Automation and optimization device for the fabrication of sensors with nanomaterials

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Abstract— This work presents a device, “dropcaster”, developed to automate and optimize the deposition process of the sensitive layer of gas sensors using the drop-casting technique. It is designed to development sensors in the research phase of different materials and the study of their behavior and response to different gaseous compounds.

Keywords—deposition, drop-casting, gas sensors, sensitive layer, dropcaster, nanomaterials.

I. INTRODUCTION

Drop-casting is a drip deposition method with different nanostructures, using a micropipette, which can be used to generate sensitive layers in gas sensors. This technique is characterized by simplicity, low cost, and versatility, allowing the deposition of many nanostructures with different shapes and sizes [1, 2].

This deposition method is affected by different parameters such as the surface tension and volatility of the solvent used, the wettability of the surface to be deposited, the composition of the solution, or the drop impact velocity. In addition, the size of the droplet must be considered depending on the dimensions of the surface [3].

Although it is a simple process, it can be tedious to deposit it manually and could damage the deposition surface. For this reason, a device called *dropcaster* was designed to automate and optimize this process.

II. EXPERIMENTAL

A. Sensors descriptions

Two types of micromachined silicon substrates (micro-hotplates) were developed by CNM (National Microelectronics Centre, Barcelona) [4] and LAAS (Laboratory for Analysis and Architecture of Systems, Toulouse) [5] are used. These devices are assembled in a TO-8 package, with 12 and 16 pins, respectively. These

incorporate four membranes on which the sensitive material can be deposited. Both devices have micro-heaters that allow reaching temperatures up to 500°C and interdigitated electrodes (IDTs) to measure the resistance variation in the presence of different gases at different temperatures. The active surface area is 0.16 mm² and 0.264 mm² for the CNM and CNRS substrates, respectively. Fig. 1 shows the two substrates used, where the four membranes, IDTs, and heaters can be viewed.

Fig. 1. Micromachined silicon substrates of (a) LAAS-CNRS, (b) CNM-CSIC, with the four membranes that compose each sensor, and a detail (bottom right) of the characteristics of the microplates: membrane, IDTs, and heater (dimensions in μm).

B. Dropcaster and setup

Different nanomaterial solutions can be deposited with the *dropcaster*. The structure of the device is composed of two aluminum profiles (40x40 mm) on which the equipment is supported. The parts have been designed using Fusion360 (Autodesk®, California, USA) and manufactured with a 3D printer in polylactic acid (PLA). Fig. 2 shows the rendering of the 3D design and an image of the device already manufactured.

Fig. 2. Dropcaster. (a) Rendering of 3D design. (b) Dropcaster fabricated and assembled.

Due to the small size of the deposition surface used, micro syringes model Hamilton 701 of 10 μ L and a 26sG gauge needle are used. Therefore, the *dropcaster* parts were custom designed for this application but could be adapted to other syringes of different sizes. A DC stepper motor is used to move the syringe plunger and deposit the material on the sensor membrane.

An Arduino Mega 2560 is used to control the *dropcaster*. The equipment incorporates a 3.2" TFT LCD touch screen with which the deposition process can be configured. A graphical interface was programmed using Arduino, through which the process can be started or stopped, and parameters such as drop size, deposition speed, or waiting time between each drop can be controlled.

On the other hand, the needle must be close enough to the surface of the sensor because the deposited droplets are tiny (50 nL approx.) to deposit the material. Otherwise, it would remain at the end of the needle. Therefore, to position the needle quickly and accurately, a mini camera, controlled by a Raspberry Pi 4 B, was used. Fig. 3 shows an image obtained with this mini camera of the moment when a drop is deposited on the sensor surface.

Fig. 3. Deposition of the material on the sensor surface, as seen from the mini camera, incorporated into the dropcaster.

This HD camera (1080p) has a resolution of 5 MP and a manually adjustable focus. Fig. 4 shows the support where the camera and the Raspberry Pi are placed, designed with the program mentioned above, and manufactured in PLA.

Fig. 4. The support to place the mini camera and the raspberry pi used to position the needle and visualize the deposition process.

A programmable power supply (model HM7044) heats the heating resistor integrated into the membrane of silicon to promote rapid evaporation of the solvent and speed up the process. Finally, a Keithley multimeter (model 2700) is used to monitor the resistance value of the sensor during the process and stop the process when a specific value is reached. Fig. 5 shows the laboratory setup used. The external screen is used to view the image coming from the Raspberry Pi.

Fig. 5. Dropcaster setup.

III. RESULTS AND DISCUSSIONS

The *dropcaster* allows the deposit of different materials on each sensor membrane, obtaining a matrix of 4 sensors that can respond differently to the same gas. This device was used to deposit different types of solutions with ZnO, TiO₂, SnO₂, and ITO nanoparticles, and in some cases with dopants such as Pd, Pt, Au, and Rh. 2D materials such as graphene, MXenes, and MoS₂ were also deposited.

The manual deposition was compared with that performed with the *dropcaster* to justify the design of this device. Fig. 6 shows the deposits obtained by a manual and automatic drop-casting on two substrates of the CNRS. In both cases, a pristine graphene dispersion in water (1%) was deposited. Water is generally used as the solvent for this

technique, as it has higher surface tension and can be evaporated quickly using the heating of the sensor.

Fig. 6a shows a sensor in which the four membranes were deposited manually using the drop-casting technique. The materials deposited on each membrane overlap each other, which can cause electrical problems, and some of the contacts may break. The lower-right membrane broke during the process due to the lack of precision in this process when carried out manually.

On the other hand, Fig. 6b shows a sensor that was deposited with the *dropcaster*. The deposited material is only in the sensitive area of each membrane. The upper-left membrane has not deposited material to compare with the rest.

Fig. 6. Deposition performed on CNRS sensors of a 1% pristine graphene solution. (a) Manual drop-casting. (b) Using the dropcaster.

The improvement in the deposition process is also observed in the subsequent response of the sensors. These are exposed to a specific gas. For this purpose, a gas line was used to generate controlled mixtures of different gases at the concentration to be measured and to monitor the change in sensor response. The sensor is placed in a hermetic measuring cell, into which the generated gas mixture is introduced.

In this case, to check the difference in response between the two sensors, acetone at 0.5 ppm concentration was used, and five measurements were carried out. Each measurement is composed of a desorption phase and an absorption phase. In the first one, the sensor is exposed to a dry air atmosphere to favor its cleaning. While in the second one, it is exposed to the gas to be measured. Fig. 7 shows the difference in response between the measurements made with each of the sensors. Due to acetone is a reducing gas, equation 1 is used to calculate the sensor response, where R_a and R correspond to the sensor resistance under exposure to air and the selected gas, respectively.

$$Response = R_a/R \quad (1)$$

Fig. 7. The difference in response between the manual deposition method and the dropcaster.

IV. CONCLUSIONS

With this device, a substantial improvement has been achieved in the sensor manufacturing process using the drop-casting technique. In addition to the time optimization achieved by automating the process, more precise depositions can be made only in the sensitive area of the sensor. It has also been possible to observe a better distribution of nanomaterials on the sensor surface and a higher sensor response than previous results.

Thus, by increasing the accuracy and repeatability of the process, two important improvements are achieved. On the one hand, potential electrical problems are avoided if the deposited droplets are large enough to accumulate material on the contacts. This can contribute to increased durability of the sensor over time and prevent it from breaking more easily.

Moreover, the *dropcaster* prevents the needle tip from punching the membrane in the depositions, thanks to the mini camera for positioning.

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