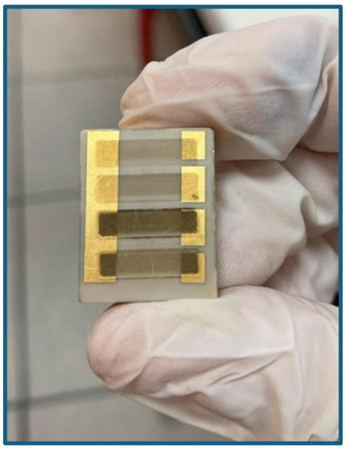
CROZAT Ilan

4A GPSE

Years 2024 – 2025

Realisation and installation of electrodes to study the electrical properties of graphene.



Project mentors : ***Barthelemy ASPE, University lecturer***

Arnaud STOLZ, University lecturer

Acknowledgements

First of all, I'd like to thank Mr Aspe, who supervised and guided me, and made himself very available and present throughout the project.

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I) Introduction

1) Context

In our time, we have become aware of the importance of having food, air, a source of hydration and, more generally, a clean environment that is not polluted by the many chemical products that are harmful to our bodies.

The industrial development that humanity has undergone in recent history has led to the massive use of raw materials that have been transformed and processed to meet the energy and food needs of the world's population, which has been growing exponentially since the 18th century, especially in urban areas.

This increase in productivity, coupled with the discovery of more calorific energies, has led to greater consumption, and therefore an even greater quantity of energy to meet these needs. The transformation and combustion of these raw materials to obtain this energy (coal, oil, etc.), as well as various other factors, have contributed to air pollution: in the European Union, the number of premature deaths in 2024 due to fine particles exceeds 200,000, and threatens the biodiversity of forests.

2) Issues

Several laws and regulations have therefore been introduced, and all industries (especially in the European Union) are obliged to reduce their emissions or face a tax (carbon tax). We are therefore looking to create more flexible and accurate pollution sensors. These innovations are based on the use of innovative materials and excellent on-board electronics. It is in this context that graphene-based sensors have been developed, using its special physical properties.

3) The sensor

a) Graphene

Otherwise known as the ‘miracle material’, graphene is being extensively studied for its properties. It is a 2D sheet of carbon one atom thick, estimated to be 100 times stronger than steel in proportion. However, it is not very resistant to impact, but it can be assembled with a polymer in a molecular ‘sandwich’ (1) to solve the problem of fragility. What's more, it is the material with the best measured thermal conduction (twenty times better than aluminium), as well as surprising mechanical properties, which is promising for the creation of new super-strong materials.

Graphene is mainly studied in physics for its unique electronic properties. In this two-dimensional system, the movement of electrons is very specific, making it a highly conductive material: electrons can travel at speeds of up to 1,000 km/s without losing energy (ten times faster than electrons in silicon, the mainstay of microelectronics).

b) Electronic applying

Because of these properties, graphene is at the forefront of the creation of new ultra-fast transistors. Graphene would therefore be integrated into the printed circuits of our electronic devices, making them much thinner and more efficient. It also holds great promise for improving our materials storage technologies and making them more energy-efficient. What's more, graphene is transparent due to its thinness: this optical property, combined with its high conductivity, makes it the material of choice for energy conversion (electrons into photons), a technology used for plasma and touch screens, as well as to make solar panels more efficient.

As previously mentioned, graphene is also used in sensor technologies to detect the presence of pollutants in an environment.

c) Global project

It is in this context that this project takes place. It has three objectives :

- The design and development of the process-flow for depositing the electrodes
- Electrodes manufactured in a clean room
- Graphene identification and electrical/dimensional characterisation

The graphene substrates will be supplied by a parallel project that is correlated to this one: the study of the dimensions of the graphene surface on the samples has been carried out jointly, to have coherence in the evolution of the project.

II) Functional blocks

1) Diagramme des cas d'usage

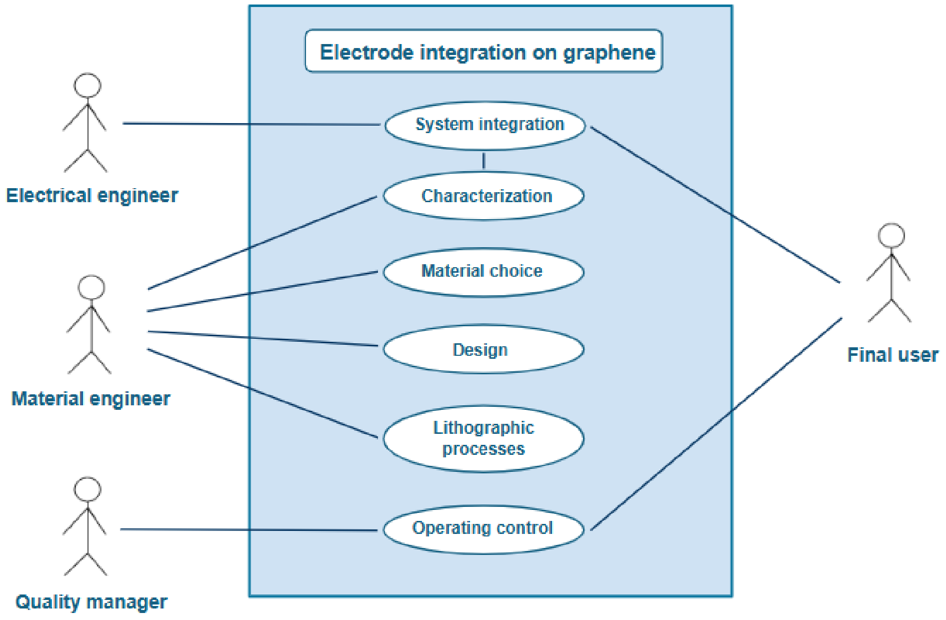


Figure 1 : Usage case diagram

1- Business plan

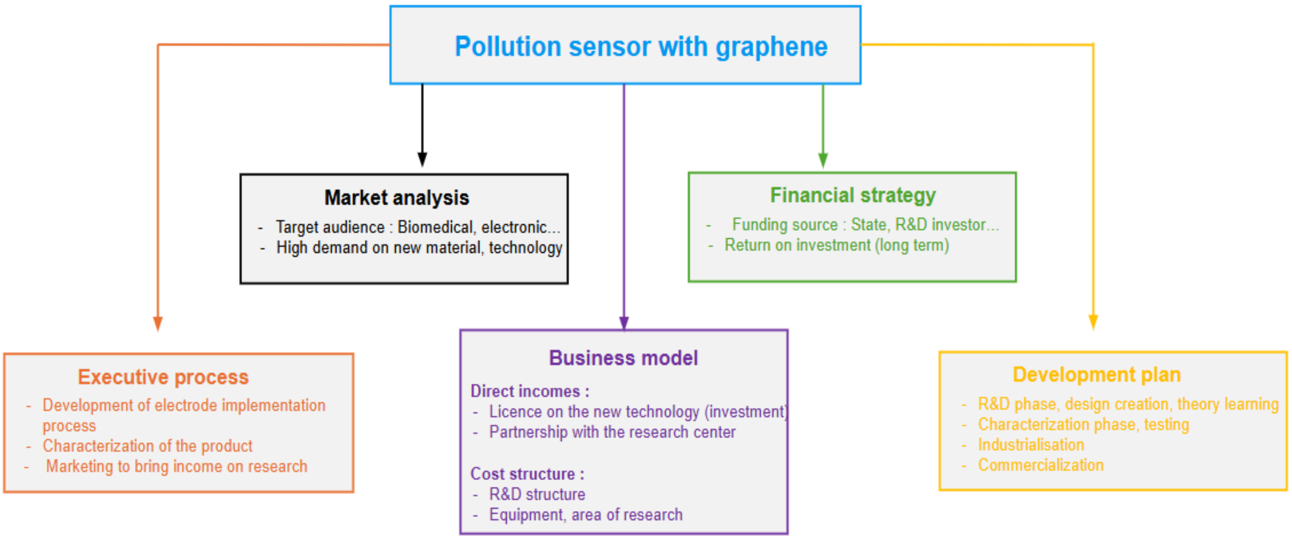


Figure 2 : Buisness plan diagram

2- Octopus

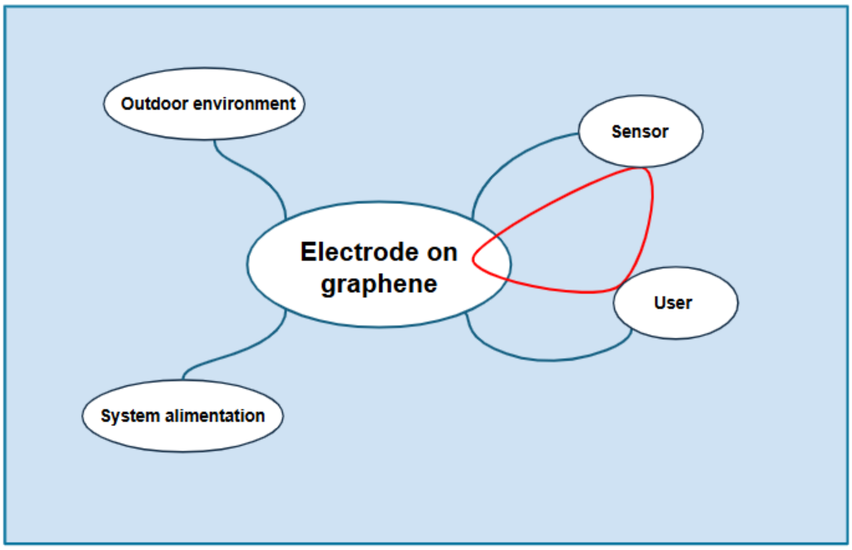


Figure 3 : Octopus diagram

III) Project purpose

1) Peek substrat

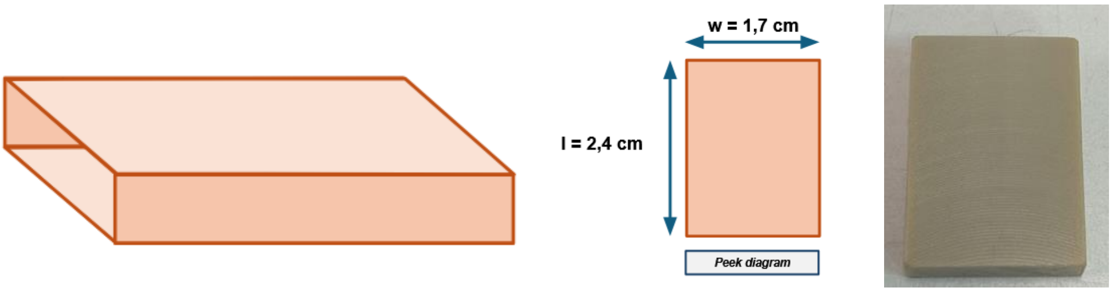


Figure 4 : Peek substrat diagram and picture

The carbon has been made on a "Polyether ketone", a colourless organic plastic polymer substrate (Peek) of 2,4cm x 1,7cm. A laser was projected onto the substrate to burn it, leaving behind carbon atoms. The difficulty was to determine whether this carbon was conductive. Graphene is conductive because: It's a two-dimensional material, which facilitates conductivity, and the atomic structure is one-dimensional.

The aim of the project is to produce a carbon with properties similar to graphene. To do this, we need to characterize it electrically and determine the thickness of the carbon we have.

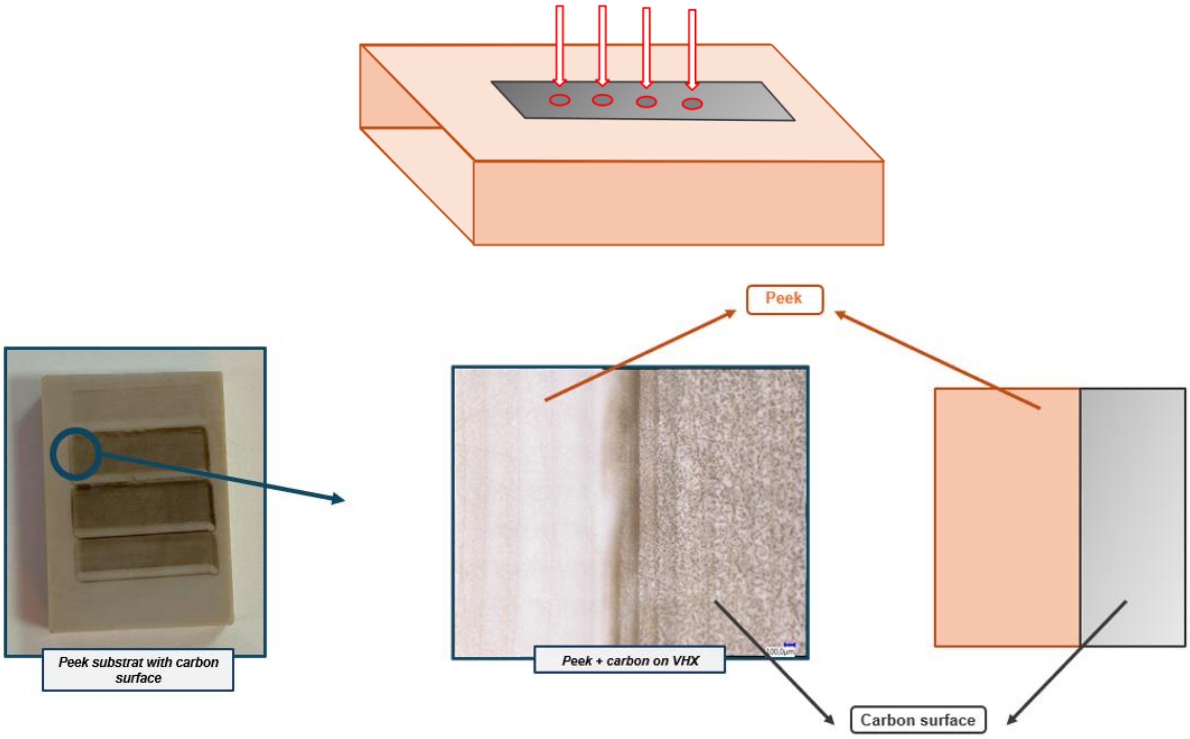


Figure 5 : Carbon on peek, diagrams and pictures

We observe on the digital carbon microscope. You can clearly see the carbon atoms, which stand out from the peek because of their dark colour and frog-egg shape. After the process, we will observe if the carbon has been damaged.

2- Electrode

Once the carbon surface has been acquired, one of the aims of the project is to deposit electrodes on either side of the surface. This is a complex stage because the electrodes have to be placed while keeping the carbon on the surface (so as not to degrade it).

In order to place our electrodes on the peek substrate, we are going to use a UV photolithography technique. We have several solutions at our disposal, and in order to optimise the rendering of the profile and the characteristics of our electrodes, a preliminary study is required. We will therefore try to determine several solutions:

- The choice of lithographic process
- The metals that will make up the electrodes
- The design of the mask

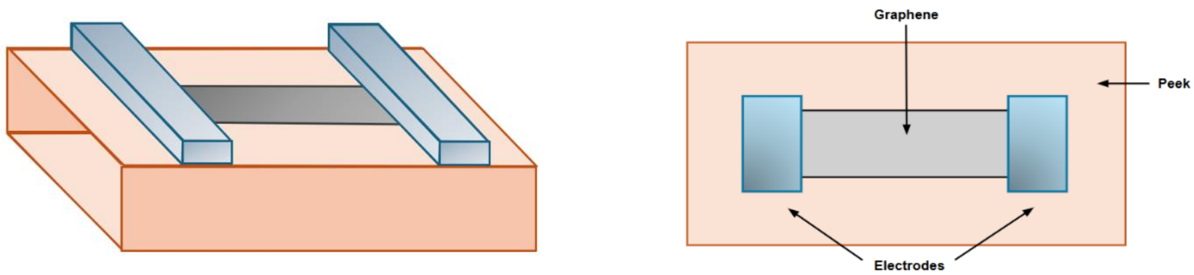


Figure 6 : Electode on substrate diagrams

3- Objectif and difficulties

It is in this context that this project takes place. It has three objectives:

- The design and development of the process-flow for depositing the electrodes
- Electrodes manufactured in a clean room
- Graphene identification and electrical/dimensional characterisation

The graphene substrates will be supplied by a parallel project that is correlated to this one: the study of the dimensions of the graphene surface on the samples has been carried out jointly, to have coherence in the evolution of the project.

However, with have several difficulties to reach these aims. First, the Peek is a substrate on which it is not usual to make graphene. This is why identifying graphene is one of our objectives: we are going to create on carbon by burning the peek surface. As graphene is a two-dimensional material, some characterisation would enable us to determine the thickness of the carbon we have (the use of the word graphene is a misuse of language in our case, as it is not two-dimensional). Furthermore, all cleanroom equipment is suitable for silicon wafers, and is not adapted to this type of substrate with such dimensions.

But this process does have its advantages:

- Peek has good thermal and mechanical properties, and this can be useful when using it in different environments.
- Make carbon directly on the material (instead of producing it next to the material and laying it down as is customary). Once the laser process has been optimised, we will be able to achieve high precision and modulation.

IV) Conception

1) Fabrication process

Several processes have been studied for making these electrodes. The type of resin will influence the steps in the process and the design of the mask, so it is important to decide beforehand on the type of resist and the manufacturing process that will be used to lay the electrodes. Here is a non-exhaustive list of the different processes that have been studied: positive resist, negative resist and T-pop.

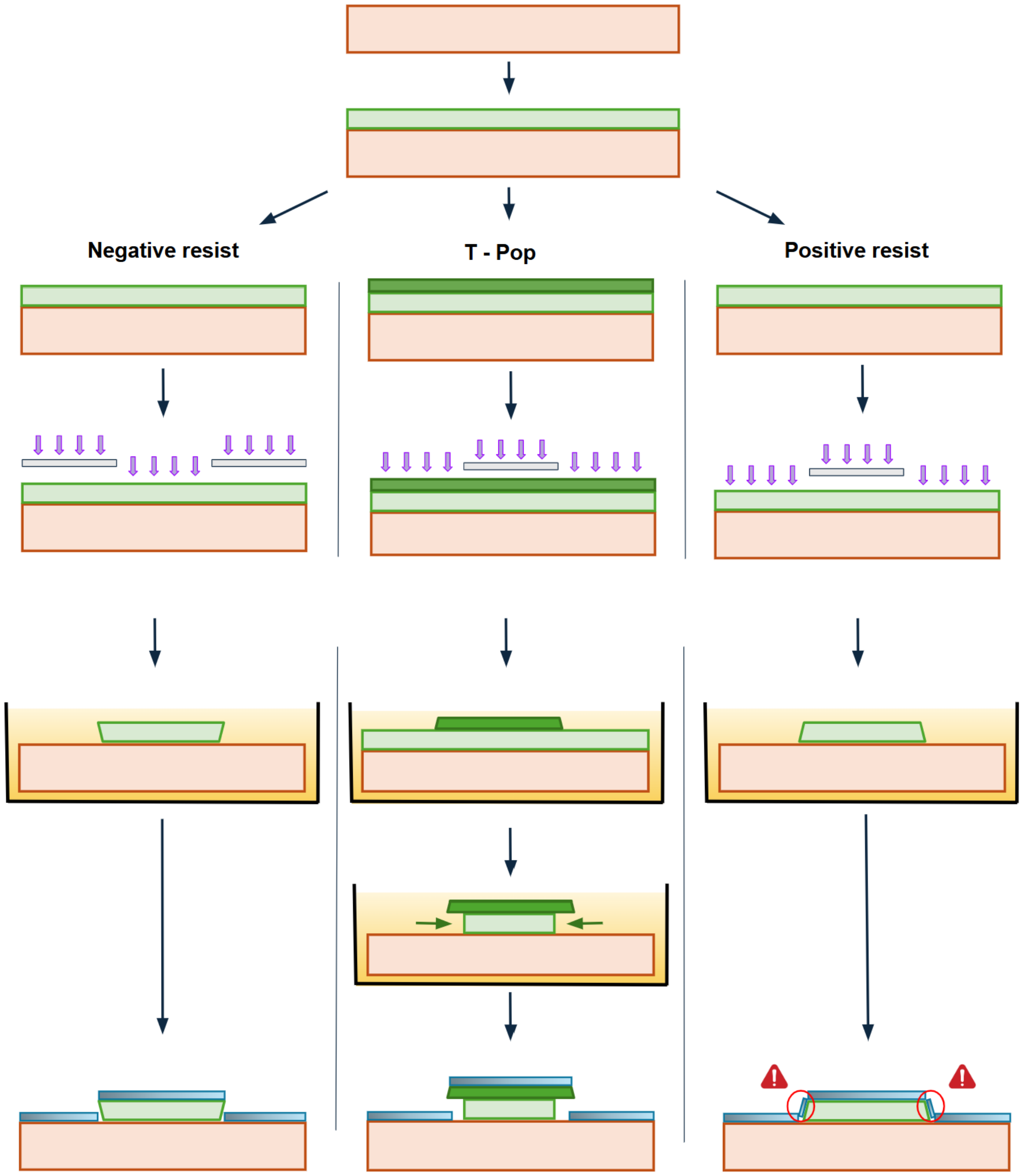


Figure 7 : Process-flow diagram

During the study, it was concluded that a process with only one layer of positive resist could potentially present a problem during the lift-off of the resist. In fact, the resin profile obtained using only a positive resist in a UV photolithography process (by UV Cube or aligner) leaves open the possibility that metal during deposition could be an obstacle to our lift-off, and therefore that the resist would not lift off as expected (see diagram, 'Positive resist'). We therefore retained two possibilities: the negative resist technique, or the T-pop profile.

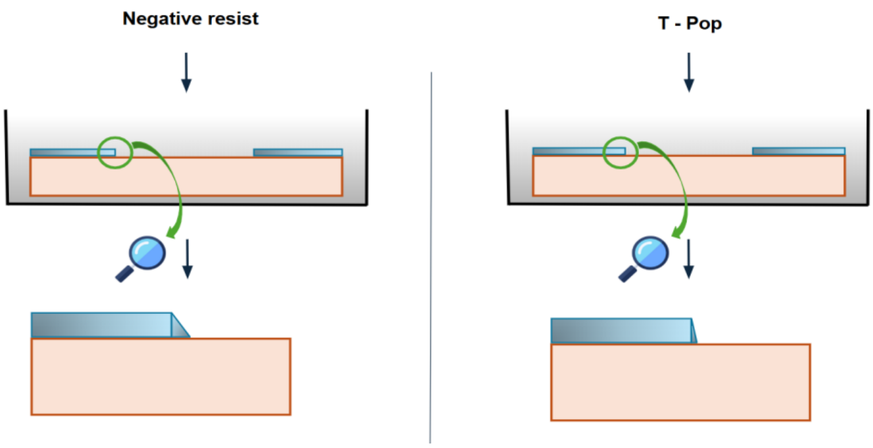


Figure 8 : Metal shape between T-pop and positive process-flow diagrams

In theory, these two processes will produce a slightly different metal profile. As noted above, the T-Pop technique acts as a protective barrier for the different stages of our process. In addition, this technique gives us a more precise pattern and smoother lines. This is why we decided to make our electrodes by using the T-Pop technique.

Although an etching process offers a number of advantages, it was not chosen. Both were possible, but since the main missing resource was time, we opted for the lift-off process because it requires a step, and we had experience of this type of process. In theory, these two processes will produce a slightly different metal profile.

2) Mask

The mask will be an essential part of our manufacturing process. It will enable us to give our product the shape and design we want. More specifically, we want to place metal on the graphene surface in such a way as to characterise it electrically.

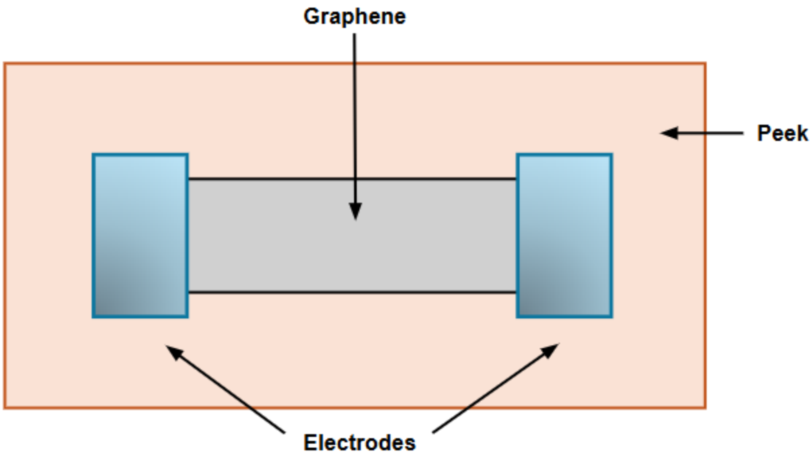


Figure 9 : Global view of the product diagram

In order to place the electrodes on the substrate, several models were studied. The key was to have metal on both sides of the graphene surface, enabling its resistivity to be characterised.

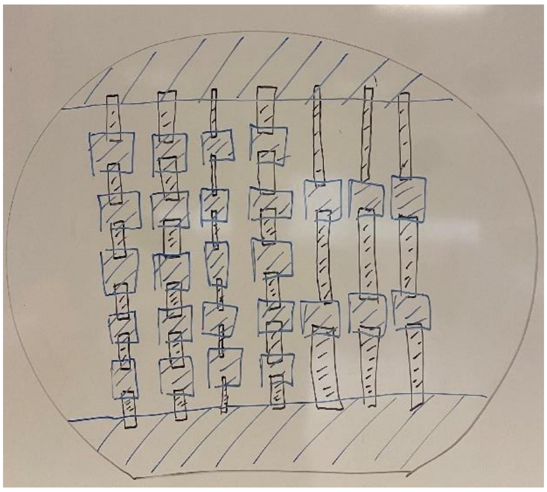


Figure 10 : Diagram of an idea developped for the mask

The model above was first thought up (the striped blue representing the metal, and the black the graphene surface). However, when the mask was designed, the graphene had not yet been laid. It was therefore difficult to accurately anticipate such a complex mask. He therefore decided to design several masks with a "single" design, and then a single mask containing a single model for our electrodes.

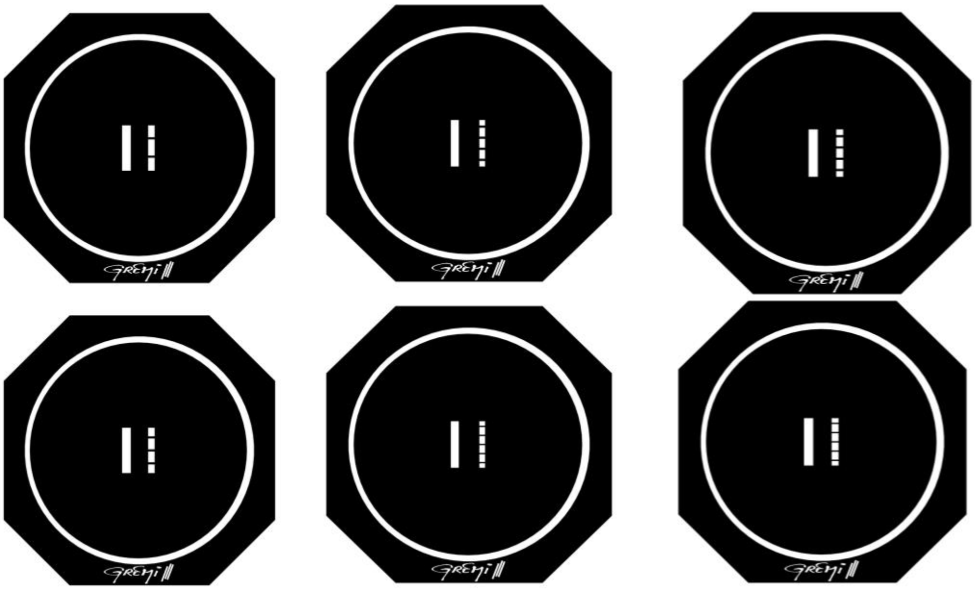


Figure 11 : The 6 mask developped

You can see the six different masks that have been printed with only one model on each, centred in the middle of the mask. For the photolithography (UV projection), several options were available for its production in a clean room:

- Use the aligner to project the UV precisely onto the substrate. However, it has to be switched on for half an hour beforehand. However, as the glass plates needed to insert the aligner are not available in clean rooms, its use was ruled out.

- The use of the UV cube, which is a quick way of carrying out the projection. In the end, this solution was chosen, although it is suitable for 10x10 circular silicon wafers. The masks were therefore just placed on the substrate, centralising the model on the mask, which enabled the mask to be balanced.

3) Carbon thickness

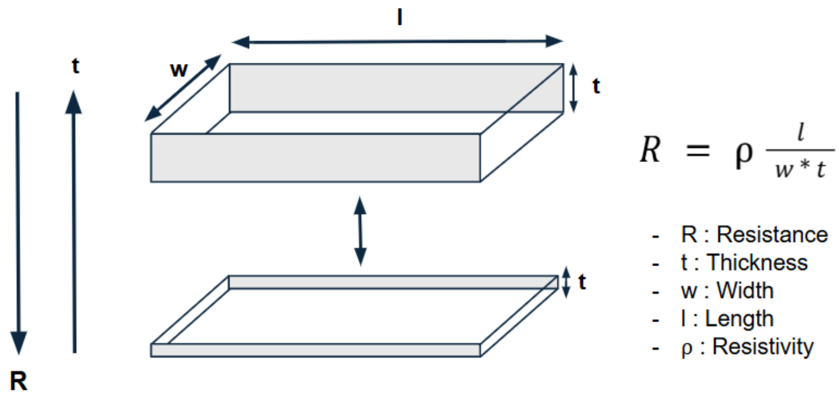


Figure 12 : Relation between thickness and resistance diagram

As mentioned previously, one of the objectives would be to characterise the depth of carbon on our substrate. In fact, there is a link between the thickness of the carbon and its resistance to current (given by the formula above). Then, it is possible to measure the resistance of the carbon and calculate the thickness of carbon we have with the remaining data.

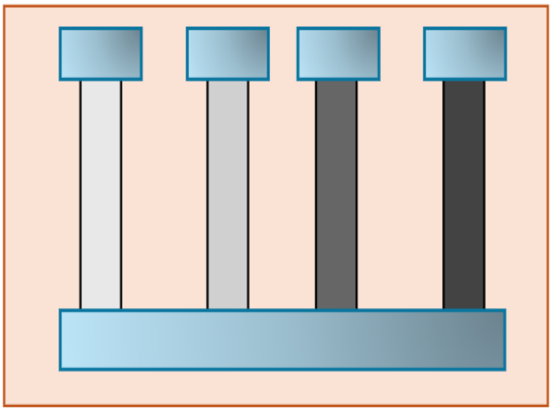


Figure 13 : Several type of surface diagram

It is the sizing and calibration of the laser that will give a certain surface with a certain carbon thickness. In aim to study its properties at different thicknesses, several carbon surfaces with different laser calibrations were supplied.

V) Fabrication and observation

1) Process-flow applying

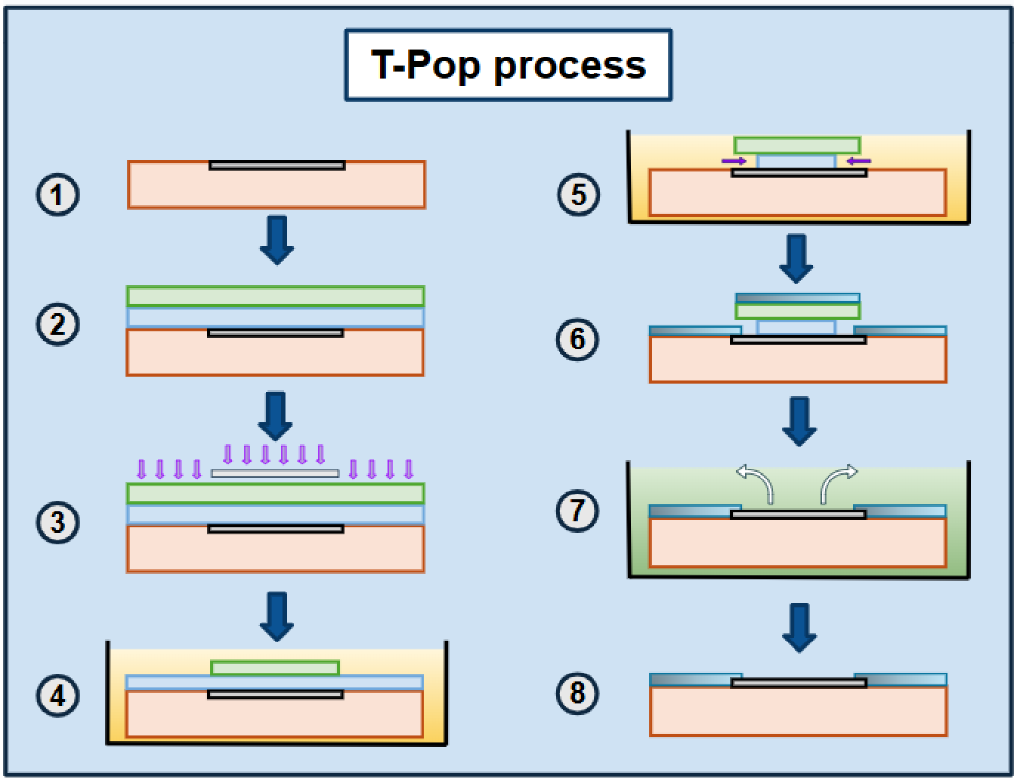


Figure 14 : Electode T-pop process-flow diagrams

(1) The carbon is produced on the substrate using a laser. **(2)** The resist is then deposited and distributed on the substrate and graphite using the spinner. Two positive resists are deposited: LOR20B as the bottom layer (in 2 step: 500 rpm/min during 5 second, then 3200 rpm/min during 45 second), then warmed for 10 minutes at 160°C. S1813 is then applied to the top layer (3200 rpm for 45 seconds), followed by a 2-minute anneal at 115°C. **(3)** The mask is placed on the substrate and placed in the UV cube. It is programmed at 150 mJ/m^2 in accordance with the S1813 datasheet. **(4)** After UV exposure, the substrate is placed in the developer for two minutes. This will remove the resist that has not been protected from UV by the mask. **(5)** In addition, the LOR20B is hollowed out horizontally by the developer, giving the resist the T-Pop profile. **(6)** The sample is placed in the PULP. After creating a vacuum, the metal is deposited by sputtering: a layer of titanium, followed by a layer of gold. The advantage of the titanium layer is its ability to adhere to surfaces. Gold, on the other hand, is a very good electrical conductor and is highly resistant to heat and oxidation. **(7)** After deposition, we remove the remaining resist by lift-off (we place it in a solvent, SVC14 in our case), then we rinse our product with acetone to remove any organic elements remaining on the substrate. **(8)** This gives us our final product: the carbon surface, with electrodes on either side.

2) Resist gap

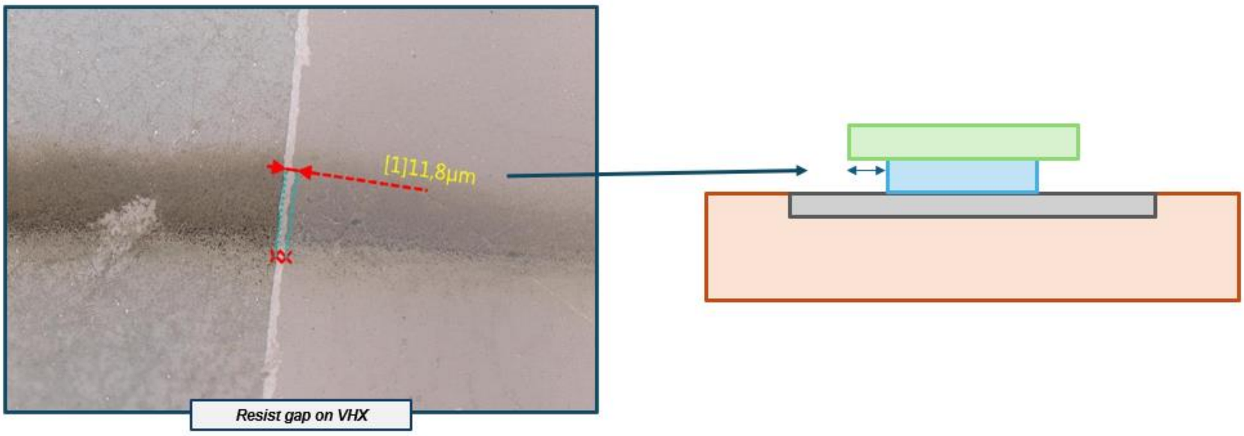


Figure 15 : Resist gap on VHX, diagram

At the development stage, after UV spraying, the VHX shows that between the resin and the peek, there is a small area on average 10mm wide in which the thickness is different. This simply means that our T-Pop profile has worked.

3) Product

After the whole process-flow, we obtain the following product :

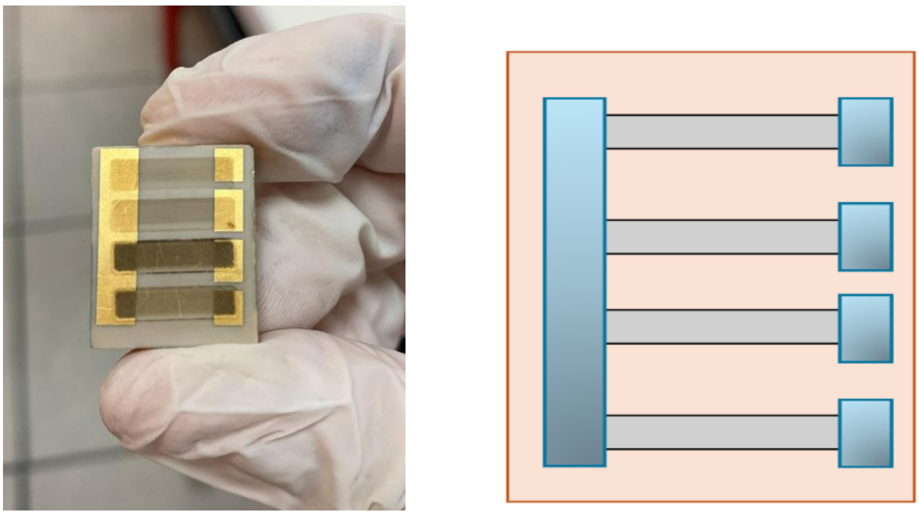
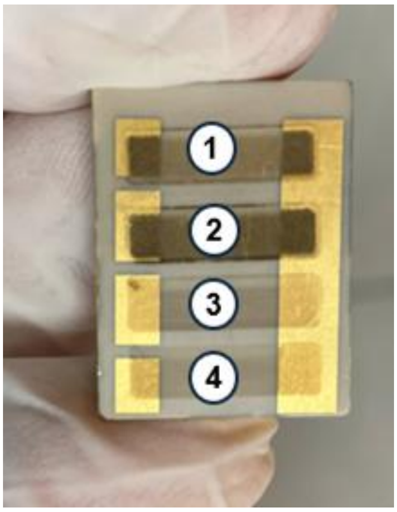


Figure 16 : Final product picture, diagram

You can see the metal on the sample, with the patterns you wanted to give the electrodes. This means that both the metal deposition and the lift-off have worked.

4) Observation on VHX

Once our product had been manufactured, the sample was observed using VHX to compare the before and after metal deposition: one image shows the substrate with only the resist after the development stage, and the other shows the final sample with the metal.



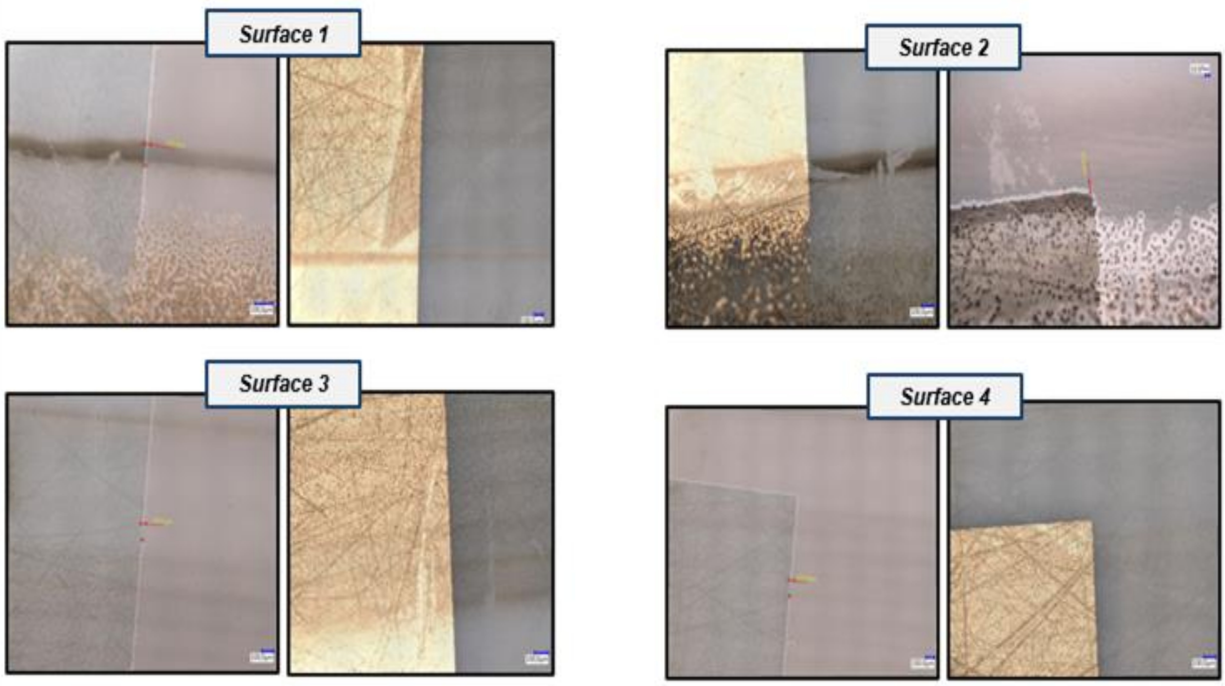


Figure 17 : View of the substrat before and after metal deposit

The VHX shows that the metal has deposited well. One disturbing fact was the impossibility of measuring metal thickness, in all likelihood due to insufficient time or power for metallization.

We note that some carbon thicknesses are deeper than others (such as surface two), while others are much shallower (surface 4, where the carbon is almost invisible). It would therefore be interesting to measure resistance in order to determine whether thickness really does play a major role in the conductivity of our surface.

VI) Characterization

Having achieved the first two objectives, the final one is to characterise the substrate electically. To do this, we decided to use a machine that places a tip on the two electrodes (see photo above), and reads the voltage by varying the current. In our case, the current varied from 10^-5 mA to 10^-4 mA (10 samples, in steps of 1*10^-5).

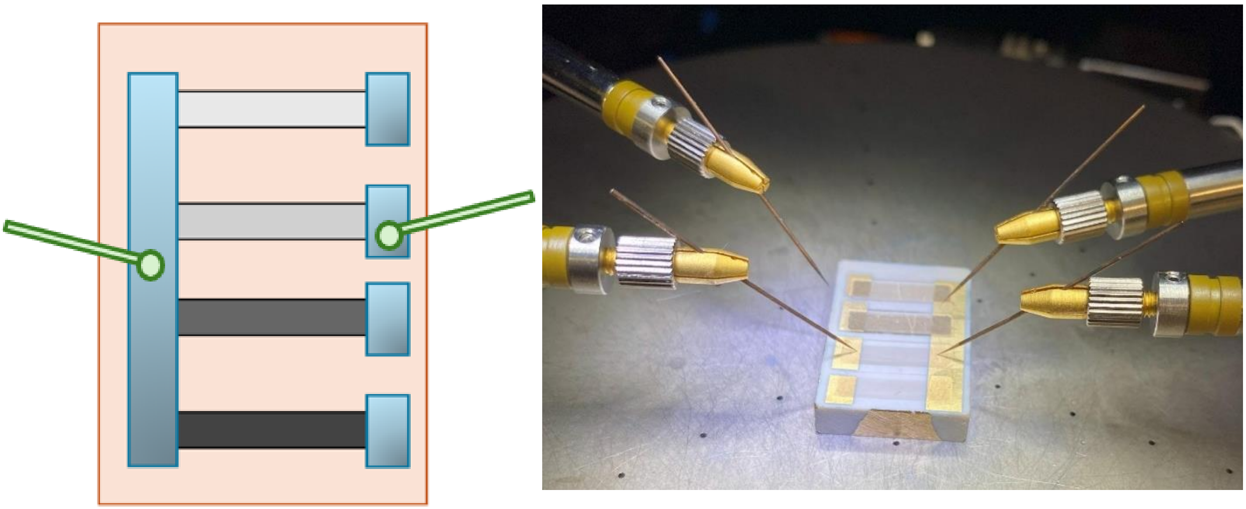


Figure 18 : Characterization picture, diagram

However, we were faced with a problem of coherence. We were unable to measure the resistance, due to a problem with the machine's programming (several tests on different materials were carried out to confirm this incoherence).

A multimeter was then used to determine the resistance of the carbon surface. This method is less precise but can give us an order of magnitude.

Once again, the resistance could not be read on the multimeter. The multimeter has a measuring capacity of up to MOhm, which means that our surface has a resistance bigger than this order of magnitude. It is therefore not conductive, as we wanted to demonstrate.

There are several reasons for this issue:

- The carbon has been damaged during the manufacturing process, impairing its conductive properties
- Even if this has normally been checked beforehand, the surface may not have been conductive from the outset. It would therefore be appropriate to test its conductivity more rigorously before any manufacturing stage.

Conclusion

This project successfully met several key objectives. First, a process flow for electrode fabrication on a Peek substrate was designed. Additionally, electrodes were fabricated on a carbon-containing substrate. However, the characterization and identification of graphene remain to be completed, representing an area for future improvement, by developing a more developed characterisation process and taking care at the possible reasons for the conductivity problem.

The project offers promising prospects, including improving the process flow, enhancing the overall design and conception, and experimenting with different materials and equipment (such as for the metal deposit, or the radiation exposure).

In terms of skills, this project enabled the acquisition of Level 1 competencies like performing microfabrication steps in a cleanroom environment and writing progress reports. It also enabled us to acquire Level 2 skills, such as designing a technological microfabrication process flow and ensuring effective project follow-up.

On a personal level, this was an interesting and instructive project that allowed for the development and strengthening of microfabrication skills. It is also well-aligned with the goals of my 4th-year internship.

Bibliographie

Le nombre prématuré de décès dû à la pollution : INED

https://www.ined.fr/fichier/s_rubrique/19627/extraits_urbanisation_monde.fr.pdf

L'Urbanisation du monde : European Environment Agency (EEA) https://www.eea.europa.eu/fr/highlights/le-nombre-de-deces-prematures

Combiner électronique imprimée et capteur graphène pour accélérer la détection de PFD

https://www.actu-environnement.com

Techniques de lithographie : MOOC

lms.fun-mooc.fr

Graphène, le « matériau miracle » : FICSUM

https://www.ficsum.com/dire-archives/hiver-2015/technologie-graphene-le-materiau-miracle/

« Réalisation de FET en graphène pour détecter les micropolluants dans l'eau » , Victor DINIEL