Integrated Circuit Manufacturing with Plasma-Activated Chemical Treatment (IMPACT): Enhancing the Chemistry of Chip Fabrication

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Abstract: Combining low-temperature plasmas with the wet chemical steps involved in semiconductor device manufacturing presents new opportunities for improving the next generation of devices. An atmospheric pressure plasma jet device is applied in a custom reactor to enhance the chemical reactivity of solutions used for wet chemical stripping, and subsequent chemical analyses are performed. The performance of these activated solutions is also evaluated with respect to reactivity and stripping time.

Keywords: Plasma-liquid interactions, plasma chemistry, chemical radicals, wet chemistry

1. Introduction

Low-temperature plasmas are ubiquitous in semiconductor processing; advancements in plasma technology have enabled smaller features to be patterned on devices. As we approach fundamental limits dictated by Moore's Law, we are also searching for ways to simplify the process or reduce the time that wafers must spend at each of the myriad steps in the process.

While much of the work devoted to plasma processing of devices has focused on the plasmas used for deposition, etching, lithography, etc., another avenue for advancement that can be explored involves the chemical reagents used in preparing the wafer. It is well-known that low-temperature plasmas can enhance the reactivity of aqueous solutions [1], therefore, we have applied atmospheric plasmas to the aqueous solutions used in chemical stripping.

2. Experimental Apparatus

In these studies, an atmospheric-pressure dielectric barrier discharge plasma jet (**Figure 1**) is used to treat various solutions involved in the wet cleaning process. An AC power supply operating at approx. 20 kHz and up to 20 kV is used to drive the plasma. A needle is the powered electrode and is positioned within a quartz capillary tube; the counter (grounded) electrode is an insulated stainless-steel collar which surrounds the quartz tube.

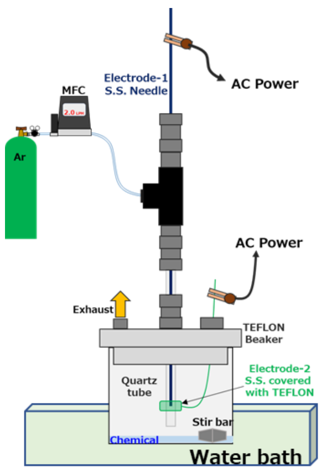

Fig. 1. Schematic of plasma jet tool used for IMPACT.

A relatively high flow of argon passing through the dielectric barrier discharge between the needle electrode and the walls of the quartz tube produces a jet of plasma from the tip of the device (**Figure 2**), which subsequently provides a remote (indirect) treatment of the solution. Most IMPACT treatments occur over the course of one hour, with constant stirring of the solution.

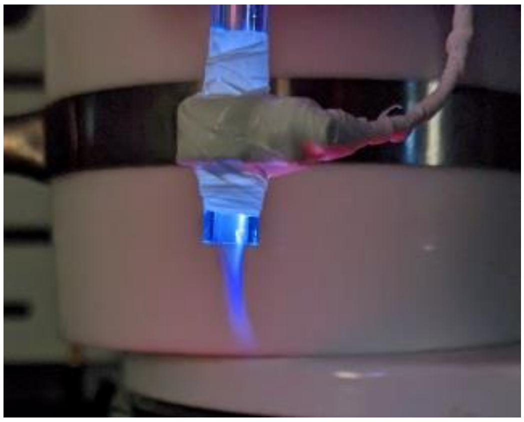

Fig. 2. The plasma jet produced by the IMPACT tool.

The reactors used in these studies were machined in-house and are comprised of solid pieces of PTFE (Teflon) and are sealed with chemically resistant o-rings. This method of construction allows for the treatment of the reactive chemicals and leads to a reduction of contaminants (primarily metals) in the solution post IMPACT treatment. Furthermore, the temperature of the reactor body (and therefore the solution being treated) is regulated with a water bath, which leads to more repeatable measurements. The IMPACT tool and its associated reactor sit within a fume hood, and exhaust lines are directed away from the operator.

3. IMPACT Induced Chemistry

Our initial experiments have demonstrated that IMPACT treatment of aqueous solutions can generate high (part per thousand) concentrations of hydrogen peroxide (H_2O_2), small amounts of hydroxyl radical ($\cdot OH$), and can alter the pH and oxidative/reductive potential (ORP) of the solution. Each of these components individually increases the reactivity of the treated solution, and the combination of these reactive species will likely increase the efficiency of chemical stripping solutions.

Initial IMPACT treatments (and computational modeling) have focused solely on water, however, we have recently begun adding various chemical species into the reactor which have historically been used as chemical stripping solutions. As the chemistry of the solution to be treated increases, as does the complexity of chemical analyses.

Presently, we are focusing on detection and analysis of short-lived radicals and other reactive species to gain a complete understanding of the plasma-treated medium. To measure some species, we have utilized various colorimetric assays to measure radical concentrations, for example, using terephthalic acid (TPA) [2] to measure the amount of ·OH produced according to **Figure 3**:

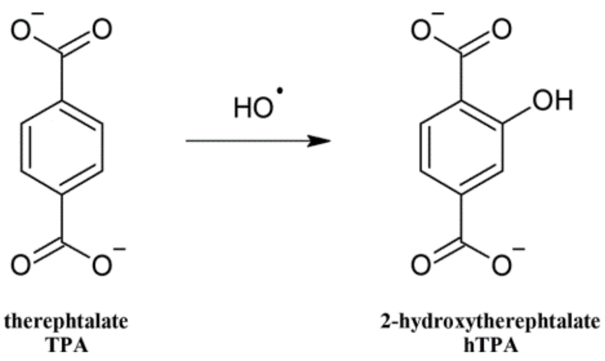

Fig. 3. Reaction of TPA for quantification of ·OH.

For some short-lived or reactive species, colorimetric assays are not effective or produce questionable results. We are therefore utilizing other methods for separating and analyzing the chemical species produced during IMPACT treatment, namely liquid chromatography, ion chromatography, and mass spectrometry. Standard methods for analyzing solutions are being developed with contributions from University of Illinois School of Chemical Sciences and Tokyo Ohka Kogyo (TOK) America.

In conjunction with our experimental work, models of the plasma-liquid interface and the bulk solution are being developed with the Crane-Zapdos [3] application within the MOOSE framework and tested to validate empirical results and to guide future experiments. Results of species concentrations under various conditions are currently being evaluated in a zero-dimensional model, and models with increasing complexity will follow, similar to the work presented in [4] for a direct-current (DC) plasma-liquid interface.

4. IMPACT on Coupon

We are also studying the effects of IMPACT treatment directly on coupons, with two primary goals: evaluating the efficacy and efficiency of IMPACT-treated liquid at removing materials from a substrate and establishing methods for plasma treating the cleaning solution as it interacts with the substrate. We believe that this instantaneous treatment takes advantage of the reactivity of species produced in the liquid and minimizes the transit time of these short-lived species to the substrate.

This series of experiments also introduces additional complexity in the form of substrate materials interacting with the IMPACT tool. Various substrate materials (glass, silicon, silicon oxide, tungsten carbide, etc.) are being exposed to IMPACT treated liquid and the resulting chemistry analyzed.

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5. References

[1] P. Bruggeman et. al, Plas. Sour. Sci. Technol., 25, 053002 (2016).
[2] F. Tampieri et. al, Analytical Chemistry, 93, 3666-3670 (2021).
[3] S. Keniley, D. Curreli, arXiv:1905.10004v1 [physics.plasm-ph]
[4] S. Keniley et. al, Plas. Sour. Sci. Technol., 31 (2022) 075001.