# Evaluation of variation of gas flow rate during pyrolysis of negative photo-resist derived carbon electrodes for electrochemical and surface optimization

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M-5052.1 Material Characterization

# Introduction

- There has been development of biological and medical devices able of using and controlling fluids in micro/nanoscale. Advantages: low sample volume, automation, portability, low cost and high throughput screening [1].
- The electrochemical analysis is one of the applications that it can be integrated in the microfluidic platforms for analytical assays. This method is commonly used by the simple implementation to measure continuously a target molecule during a redox reaction.
- Carbon is the most common material for electrodes fabrication due to the different properties that it can offer such as: wide electrochemical window, chemical inertness, low fabrication costs and biocompatibility [2,3,4].

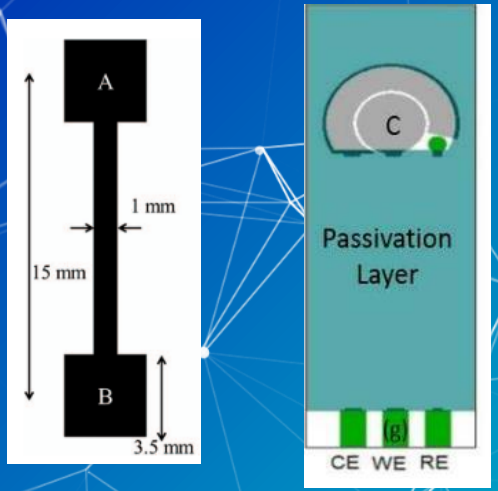



Figure 1. Examples of glassy carbon electrode design. (Left) Pure glassy carbon [3]. (Right) Combination of gold and glassy carbon for electrochemical purposes [5].

# Introduction

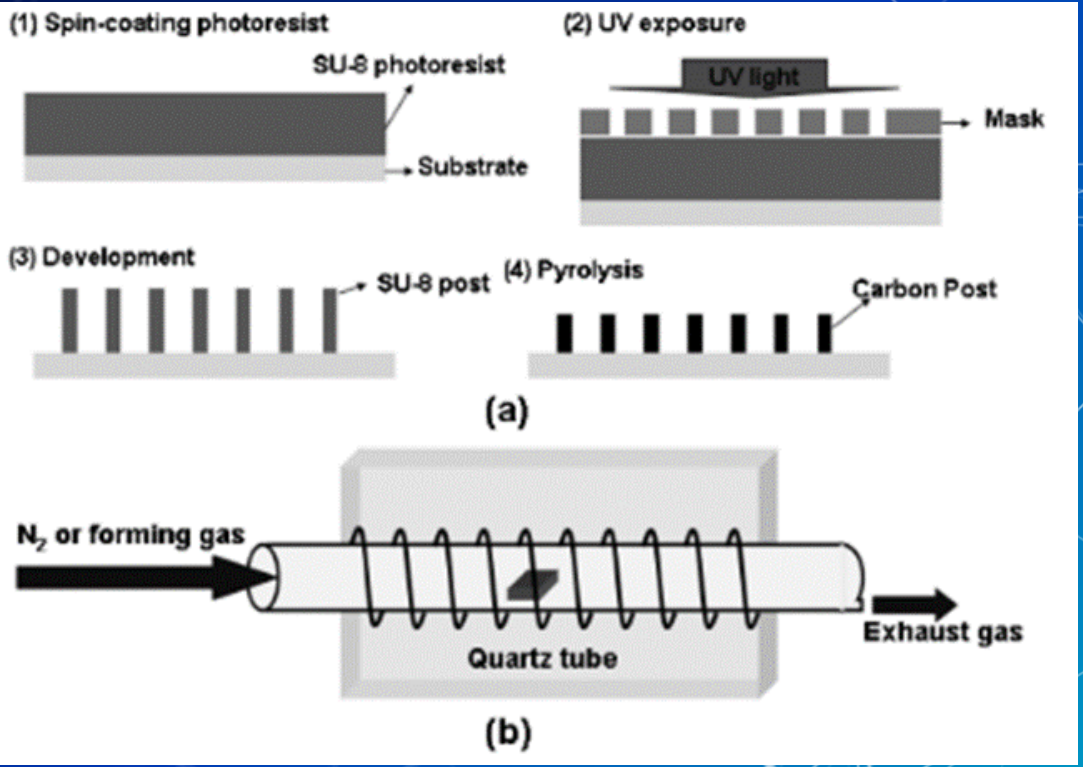



Figure 2. Standard photolithography and pyrolysis. Fabrication steps for SU-8 photoresist to glassy-like carbon [6].

# Objective

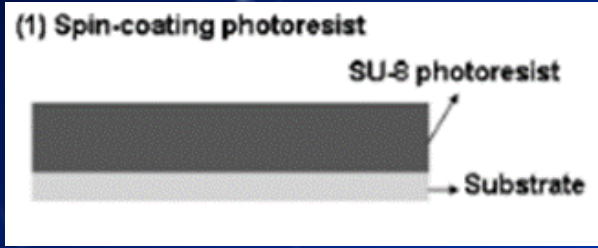
- Multiple works have focused on the optimization of parameters used during the pyrolysis such as heat ramp, dwell time in the carbonization and type of inert atmosphere [2,4,7-11].
- However, there is not a study where it quantifies the differences that the change of flow rate in the gas supply for pyrolysis can generate in the electrochemical and surface properties in the sample.
- It is important consider that it could exist a temperature gradient inside of it depending of where the entrance of the gas supply and temperature sensor are localized. This heat transfer can affect the thermal homogeneity in the samples inside of the furnace, modifying the electrochemical properties of each sample.

**Characterization techniques will provide both quantifiable and qualifiable data about the variation of electrical properties in GC electrodes by the difference of flow rate during the pyrolysis, either the position of the substrate or the physical position of the electrode through the Quartz tube.**

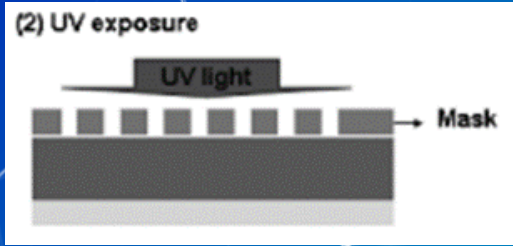
# Materials

- SU-8 2007 and SU-8 Developer
- Silicon wafers (diameter 100 mm, orientation (100), type p)
- Ultra-pure nitrogen tank (99.99%)
- Potassium chloride (KCl)
- Potassium hexacyanoferrate (II) trihydrate ($C_6FeK_4N_6 \cdot 3H_2O$)
- Potassium hexacyanoferrate (III) ($C_6FeK_3N_6$)

# Fabrication

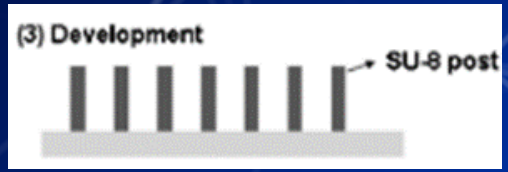



- The SU-8 was spin-coated at 3500 RPM for 30 seconds to obtain thick layers of 7 µm.
- The samples were soft baked at 95 °C for 4 minutes on a hotplate

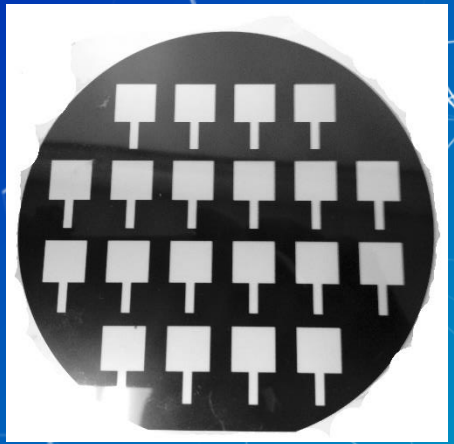



- The samples were exposed to UV light through a contact mask.
- The post-exposure bake was carried on a hotplate at 95 °C for 2.5 minutes

# Fabrication

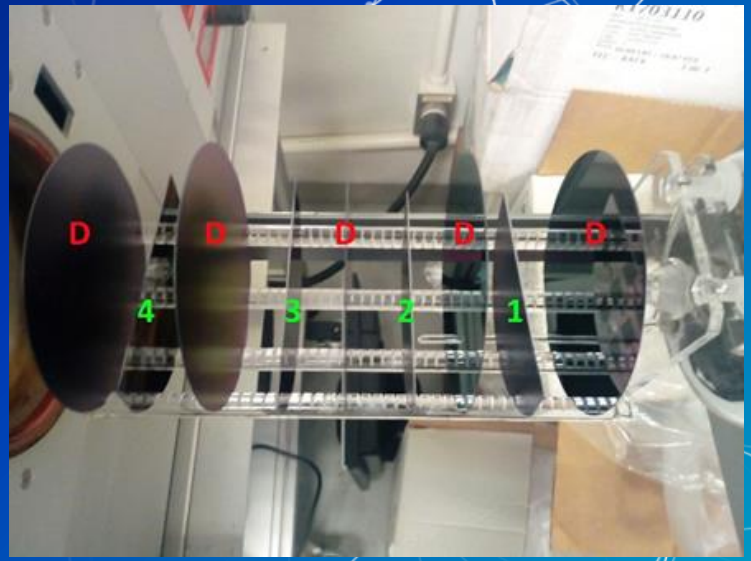


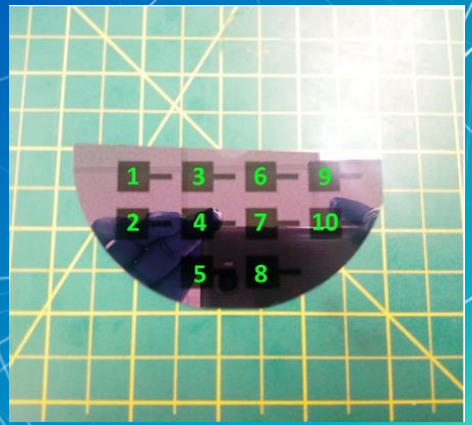

- The samples were immersed to developer for 7 minutes, with moderate agitation, to remove the unexposed polymer.
- The samples were hard baked on a hotplate at 200 °C for 1 hour.



# Fabrication


- The samples were positioned between “dummy” silicon wafers to create a homogeneous gas flow inside of the tube.
- The pyrolysis process started with room temperature (25 °C) for 1 hour.
- It was applied a heat ramp of 4.5 °C/min to achieve 300 °C .
- A second heat ramp (1.67 °C/min) to reach 600 °C [4].
- It was reached 900 °C by using a heat ramp of 5 °C/min. It was maintained the final temperature for 2 hours
- The gas flow proportioned during the pyrolysis varied in 1000 mL/min and 5500 mL/min.



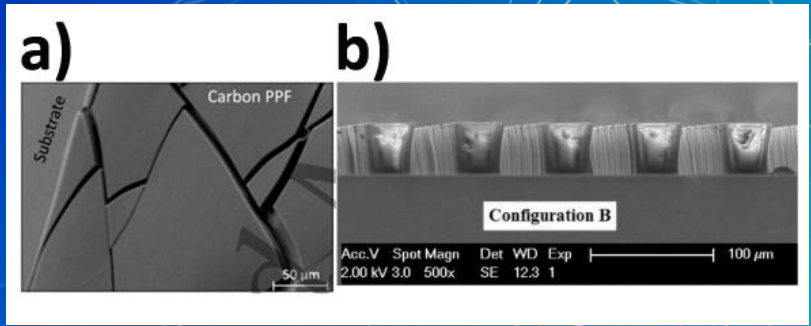



# Characterization Analysis

## Scanning Electronic Microscopy (SEM)

- Acc. Voltage 10 kV [9,12,13].
- A thin gold film will be evaporated on the top to avoid charging on non-conductive parts [8,12].

- If the change of gas flow to a lower value can affect the sample in a physical way, it would be the apparition of cracks or fractures by overstress.
- Cross-sectional images are obtained using SEM to determine the thickness of the carbon structures after pyrolysis [2].
- The shrinkage effect in the carbon structures (outgassing of non-carbon material) is related to the final temperature the type of gas used for the atmosphere, not to the gas flow.



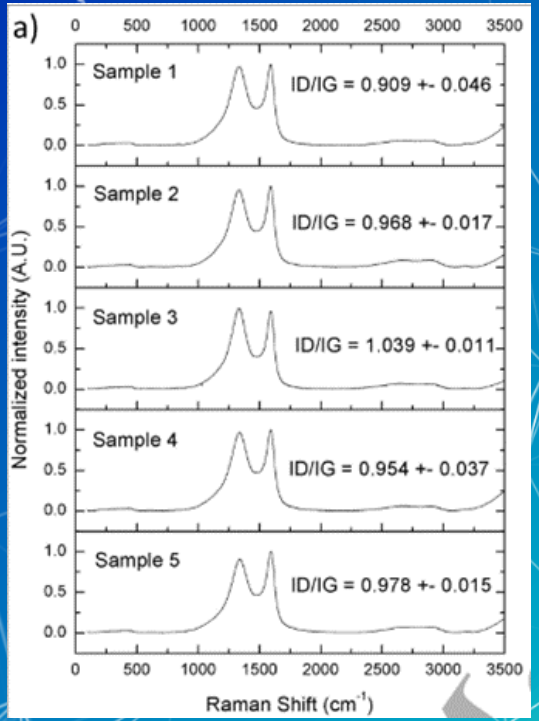

a) Fractures on pyrolyzed carbon [4]. b) Cross-sectional image of SU-8 structure after photolithography [15]

# Characterization Analysis

## Raman Spectroscopy

- It is carried out at 532 nm (Ar-ion laser, 10 mW)
- Range 1000-1800 cm^-1

- It is expected to obtain not only the characteristic G-band (graphite, C-C vibrational mode, 1590 cm-1) and D-band (amorphous, Disorder, 1330 cm-1) but a low D/G ratio [2,3].
- If the D/G ratio of multiple samples in the gas flow 5500 mL/min and 1000 mL/min does not vary, we could conclude that the gas flow does not affect the graphitization of the glassy carbon electrodes by the uniformity of temperature in all the furnace.



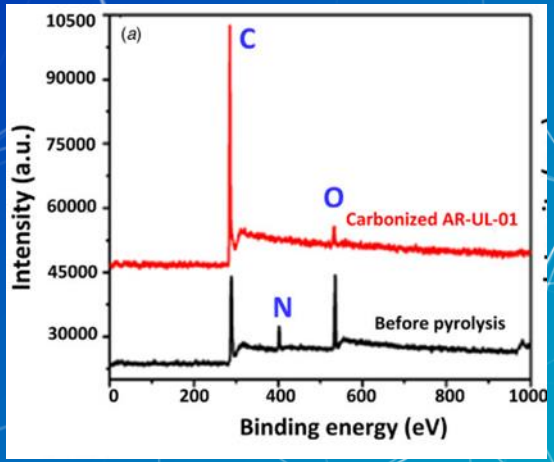

Raman spectra of pyrolyzed carbon structures [4]

# Characterization Analysis

## X-Ray photoelectron spectroscopy (XPS)

- It is recorded using a monochromatic Al Kα X-ray source while the measurement chamber is
- Maintained under <10-6 Pa vacuum.
- Range of 0 to 1000 eV

- To determine the levels of oxygen (using the ratio O1s and C1s peak area) presented in the electrodes while there was variation of gas flow [14].
- The peaks that appears after applying pyrolysis are carbon (284.6 eV, related to C=C) and oxygen (531 eV).
- If the O/C ratio obtained from all the samples in the two gas flows does not present a significant difference, it is possible to conclude that the gas flow does not affect the inert atmosphere during the pre-carbonization step.



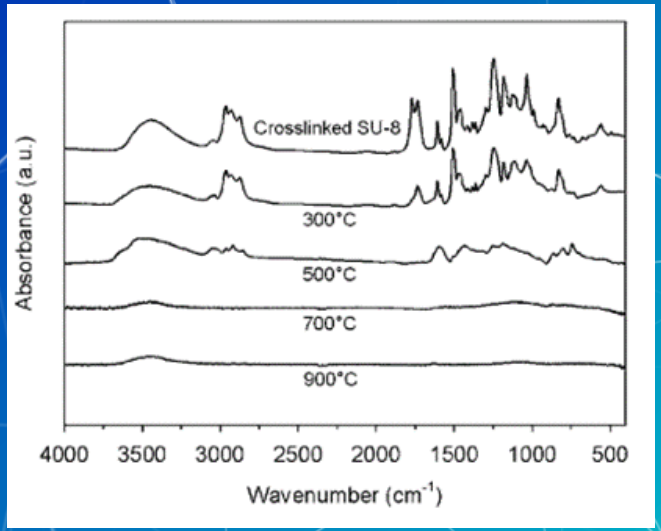

XPS pattern of pyrolyzed (positive photoresist) carbon structures [8]

# Characterization Analysis

## Attenuated total reflectance-Fourier Transform Infrared spectroscopy (ATR-FTIR)

- It is performed on a solid sample (pyrolyzed carbon structure above of silicon substrate) through a diamond ATR crystal
- Range 500-4000 cm^-1

- >700 °C the spectrum does not present any significant peak because the material was able of completing the carbonization (infrared inactive).
- Nam et al. [13] showed that is possible to observe a small peak in 1503 cm^-1, related to the carbonization of the material.
- We are expecting to obtain smooth line in the spectra of the samples, demonstrating the glassy carbon electrodes were successful to eject the rest of the oxygen and hydrogen

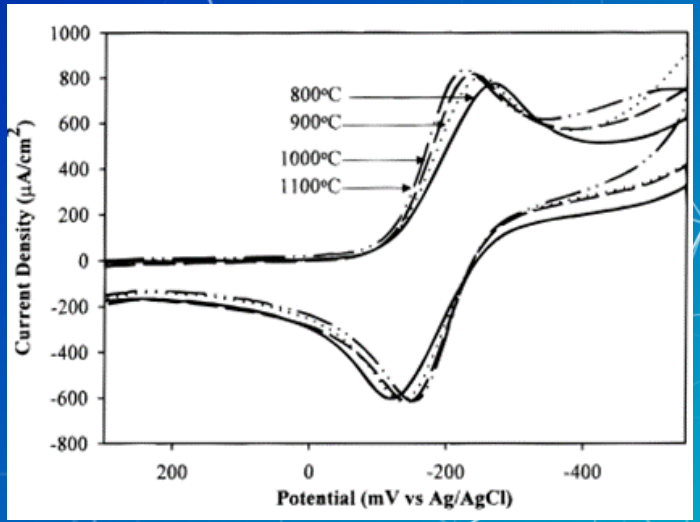



FTIR Spectra of carbon structure on different temperatures[8]

# Characterization Analysis

## Cyclic Voltammetry (CV)

- Potensiostat Chi Instruments 760E
- 300 µL 10 mM ferri-ferrocyanide in potassium chloride (KCl)
- Scan rate of 20-200 mV/s from -600 to 600 mV
- Three electrode configuration: Working- GCE, counter- platinum, reference-AgCl
- It was employed to assess the electrochemical kinetics of the surface towards oxidation and reduction reactions of molecular species.
- Singh et al. [9] and Mardegan et al. [3] concluded that the reduction of the difference of potentials (ΔE) between the anodic and cathodic peaks as well as the increase of current peak (Ip), are signals of a high conductivity of the glassy carbon electrodes.
- Homogeneity.



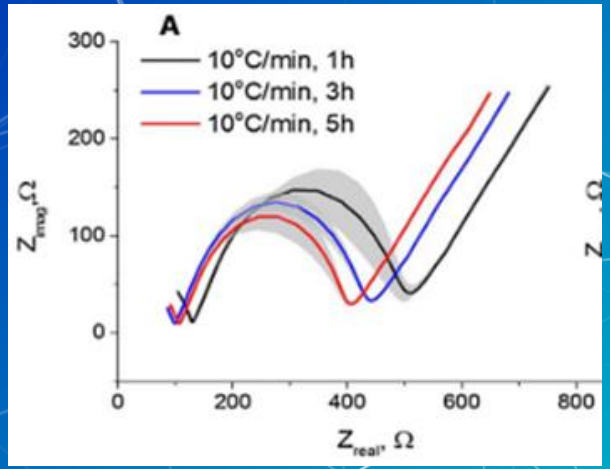

[17]

# Characterization Analysis

## Electrochemical Impedance Spectroscopy (EIS)

- Potensiostat Chi Instruments 760E
- 300 µL 10 mM ferri-ferrocyanide in potassium chloride (KCl)
- Frequency range of 0.1-106 Hz with a sinusoidal signal of 10 mV (10 acquisitions points per decade).
- Three electrode configuration: Working- GCE, counter-platinum, reference-AgCl

- According with Hassan et al. [2], it is expected that the diameter of the big semi-circle represents the charge transfer resistance and the intersection of the linear part in the X axis is the solution and electrode resistance.
- We expected to obtain similar resistance in the samples where the samples were taken from different parts of the Quartz furnace.




[2]

# Conclusion

- The reduction of the gas flow can generate benefits such as: Decreasing of costs on materials, less amount of overstressed electrodes, repeatability in electrochemical properties.
- It is recommended to create a simulation to visualize until which minimum gas flow value is created a temperature gradient. It is assumed that the heat transfer is done by convection and radiation.
- The proposed characterization techniques will help to know the quality of our fabrication methods, specially in the pyrolysis (which is open to improvement).
- It was not considered techniques such as thermal analysis and X-ray Dispersion (XRD) because we assume that the2 pyrolysis can generate the glassy transition and shrinkage is a “must” event.

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