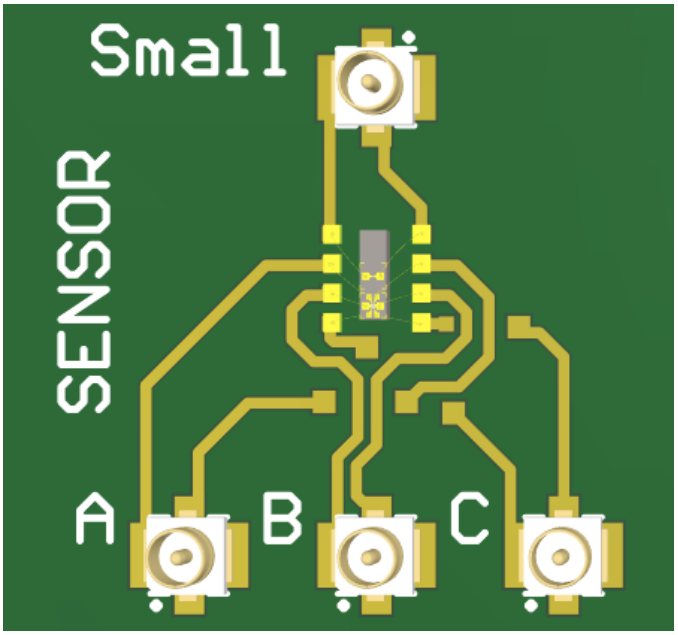

Fig. 4. PCB for the sensor interface with direct connections.

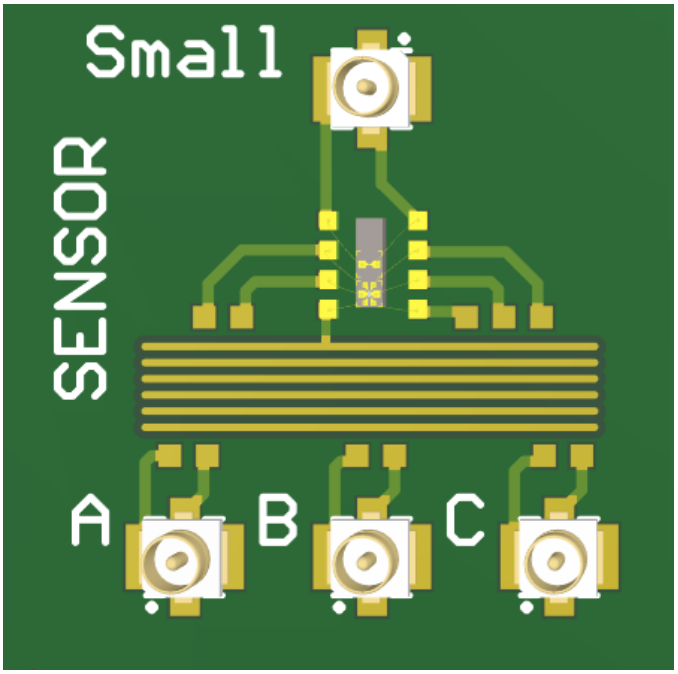

Fig. 5. PCB for the sensor interface with matrix interconnection capability.

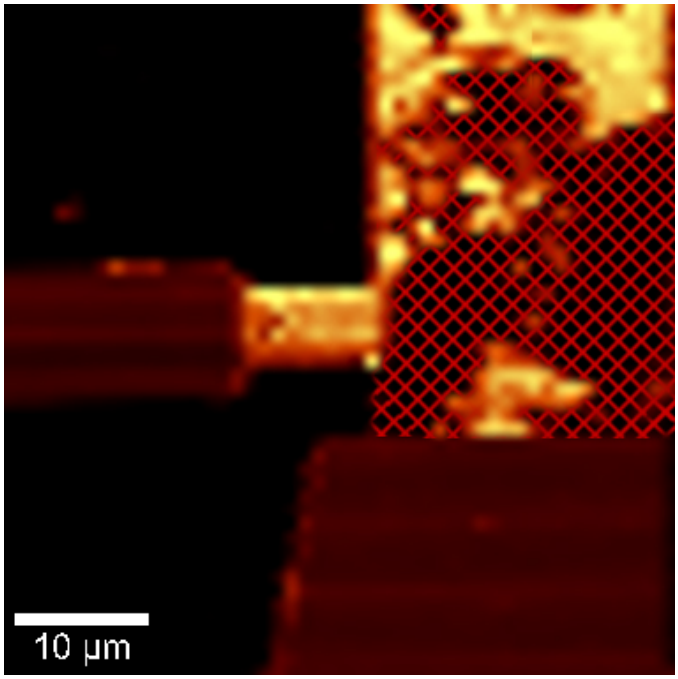

Fig. 6. The red area is missing graphene. Image is from a Witec Alpha 300R Raman imager. Red mesh is edited in for clarity.

Acknowledgment

First of all, I thank Lord Most High for creating such an interesting universe that we study until now and humbly still don't understand a lot, and I thank Him for giving me the ability to gain wisdom, learn and understand concepts I write about in this paper. I thank to my great supervisor doc. Mgr. Dinara Sobola PhD. for her help in overcoming obstacles that occurred while progressing in this research. Thanks to Brno Universtity of Technology for providing the necessary equipment for the research, Gatema company for the help in manufacturing of necessary PCB parts, and several colleagues for their advices and practical help.

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