SBIR Opportunities for University Research and Development

Jane P. Chang
Department of Chemical Engineering
University of California, Los Angeles, CA 90095

Abstract

NSF SBIR program supports a collaborative research and development effort between UCLA and Surfx Technologies LLC. This paper discusses the benefits of participation in the NSF SBIR Phase II research on "Environmentally Benign, High Pressure Plasma Cleaning Tool for Photoresists." Specifically, this research aims to commercialize an atmospheric plasma processing system for photoresist ashing and provides an excellent opportunity for graduate students to experiment with a commercial semiconductor manufacturing system. Specific research tasks summarized here includes (1) the modeling of atmospheric plasma reactor to aid the improvement of the reactor design, (2) the new design of the plasma sources, (3) the spectroscopic characterization of the photoresist surfaces, (4) the effect of process conditions on the attainable photoresist etch rates, and (5) the deposition of dielectric materials. This unique research partnership requires frequent communications with the sponsor to quickly modify the research scope or adapt radical changes to accommodate the new development and interests of the sponsor in commercializing the technology.

Company Profile

Surfx Technologies LLC was founded in 1999 to bring to the marketplace new tools for nanotechnology. The company's atmospheric plasma products are based upon inventions exclusively licensed from the University of California, Los Angeles (UCLA). Patents are pending on these inventions both in the United States and internationally. The company sold its first product, the Atomflo™-250, in May 2002.

Research Progress

To design an environmentally benign and atmosphere pressure plasma tool for photoresist etching and dielectric deposition, the computation modeling was first performed to optimize an 8" plasma reactor by designing a suitable baffle that distributes the gas evenly through the perforated electrodes and onto a wafer. The optimum design yielded a uniform velocity profile of 0.455 ± 0.025 m/s. New plasma heads with different grounded electrodes were then designed and fabricated to study the effect of electrode geometry on the etch rate of photoresist. Etching of photoresist was studied as a function of the total gas flow rate, the oxygen partial pressure, the total power, the size of the perforated holes on the electrode, and the electrode to substrate distance. The optimal new design yielded a maximum etch rate of 0.85 μm/min, compare to 0.53 μm/min achieved by the standard design manufactured by Surfx. Additional research effort on deposition of silicon nitride with the atmospheric plasma source was investigated and yielded a maximum deposition rate of 130 ± 15 nm/min. Specific research details are summarized below:

1. Modeling of the Plasma Reactor

A computational fluid dynamic model of an atmospheric pressure plasma reactor was developed using FEMLAB. This model was formulated to simulate the velocity profile of the gas in a plasma source, housed in a chamber, and to optimize the velocity uniform at the wafer surface. The design consisted of two perforated electrodes, 8" in diameter, with a wafer placed 3 mm away from the electrodes. The conditions used in the simulations were: helium gas, 80 Torr total pressure, and 8.3 m/s inlet velocity.

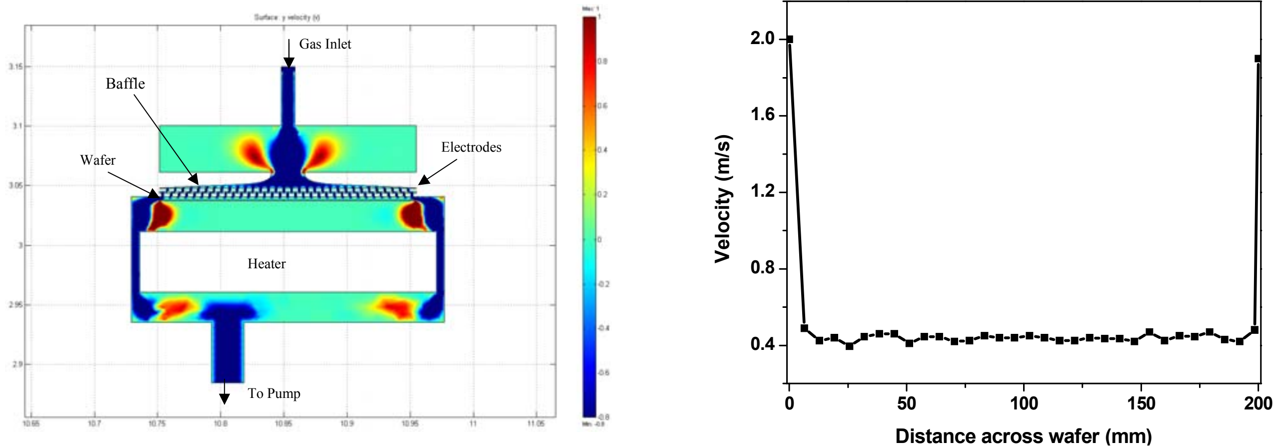


Figure 1. Velocity profile in the plasma reactor.

Figure 1 shows the simulation setup including the heater, wafer, electrodes, and the baffle. The scale on the right hand side indicates the velocity in m/s, where negative values denote a downward direction. The gas enters the reactor through the top, experiences minimal lateral diffusion, then passes through the two perforated electrodes before impinging upon the wafer. The velocity profile at 1.3 mm above the wafer is shown in Figure 2. The velocity in this profile is 0.455 ± 0.025 m/s. The baffle configuration was modified to yield this low standard deviation. It was discovered that the maximum pressure variation in the entire chamber, including above the wafer, was merely 0.2%. This model was also applied to a similar reactor with 4" diameter electrodes. The baffle dimensions had to be modified to produce a uniform velocity profile along the wafer. In these simulations, the velocity at 1.3 mm above the wafer was 0.438 ± 0.013 m/s, with only a 0.05% pressure deviation in the chamber.

2. Design of new plasma sources

New plasma heads with perforated electrodes were designed to study the effect of electrode geometry on the etch rate of photoresist. The goal was to keep the total open area constant but vary the number of holes and their diameters. Three different grounded electrodes were constructed for the 1" plasma source (the AtomFlo™), and Surfx Technologies, LLC, donated an additional one. Shown in Figure 3 are pictures of a helium plasma at 20 W in these four electrodes. The differences between these electrodes are the hole sizes and number of holes, however, the percentage of open area is kept constant at 15%.

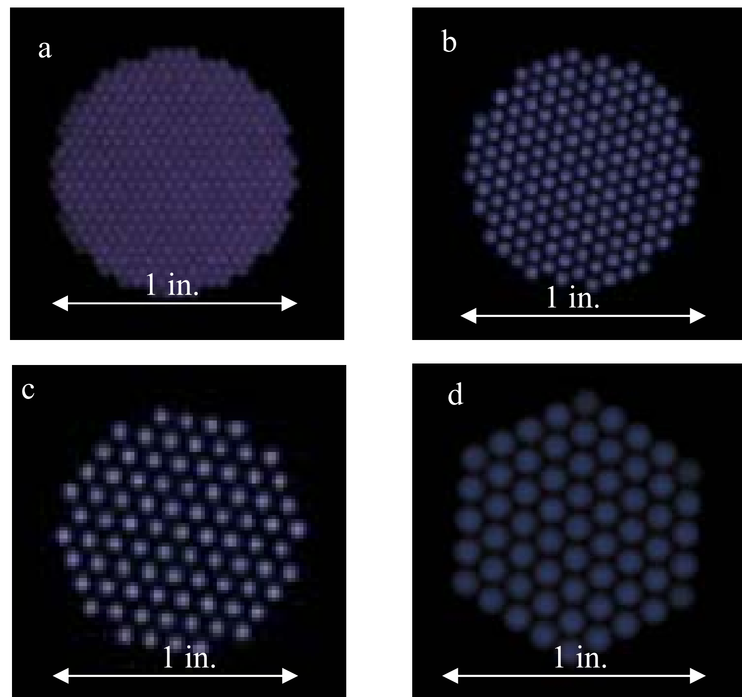


Figure 3. Pictures of the 1” plasma source with different grounded electrodes with the following hole diameters: a) 0.023” b) 0.031” c) 0.041” d) 0.050”.

These pictures are taken looking into the plasma. The differences in the discharges are clearly illustrated. Note that the standard AtomFlo™ used by Surfx Technologies is the one shown in Figure 3b.

3. Plasma Etching of Photoresist

Silicon wafers coated with AZ5214-E photoresist were ion implanted with phosphorous at a dose of 1×10^{16} cm^{-2} at 30 keV. These films were characterized with infrared spectroscopy (IR), x-ray photoemission spectroscopy (XPS), and scanning electron microscopy (SEM). Shown in Figure 4 are the IR spectra for regular and ion-implanted photoresist films. The two films are of comparable thickness (~1.5 μm). Hydroxyl peaks are observed at around 3500 cm^{-1}, which is due to the OH stretch, and at 1380 and 1270 cm^{-1} due to OH stretch in phenols. The peaks at 3000, 2900, and 2850 cm^{-1} represent the CH_3 asymmetric stretch, CH_2 asymmetric stretch, and CH_2 symmetric stretch, respectively. The peak at 1500 cm^{-1} is either due to CH_3 deformation or CH_2 scissor vibration. The features at 1550 and 1500 cm^{-1} are due to C=C aromatic stretch and the peak at 2140 cm^{-1} represents the SiH stretch. From the IR data, no discernable differences are detected between the two films. A possible reason is that ion implantation forms a crust only on the surface of the film that looses its aromatic structure and becomes hard to remove, yet IR spectroscopy analyses the film as a bulk. To examine the surface of the films, XPS was performed. Figure 5 shows the XPS spectra for the surfaces of the regular and ion-implanted photoresist films. In both spectra, oxygen Auger, O 1s, and C 1s peaks were observed at binding energies of 997 and 976, 532, and 283.4 eV, respectively. In the ion-implanted sample a weak phosphorous 2p peak was observed at 137 eV.

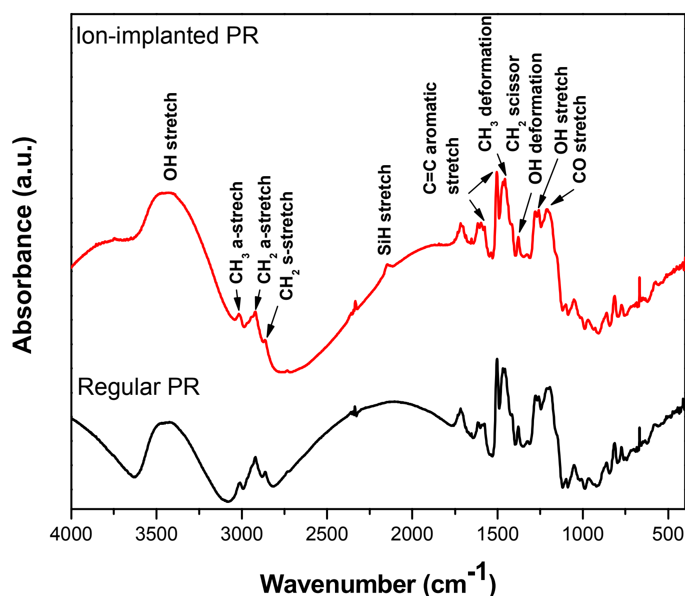
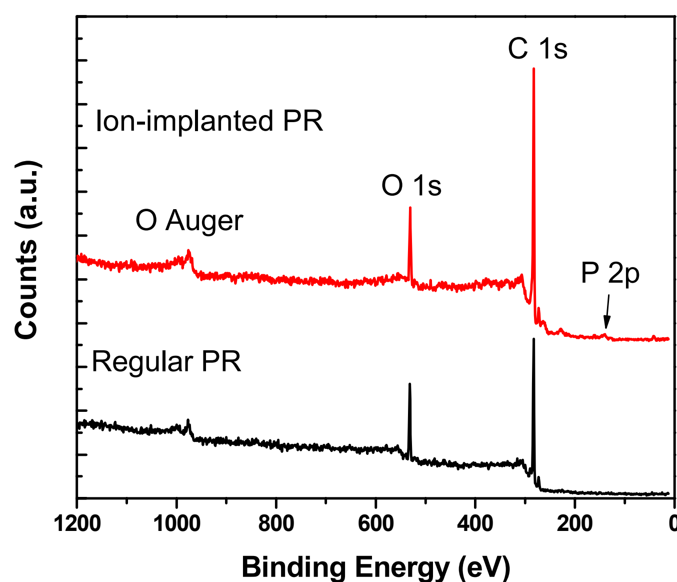


Figure 4. Infrared spectra of regular and ion-implanted photoresist.



The atomic compositions of the ion implanted photoresist are 86.5 % C, 13.3% O, and 0.2% P. Further analysis of the data revealed that when the photoresist is heavily implanted, the carbon composition increased while the oxygen composition decreased. The C:O ratio increased from 4.3 to 6.5, when the photoresist is ion-implanted. This is expected because when the photoresist is heavily implanted it forms a graphite-like structure with C-C bonds, while losing some of its aromatic structure.

In order to assess the differences between these four electrodes, they were all used to etch the positive photoresist (AZ5214-E). The conditions used in these experiments were: 745 Torr He, 15 Torr O_2, 50 W total power, 1000 rpm wafer spin rate, 2 mm electrode-to-substrate

spacing, and 5 minutes processing time. The process time was kept constant for all the experiments to ensure that the gas temperature remains the same, ~70°C, after 5 minutes. Before the first trial in each of the electrodes, the plasma was run at the above specified conditions for 5 minutes to warm up the system. The results for the etch rate with the different electrodes are shown in Figure 6. The letters A, B, C, and D on the x-axis correspond to the electrodes in Figure 3a, 3b, 3c, and 3d, respectively, where A is the one with the smallest hole diameter and D is the one with the biggest hole diameter.

It is clear that the electrode with the largest hole size etches photoresist at the highest rate, 0.34 μm/min, while the one with the smallest hole size has the lowest rate of 0.04 μm/min. This is almost an order of magnitude difference in the etch rate. Comparing source D with B, which is the standard sized one used at Surfx, the etch rate was improved by a factor of 2 by simply increasing the hold diameter by 0.020". The electrode with the largest hole is termed the new design and examined in detail for the attainable etch rate.

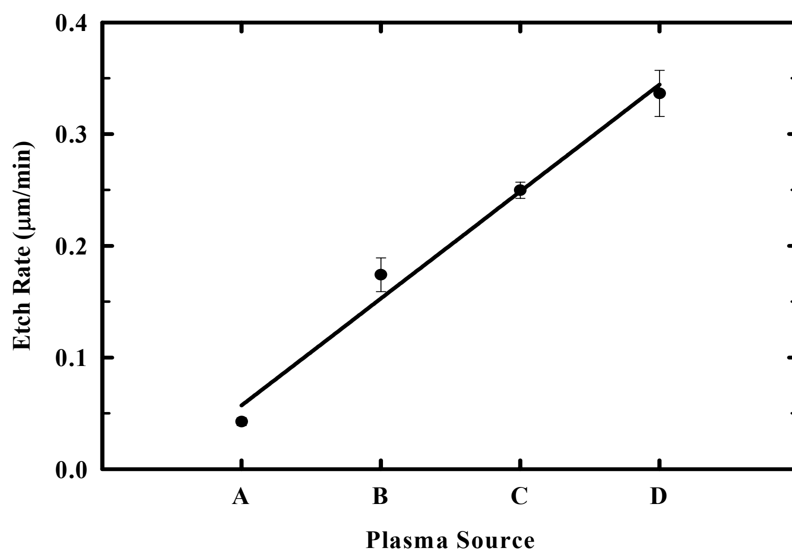


Figure 6. Etch rate for the different plasma electrodes.

To find the optimum conditions for etching photoresist, the effect of the oxygen partial pressure was first determined. Experiments were performed on the electrode with the new design and the standard one, respectively. The following conditions were common to all the experiments: 30 L/min He flow rate, 50 W total power, 1000 rpm wafer spin rate, 2 mm electrode-to-substrate spacing, and 2 minutes processing time. In the standard design, the etch rate increased to 0.22 μm/min as the O_2 partial pressure increased from 0 to approximately 5 Torr. Thereafter, the etch rate decreased gradually to 0.15 μm/min at 25 Torr. Similar experiments were performed on the new design and the etch rate reached a maximum of 0.32 μm/min at an oxygen partial pressure of ~ 10 Torr. Table 1 summarizes the effect of various operating conditions on the attainable maximum etch rate between the new design and the standard one.

Table 1. The effect of operating conditions on the maximum etch rate.

	Standard AtomFlo™ design	New design
The total gas flow rate	0.30 μm/min above 40 L/min	0.60 μm/min at 35 L/min
Oxygen partial pressure	0.22μm/min at 5 Torr	0.32μm/min at 10 Torr
The delivered power	0.45 μm/min at 80 W	0.76 μm/min at 70 W
The electrode to substrate distance	0.4 μm/min at 1 mm	0.6 μm/min at 1 mm

By optimizing all the process conditions, the standard design exhibited a maximum rate of 0.53 μm/min, while the new design yielded a maximum rate of 0.85 μm/min. This significant increase in the etch rate is essential to the commercialization of this system.

Scanning electron microscope (SEM) images were taken on the heavily implanted photoresist that have been exposed to an atmospheric pressure helium-oxygen plasma in both the standard AtomFlo™ and the new design. The operating conditions were 50 W (62 W/cm^3), 5 Torr O_2, 40 L/min total flow rate, 1 mm gap spacing, 1000 rpm, and 5 mins processing time in the standard AtomFlo™. In the new design, the oxygen partial pressure was increased to 10 Torr, while the other parameters were kept constant. Both plasma sources yielded small etch rates of about 180 Å/min. Shown in Figure 7 are SEM images of the sample before and after exposure to the plasma. It can be seen that after the film has been processed, there are small islands of material removed.

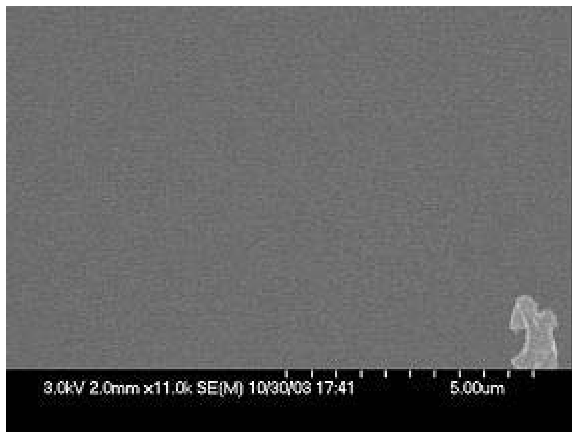


Figure 7a. Ion-implanted photoresist before processing.

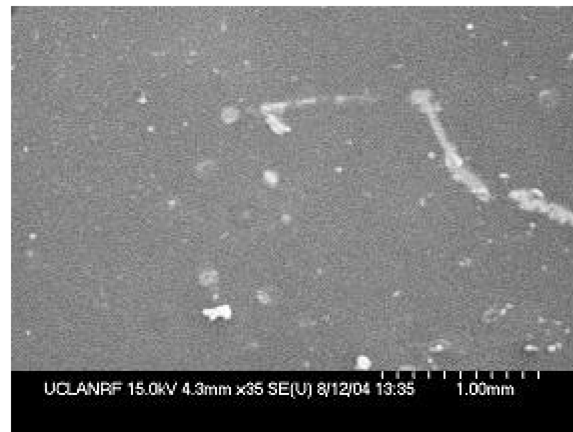


Figure 7b. Photoresist in 6a after 5mins exposure to a He/O_2 plasma.

<u>4. Plasma Enhanced Deposition of Silicon Nitride</u>

To extend the applicability of this atmospheric plasma source, the plasma-enhanced chemical vapor deposition (PECVD) of silicon nitride was studied at atmospheric pressure using a helium/nitrogen plasma with silane added to the downstream of the discharge. We observed a maximum deposition rate of 130±15 nm/min at 0.34 Torr silane, 18.0 Torr N_2, 450°C and an electrode-to-wafer spacing of 6.0 mm. The film properties were characterized by infrared spectroscopy and Rutherford backscattering spectroscopy. The hydrogen and

oxygen impurity concentrations in the films depend mainly on the substrate temperature, decreasing as the temperature is raised. Minimum H and O content of 13.0 and 3.6 atom% have been achieved at 500°C. Infrared spectra of the films indicate that most of the hydrogen bonds to nitrogen atoms. Shown in Figure 8 is the hydrogen content in the films as a function of the N_2 to SiH_4 partial pressure. A scanning electron microscope image of a Si_3N_4 film deposited at 10 Torr N_2, 750 Torr He, 0.34 Torr SiH_4, 4.4 W/cm^2 and 350 °C on a patterned GaAs wafer is presented in Figure 9. Note that good conformal deposition is achieved.

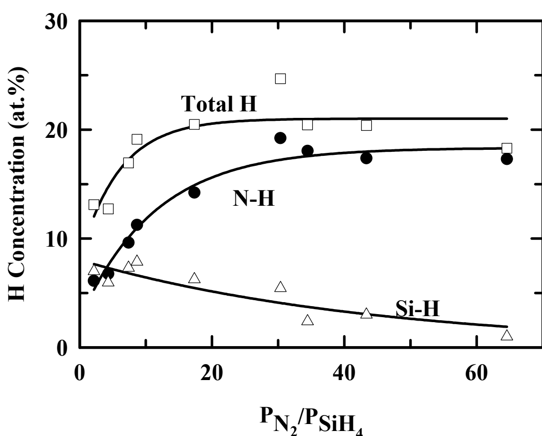


Figure 8. The hydrogen content in the films as a function of N_2 to SiH_4 partial pressures.

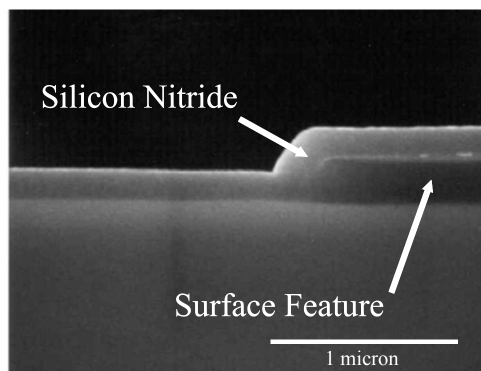


Figure 9. SEM image of a silicon nitride film on a patterned GaAs wafer.

Interactions between Surfx Technologies LLC and with UCLA

With this SBIR grant, two graduate students were trained in photoresist etching, characterization, and the plasma enhanced chemical vapor deposition. They carried out a systematic study to assess the effect of processing conditions on the photoresist etch rates and obtained experience in the modeling and fabrication of a plasma reactor and analysis of films using X-ray photoemission spectroscopy, Infrared spectroscopy, and Scanning electron microscopy.

Regular communications occurred between the PI and graduate students at UCLA and Surfx Technologies. Conference calls took place on a bi-weekly basis. During these discussions, the PI and graduate students at UCLA explained their research results and planed for further work. Monthly progress reports were sent to the sponsor. Dr. Steve Babayan from Surfx Technologies made visits to UCLA on several occasions to discuss research plans.

Sponsors at Surfx Technologies are consistently pleased with the monthly progress, and gave valuable feedback and suggestions during these meetings that shaped the direction of future studies. A couple of months into the project, the sponsors decided to modify the research focus to include both plasma enhanced deposition work and plasma assisted surface treatment. The Sponsor believed that it would be more beneficial to them to expand the applicability of this plasma source. The same plasma source and characterization techniques

were used for the etching experiments as the deposition ones, keeping the scope of the new project similar to that of the original one.

Summary

NSF SBIR program is a unique program that enables the collaborative research and development effort between universities and industrial sponsors. In this case, UCLA and Surfx Technologies LLC jointly developed an environmentally benign, atmosphere pressure plasma tool for photoresist etching and dielectric deposition. This joint collaboration effort is successfully through frequent communications with the sponsor and flexibility in adapting new changes and demands in research and development. It also provides an excellent opportunity for graduate students to learn about a commercial semiconductor manufacturing system and the state-of-the-art requirement in materials synthesis and processing development.