Lab 4 – Plasma Technology

Pre-Lab Reading:

In the domain of nanotechnology, where manipulation occurs atom by atom, **surface modification** reigns supreme. Here, we delve into the world of **plasma**, not light, for shaping surfaces at this minute scale. Imagine a sterile chamber, devoid of air, awaiting transformation. A chosen gas, like argon, becomes the canvas, its potential untapped. Then, a burst of energy ignites the process. Like an invisible brush, it strips electrons from the gas atoms, creating a swirling dance of charged particles: ions and electrons, our sculpting tools.

This energized mixture, no longer gas but plasma, becomes our sculpting medium. Plasmas can be thought of as an alphabet soup of energized species. *Figure 4.1* depicts a hypothetical CF_4 plasma, which contains much more than just CF_4 – it also contains ions, free radicals, which are unstable fragments of the CF_4 after it has been ripped apart, and electrons. With unparalleled precision, such an energized mixture can remove unwanted atoms, etching intricate features directly onto the canvas. Picture miniature channels for microfluidic devices or nanogratings for solar cells, sculpted atom by atom. Plasma's capabilities extend beyond removal. Think of it as a molecular paintbrush, wielding a vast array of functional groups. Each touch imbues the surface with desired properties: biocompatibility for medical implants, conductivity for electronics – plasma makes it possible.

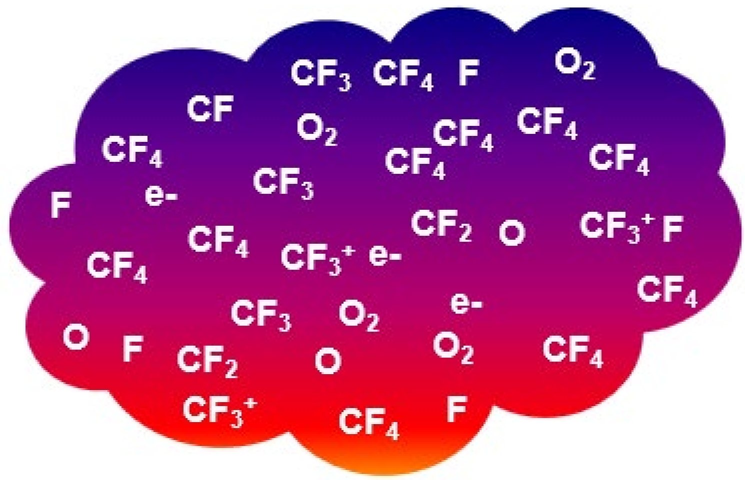

Figure 4.1: Depiction of a CF_4 plasma cloud - illustrating the various types of intermediate species that may exist in a plasma environment.

Unlike traditional sculptors, plasma works silently within its vacuum chamber. No tools clang, no paint splatters, just the silent ballet of charged particles transforming surfaces atom by atom. Yet, the results are tangible: stronger, cleaner, more versatile surfaces emerge, ready for diverse applications. From light-harvesting nanostructures to medical biosensors, plasma's touch leaves its mark on various fields. In the hands of skilled scientists, it's a crucial tool, enabling the creation of materials with previously unimaginable properties.

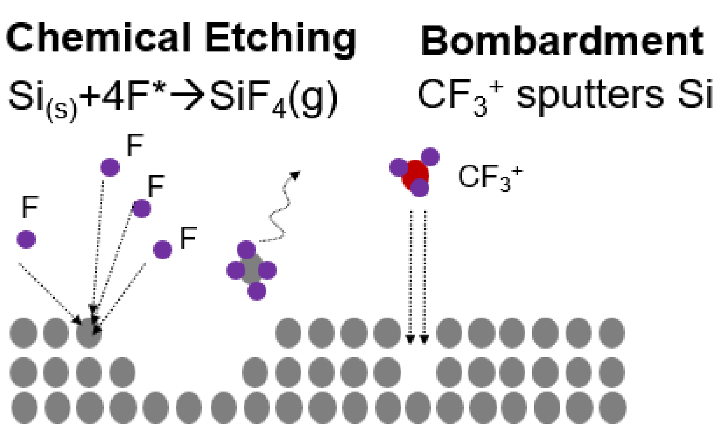

Figure 4.2: In a plasma, the free radicals serve to perform selective chemical material removal while the ions serve to perform physical non-chemical material removal.

Mastering this atomic-level sculpting isn't simple. Plasma treatments require precise calibration and process optimization, akin to a scientist meticulously adjusting parameters in a complex experiment. Imagine a diverse landscape that is to be transformed into a golf course. The hilly landscape contains dirt, grass, soil, weeds, concrete, asphalt, and a variety of other surfaces. If we were to dig small but deep holes all over the landscape to create the holes for the golf course, irrespective of what the surface was made of, the ions from our CF_4 plasma, namely the highly energetic CF_3^+ species, would serve this purpose. Instead, if our goal was to kill all the weeds on the landscape but leave the other surfaces intact, then we would now employ the free radical portion of the plasma to selectively remove the weeds but leave the remaining surfaces intact. In an analogous fashion, *Figure 4.2* illustrates how the ions (e.g., CF_3^+) from a plasma can be used to perform physical "**anisotropic**" etching or "digging" while the radicals (e.g., F) from the plasma can be used to perform the selective "**isotropic**" etching or "weeding".

The highly energetic species of plasma can be used for various applications including etching materials, depositing materials, and chemically modifying their surfaces. In the semiconductor industry the strengths and unique abilities of plasmas are applied in complex systems and equipment such as **dry etching** and thin film deposition tools. In these systems, the plasma environment is supported by a variety of infrastructure including vacuum equipment, semiconductor process gases, and electronics as shown in *Figure 4.3*.

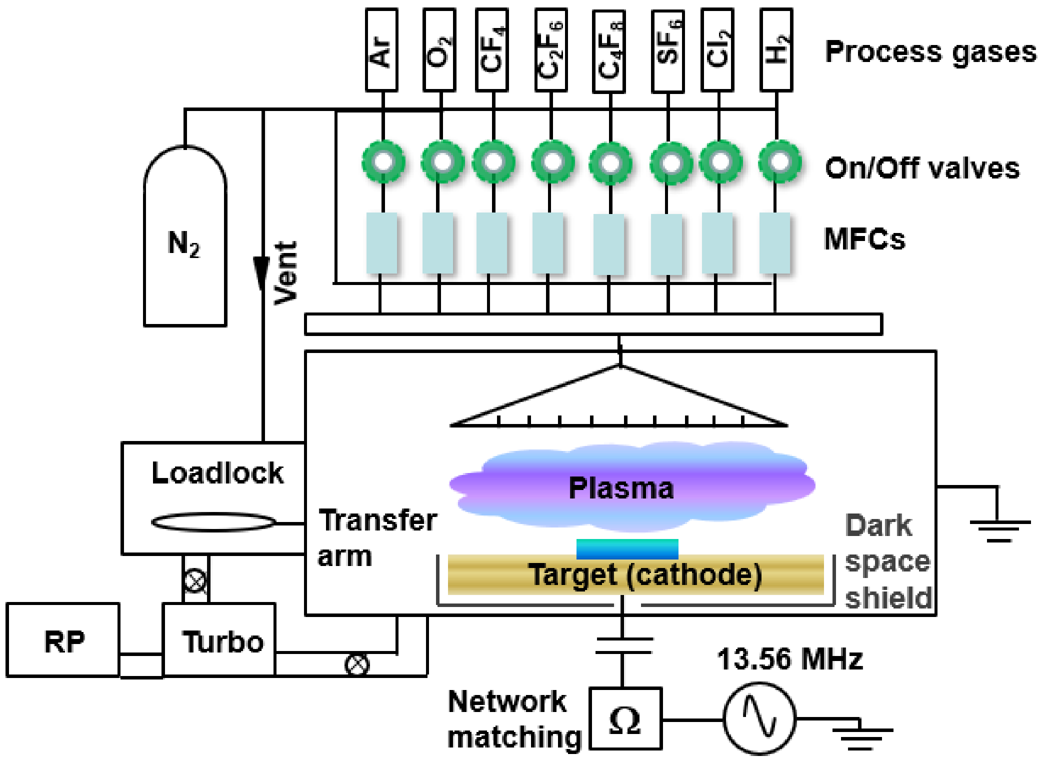

Figure 4.3: Block diagram of components that may be found on a typical plasma tool used in the semiconductor manufacturing industry. Shown is a Reactive Ion Etch (RIE) tool.

Objective:

The objective of this lab is for students to learn the applications of plasma and create a plasma utilizing lab glassware and a vacuum pump. Students will understand and utilize plasma in surface modification applications by first creating a basic plasma, then performing a surface modification experiment. The educator will provide a detailed experimental appendix for students to follow to perform the process.

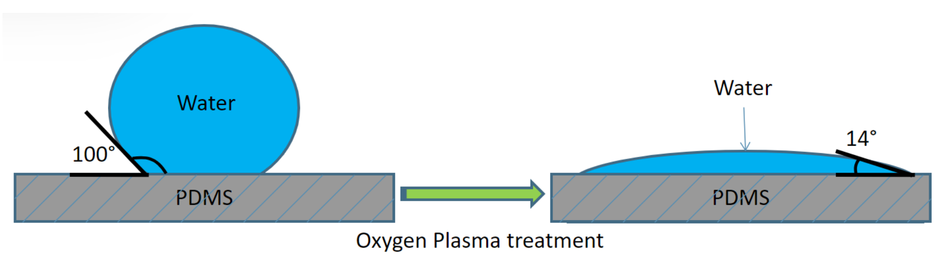

Figure 4.4: Example of wetting angle changing

Background:

Within nanotechnology, there is an important process known as surface modification. The ability to modify a surface to have specific properties is integral to many processes within the field of nanotechnology. This is mainly done using plasma, the enigmatic fourth state of matter. Unlike the familiar solid, liquid, and gas states, plasma exists as a highly energized mix of charged particles: ions, electrons, and radicals. This unique composition empowers it to act as a versatile "nanosculptor," capable of both removing and adding material with unparalleled precision.

Imagine a vacuum chamber, this clean environment allows technicians to control the atmosphere and conditions within the enclosed space, allowing for specific process to occur. This chamber becomes the arena where a chosen gas, like argon or oxygen, is introduced at low pressure, which is the predecessor to the introduction of plasma to the space. Once the environment within the chamber meets the proper conditions, energy is added. This is not through light, but through a calibrated application of electric fields, radio waves, or microwaves. This applied energy rips electrons from atoms as well as breaks molecules apart. As electrons are stripped away, a cascade effect initiates, transforming the once neutral gas into a field of charged particles. These charged particles, positively charged ions and free electrons, form the core of plasma – our key to manipulating surfaces on the nanoscale.

This plasma then interacts with surfaces in diverse ways, each leading to distinct outcomes. However, this lab will mainly focus on the surface modification capabilities of plasma. When this plasma is created, it forms **free radicals**, which are highly energetic molecular fragments that aggressively bond with almost any material they encounter. The specific materials that the free radicals bond with are determined by the atom of the free radical itself. For example, a free radical of oxygen (O*) will willingly bond with almost any organic or carbon-based material that it comes in contact with, while a fluoride free radical (F*) will bond with oxygen and silicon materials.

By harnessing these properties, various processes intrinsic to nanotechnology can be completed. Using an oxygen-based plasma, a process known as '**ashing**' can occur. This process is where organic material can be stripped or cleaned from the surface of a harder material. In industry, ashing is used to clean substrates better than humans or other machines could feasibly do. Additionally, some tools in nanotechnology have "plasma cleaners", which are systems within these tools that create a plasma to remove any residue or contamination from inside of the vacuum chamber. An additional use of plasma is in the process of etching, a process used to create the chips found in phones, laptops, and other devices. Etching uses the same principles as ashing, except this time, the goal is to 'dig' into the substrate using a specifically tailored gas chemistry which can chemically target the substrate material. This allows for trenches and other structures to be fabricated, allowing for complex devices to be made. Etching, in addition to lithography, are two of the most important processes in nanofabrication.

Experiment:

SAFETY DISCLOSURE: This lab contains the use of microwaves, glassware, vacuum systems, and plasmas. Therefore, for student safety it is important to follow the instructions outlined in this handout to minimize the risk of inhalation of free radicals, burns, cuts, or other types of injuries. Students should wear standard lab PPE such as long sleeves, safety glasses, and gloves. This process should be done under a fume hood, and extreme caution should be taken after the process is complete, as the temperature of the system can exceed 750 degrees Fahrenheit. FAILURE TO ABIDE BY THESE SAFETY REGULATIONS CAN RESULT IN THE FAILURE OF THE GLASS BOTTLE USED, refer to *Figure 4.5*.

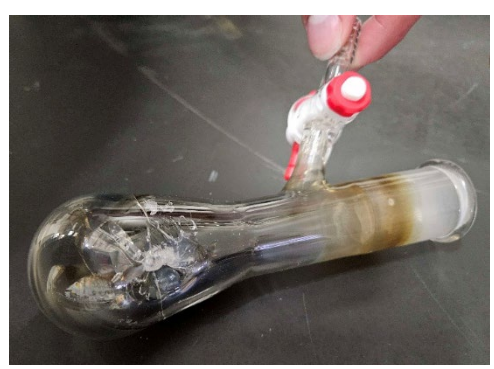

Figure 4.5: Example of an imploded flask due to disregarded safety measures

In this lab, students will build and utilize a vacuum chamber to create a plasma for surface modification. Once complete, the students will utilize the system to perform basic surface modification which will be tested using a digital microscope and a basic wetting test.

Required Materials:

1. Vacuum Flask
   a. Link
2. KJL Vacuum Trainer
   a. Hose connection nozzle
      - Link - PN: QF25-050-SHA
3. Vacuum hosing
   a. Link
4. Rubber stopper
   a. Link
5. Standard Kitchen Microwave
6. Glass Slides
   a. Link (12-550C) (Save the box)
7. Diamond Scribe
   a. Link
8. Straight Edge/Ruler
9. Pipettes
10. Glass Cutter
    a. Link
11. Forceps or Tweezers

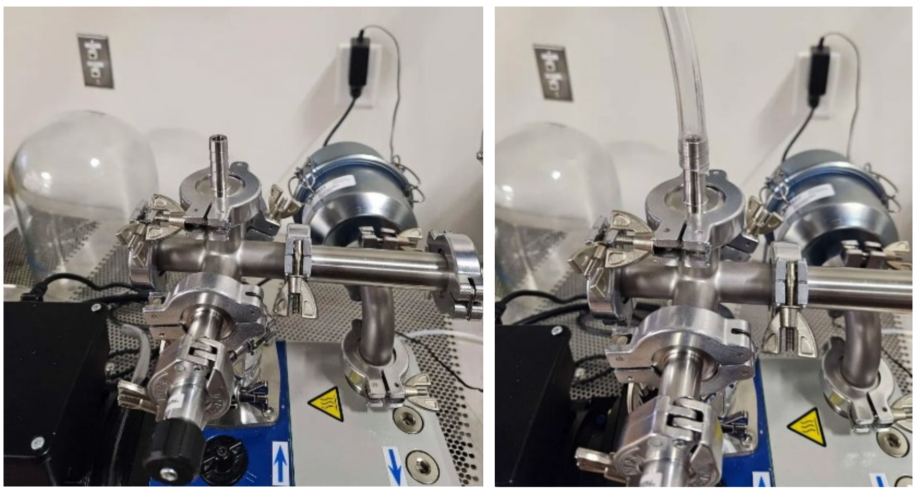

Figure 4.6: Modifying the KFL Trainer

Step 1: Modify KJL vacuum trainer for plasma application

To modify the KJL Vacuum trainer for this lab, simply remove the baseplate of the trainer and replace it with the hose nozzle. Then attach the vacuum hosing (5/16ths hose, or the second largest) to the nozzle and the other end to the removable vacuum chamber, which will be covered in the next section.

Step 2: Create removable vacuum chamber

To create the removable vacuum chamber, you will need the vacuum flask, and the rubber stopper. To place or remove things from the inside of the chamber, remove the rubber stopper as needed and remove/place the item inside of the flask. Be sure that the red, plastic nut on the back side of the valve is tightly (hand tight) against the black O-ring, or the chamber will not achieve the proper pressure. Conversely, if needed, loosening this nut will act as a vent valve, if needed.

Figure 4.7: Vacuum flask with stopper

Step 3: Test plasma generation

Before performing any experiments using the plasma system, the proper location inside of the microwave must be found to maximize the amount of RF energy interacting with the flask. To do this, first pump down the flask to approximately 50 mTorr of pressure. In the case of plasma, a lower pressure will reduce the heat and energy of the produced plasma, so being lower than this pressure (down to around 30 mTorr) will still be acceptable for this lab. Avoid any pressures between 80 mTorr and 120 mTorr, as this range will create a plasma that can exceed 750 degrees Fahrenheit under the proper conditions. This will result in the meltdown and implosion of the vacuum flask. Further, do not exceed 30 seconds of application time total as this may also result in the failure of the system.

Figure 4.8: Positioning of the vacuum flask in the microwave

Once the proper pressure is achieved, ensure that the rotating tray of the microwave is in place. If the microwave being used does not have a rotating tray, the students will need to manually move the flask around the microwave to find where the plasma is ignited most effectively. If the microwave does have a rotating tray, place the flask along the circumference of the tray, and set the microwave to 60 seconds. Refer to *Figure 4.8* for the placement of the flask in the microwave.

As the RF does not cover the entire microwave (hence why there should be a rotating tray) the plasma will not be ignited for the entire 60 seconds. The students should start the microwave and watch the flask, noting where the plasma is ignited, as well as where it is brightest. This will indicate where the RF energy is the strongest. For example, in the microwave used to test this lab, this location is in the back left corner of the microwave, as shown in *Figure 4.9*. Note this location, as it will be used throughout the rest of the lab.

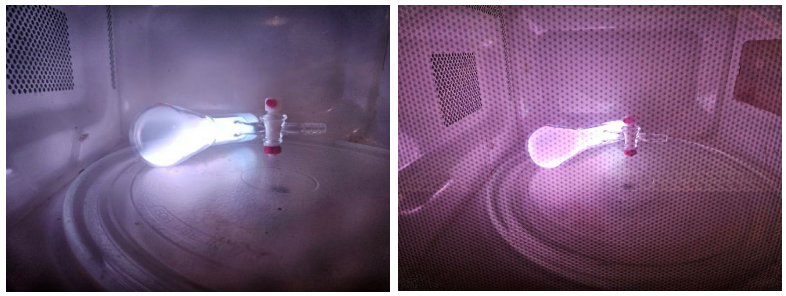

Figure 4.9: Approximate position of highest RF energy, leading to plasma ignition.

Step 4: Perform Surface modification

Figure 4.10: Glass cutting process

Once the plasma generation has been confirmed and viewed, the beginning of the surface modification section can begin. To start, retrieve a glass slide, diamond scribe, glass cutters, and a straight edge. With the glass slide in a vertical (portrait) position, use the diamond scribe and glass cutters to cut a strip approximately two centimeters in width. If the glass does not form a clean break, that is acceptable, simply be sure to handle the glass with care so as to avoid being cut.

After the glass has been cut, use a pipette to drop a singular drop of water onto the surface of the glass. Take a picture from the side of the glass and note the shape of the droplet. Is it rounded, or is it flat? Be sure to write this down. After getting a picture of the sample (*Figure 4.11*), dry it with a paper towel and retrieve the vacuum chamber created in step 3.

Figure 4.11: Initial droplet of water

Place the glass slide into the chamber with the side that was wetted facing upwards, in the neck section of the bottle. Be sure to keep this side up at all times. Carefully attach the vacuum chamber to the vacuum pump and pump the system down to 50 mTorr. Remove the chamber from the pump and place it into the microwave at the previously determined position. Turn on the microwave for ONLY 15 seconds. This will begin the surface modification process. After the process is finished, allow for the system to cool for no less than 5 minutes. After this time period is up, CAREFULLY test the heat of the vacuum chamber by feeling for any excess heat emanating from the bottle. Remove the bottle from the microwave and remove the stopper from the bottle. Remove the glass slide from the bottle USING

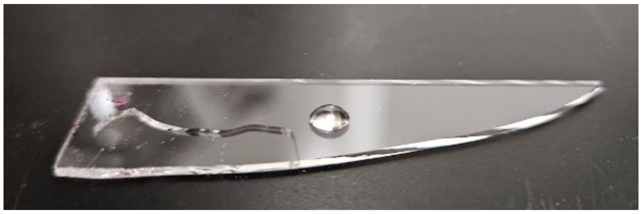
Figure 4.12: Post-modification droplet of water

FORCEPS or TWEEZERS. Do not touch the glass slide with bare hands, as this is not only a safety risk, but the oils present on human hands can reverse the process. Allow the glass slide to cool for an additional minute to ensure safety. After the slide has cooled, use the pipette to drop a similar amount of water onto the glass slide, and observe how it reacts. Is it more rounded, or flatter? Note this difference for the future.

Questions:

1. What was the initial shape of the water droplet? What was the shape after the process was completed?
2. Explain the surface modification process in your own words. How does this process work?
3. In your own words, explain how a plasma is generated in the microwave.
4. Research and describe how plasma is used in real-life applications in nanotechnology.
5. Research a tool that uses plasma as part of a process. Include details such as the industry it is used in, the cost, and any special circumstances.
6. As a supplemental activity, it may be possible to place a glass slide with sharpie written on it into the plasma system. Given that sharpie is an organic compound, what would be expected to happen to it when it is exposed to the plasma?
7. What are some safety concerns when working with plasma? Why is protective eyewear important?
8. During the plasma generation test, students were instructed to observe the plasma while wearing eye protection. What color did the plasma appear as, and did it change? Research why this occurred, and what elements may be responsible for these colors.
9. Research a specific material used during plasma processes, for example, oxygen or carbon tetrafluoride. (Do not use the examples) What is this material used for? What are the costs associated with using it? Are there any special considerations?
10. Plasmas can only form under specific conditions. What are these conditions, and why are they important?

Supplemental Activities:

1. To assist in visualizing the ashing process, cut another glass slide and write on it using a sharpie marker. Place it into the vacuum chamber and expose it to plasma. What happens to the sharpie?
2. Perform surface modification for various times – does the length of the plasma treatment influence the contact angle?
3. Observe the color of the plasma. Do a literature review to determine what gas species are most likely present in the microwave plasma.