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Letters

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Letter

Fast, downstream removal of photoresist using reactive oxygen species from the effluent of an atmospheric pressure plasma Jet

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Abstract

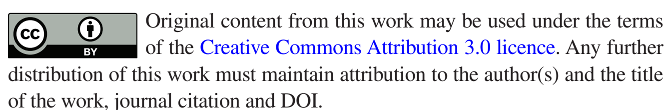
In the semiconductor industry the plasma removal of photoresist (PR) between processing steps (so-called plasma ashing) is a critical issue in enabling the creation of advanced wafer architectures associated with the next generation of devices. We investigated the feasibility of a novel atmospheric-pressure plasma jet (APPJ) to remove PR. Our device operates at atmospheric pressure, eliminating the need for low-pressure operation used in conventional plasma ashing. Also, our method uses the downstream effluent of the source, avoiding issues relating to ion bombardment, a known hinderance to atomic precision manufacturing. Two-photon absorption laser induced fluorescence (TALIF) measurements of the system has shown that the PR removal rate is directly correlated with the atomic oxygen flux to the surface. The maximum removal rates achieved were 10 μm min^{-1}, a factor of 100 improvement over typical low-pressure methods, while the quality of the etch, as assessed by attenuated total reflection fourier transform infrared spectroscopy, was found to be equal to low-pressure standards.

Keywords: photoresist, ashing, atmospheric, plasma jet, downstream

(Some figures may appear in colour only in the online journal)

In semiconductor manufacture photoresist acts as a mask to allow deposition and etching of the substrate in a controlled, localised manner. The photoresist (PR) consists of organic chain molecules that react in the presence of UV light to either harden (negative PR) or soften (positive PR), giving a pattern on the surface where soft PR is etched at a higher rate than hardened PR, leading to preferential etching of the substrate. The photoresist then must be removed to perform the next iteration of etching or deposition, which may happen multiple times for complicated architectures.

The standard option to remove the photoresist is to use a low-pressure oxygen plasma discharge in a process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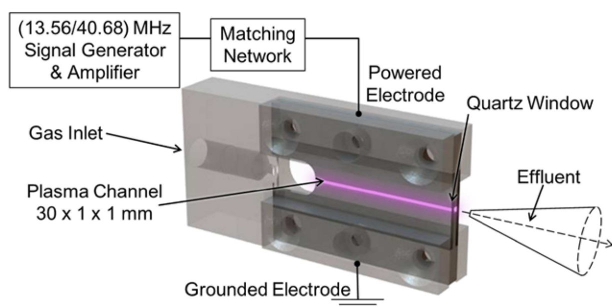

Figure 1. Diagram of atmospheric pressure plasma jet. Gas is fed into the device where it is driven into a plasma, then as it exits the plasma channel, the plasma recombines leaving the neutral radical rich effluent.

commonly known as plasma ashing, but this has limitations. Firstly the cost of operating vacuum equipment, but more importantly is the damage to the substrate surface from the plasma discharge. The sheath formed at the surface of the substrate can produce large electric fields, possibly damaging sensitive semiconductor components, however the largest issue is the ion bombardment of the surface as ions are accelerated through the sheath to the surface. This ion bombardment can cause sputtering and physical damage of the wafer, and as feature sizes get smaller, this ion bombardment has the distinct possibility of causing irremediable damage to the wafer architecture. The use of 'downstream' [1] plasma etching at low pressure, where the plasma is created separately and the radical species are directed on to the surface mitigates most of these issues, but removal rates can be compromised as a result. The etch rate of PR at low pressure downstream oxygen plasma is typically on the order of Å min^{-1} to tens of nm min^{-1} [2] compared to μm min^{-1} when the plasma is in contact.

The required use of vacuum systems can be overcome by using atmospheric pressure plasmas, and previous work has shown they are effective at removing photoresist [3–7] with high selectivity [8]. These devices show removal rates ranging from 100 nm min^{-1} to $<$1 μm min^{-1}. Unfortunately for some of these systems an active plasma is often still in contact with the wafer, resulting in possible ion bombardment and electric fields that deteriorate the surface topology. We propose as a solution to this issue, is to use the neutral effluent of an Atmospheric Pressure Plasma Jet (APPJ). The effluent is the region of recombined plasma that still contains the radical rich chemistry formed in the plasma core, but no charged species. By treating the surface with only the radical rich neutral effluent, no sheath structures associated with plasma-surface interaction are created, leaving a chemical only etchant at atmospheric pressure. In this paper, the viability of using the effluent of a plasma jet as a downstream method to strip PR at fast rates is shown with respect to controllable parameters: power input, frequency, flow rate, distance from the plasma channel exit and substrate heating.

The atmospheric pressure plasma jet used is shown in figure 1. The plasma channel consists of two parallel electrodes 1 mm apart and 1 mm in width sandwiched between two quartz glass windows to create a square cross-section of length of 30 mm [9, 10]. Helium with an admixture of 0.5% molecular oxygen is fed into the device and a plasma formed between the electrodes in the channel, creating various reactive chemical species. It has been shown that at 0.5% oxygen admixture, the most atomic oxygen can be produced [11] in the core plasma, and consequently was chosen as a fixed molecular admixture.

The electric field in the plasma channel is perpendicular to the gas flow. This means the plasma will recombine at the exit, rather than having an active plasma effluent which occurs when the electric field is parallel. Many previous atmospheric pressure plasma ashing systems use the substrate as an electrode [3, 4], or for jet like devices, have a parallel electric field and feature an active plasma effluent [5–8, 12, 13]. This active plasma effluent is undesirable, as a sheath can still possibly form at the substrate surface. At the outlet of the APPJ the plasma promptly recombines leaving a neutral effluent to transport the various chemical species from the jet to the treatment surface. The APPJ is mounted vertically with the exit facing downwards at the surface on a precision motorised stage to control position and distance from the surface. The plasma jet is driven using radio frequency (RF) voltages at 13.56 MHz or 40.68 MHz.

The S1813 positive novolac based photoresist is spun on a silicon wafer at a 1.5 μm thickness, and baked as recommended by the manufacturer. By using hard unpatterned resist, the etch rate can be assessed where on a processed wafer the remaining hardened PR must be removed along with residual soft PR. Positive resists are often used for plasma ashing investigations [3–6, 13]. Etch rate is determined by measuring the thickness of the resist using a surface profile analyser, and measuring the time taken to etch through to the visibly identifiable silicon wafer underneath.

Preliminary tests showed a significant decrease in etch rate with increased outlet to surface distance, this resulted in the jet exit being brought as close as possible to the treatment surface to maximise etch rate. At distances approaching the interelectrode distance ($<$2.5 mm) the surface acts as a ground to the powered electrode forming a discharge on the surface. To avoid this effect, but maximise etch rate, the separation was held at 3 mm.

With the initial parameters of 1 slm He with 0.5% oxygen admixture, 13.56 MHz driving frequency and a generator input power of 20 W, the etch rate achievable was 75 nm min^{-1}. However by increasing the driving frequency to 40.68 MHz, three times the fundamental, the etch rate was increased to 125 nm min^{-1}. As shown in figure 2, 40.68 MHz out competes 13.56 MHz with an approximate doubling in etch rate for the same generator input power, gas composition and flow rate. These etch rates are already comparable to those at low pressure.

Figure 3 shows a linear increase in etch rate with input RF generator power at 3 slm He flow and 0.5% O_2, with double the input power being roughly equivalent to double the etch rate. The APPJ device does not allow for a continuous increase of input power, eventually transitioning into a damaging arcing mode at high voltage. This arcing mode gives a physical upper limit to input power and further control over etch rate must be found through other mechanisms.

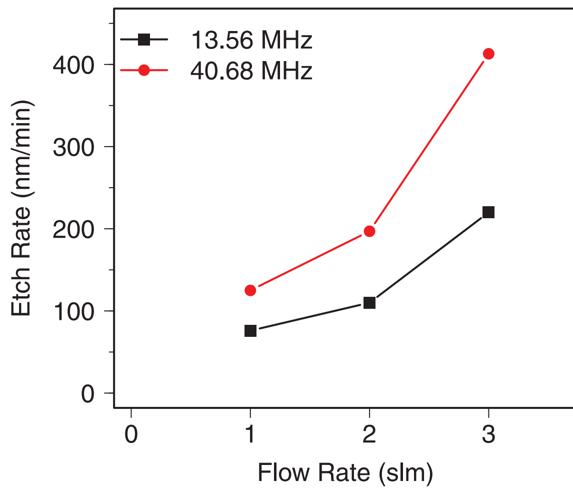

Figure 2. 40.68 MHz outperforms 13.56 MHz in etch rate for the same parameters of 0.5% O_2 in He, 20 W generator input power.

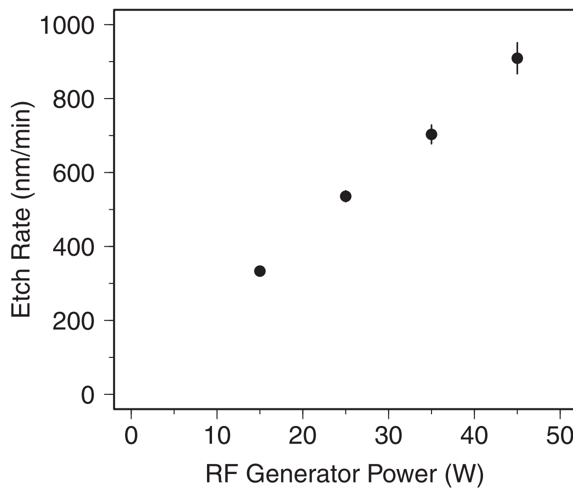

Figure 3. Measured etch rate at varying RF input powers, at 3 slm He with 0.5% O_2 admixture.

A simple method to increase the flux of reactive species to the substrate is by increasing the flow rate. In figure 4, the etch rate can be increased roughly linearly up to around 2 μm min^{-1} for greatest input power of 45 W, driving frequency of 40.68 MHz and 0.5% oxygen admixture. Once again there is a physical restriction on the maximum gas flow possible that arises from turbulences. Approaching 10 slm and above, there is an apparent deformation of the etch area.

Typically a fast rate etch area consists of a circle roughly 10 mm in diameter, with a partially etched area twice or three times this diameter again visible through the Newton's rings phenomena. At gas flows higher than 10 slm the etch area becomes highly distorted, and that these gas speeds $\sim$170 ms^{-1}, the Reynolds number is no longer that of a laminar regime. This semi-turbulent flow through the plasma channel, along with the possible flow perturbations induced by the plasma, indicates the fluid dynamics limits the flow rate, imposing another physical constraint for the current channel cross section. Turbulent flows are clearly undesirable for producing consistent ashing.

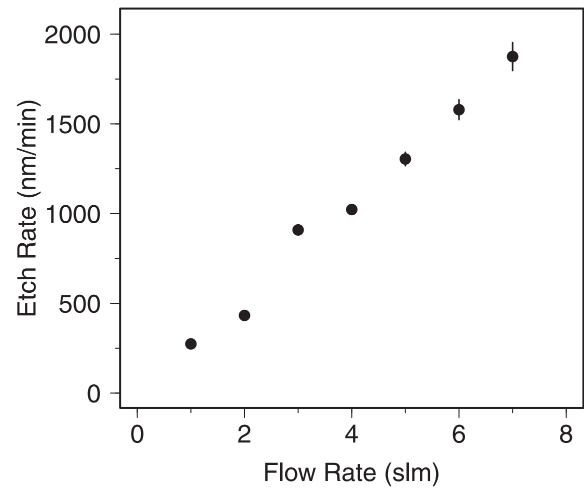

Figure 4. Etch rate has an positive correlation with flow rate. Input was held at 45 W and the gas mixture at 0.5% O_2 in helium.

At low pressure, it is a common technique to heat the substrate to temperatures up to 200 °C to increase reactivity and ashing rates [1, 14]. With the silicon wafer on a hotplate, etch rates were assessed at wafer temperatures of 60 °C, 100 °C and 140 °C, as well as with the hotplate off. There was no great enhancement with 60 °C, however the etch rate had noticeably begun to increase at 100 °C by tens of percent. The softbake temperature for both photoresists used are around 110–115 °C, and past these temperatures at 140 °C there is significant improvement in etch rate. For 140 °C, a 5 fold increase in the etch rate from 2 μm min^{-1} to 10 μm min^{-1} was observed.

The efficacy of etch is also of importance, especially with respect to residual PR [15] left on the surface which will interfere with subsequent wafer processing. attenuated total reflectance fourier transform infrared spectroscopy (ATR-FTIR) is used to assess the surface chemistry of the atmospheric ashing compared to a wafer which has undergone plasma ashing using a traditional oxygen Inductively Coupled Plasma (ICP) system. ATR-FTIR is capable of detecting single surface monolayers and has previously been used to monitor chemical quality of wafer surfaces [16]. The spectra in figure 5 shows the APPJ producing a comparable fingerprint as the ICP treatment. When comparing these spectra to the PR, the structures that are indicative of organic molecules, in the region 500–1800 cm^{-1}, are no longer visible with the etched spectra resembling the clean Si wafer. Hence we can conclude that the APPJ can remove photoresist from unpatterned Si wafers to at least an equal standard to that of traditional ICP treatments.

The rate of chemical etching of a substrate s by species x is given by (1) where Γ_x is the particle flux of reacting species, T_s is the substrate temperature [17].

$$R_{x(s)} \propto \Gamma_x \mathrm{e}^{-1/T_s} \tag{1}$$

The Γ term is a convolution of the reactive species density n_x and the rate they impinge on the surface v_x [18]. By increasing the reactive species density, the flow rate, or both, etching will be undertaken at a faster rate.

Investigations [19] and modelling [18] at low pressure have indicated a strong relationship between atomic oxygen

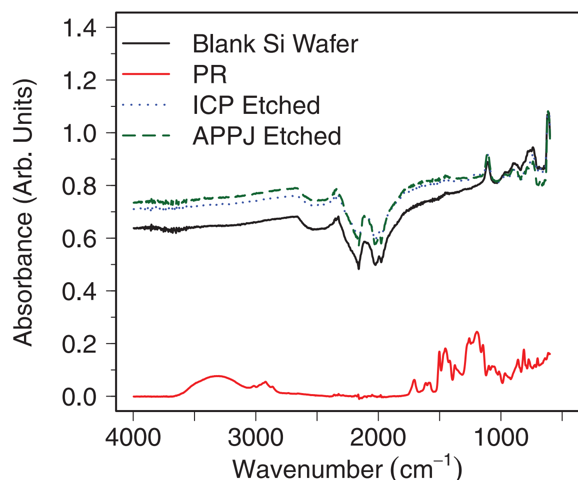

Figure 5. ATR-FTIR spectra for Si wafers before treatment, with PR, and after treatment. The ICP treated (dotted) and APPJ treated (dashed) result in the same surface chemistry.

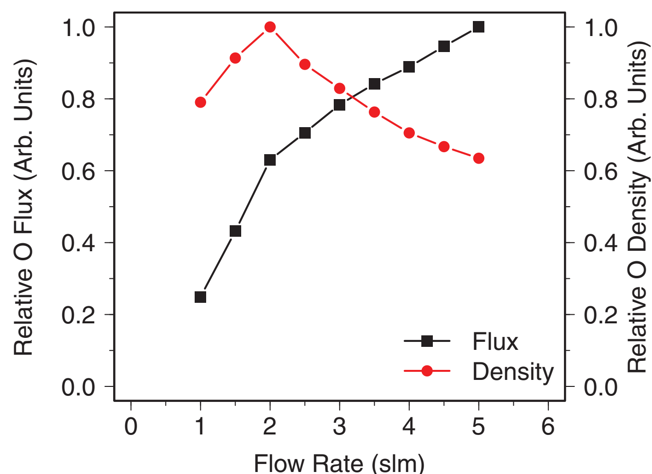

Figure 6. TALIF measurements of relative atomic oxygen density at 13.56 MHz less than 0.5 mm above the etching surface. The decreased residence time does not lessen the overall flux.

and etch rate of PR, where the atomic oxygen leads to random chain scission into eventually volatile species [16]. This behaviour has also been documented at atmospheric pressure [5, 12].

The APPJ used has been well characterised in terms of its chemistry [20–22], including two-photon absorption laser induced fluorescence (TALIF) measurements of atomic oxygen [11, 23, 24]. These measurements of atomic oxygen in both the core and effluent reveal a correlation between atomic oxygen production and etch rate. Measurements of atomic oxygen at 40.68 MHz driving frequency have not been undertaken, however modelling of dual frequencies 13.56 MHz and 40.68 MHz [25] show a better coupling of energy into the electrons for the same voltage at 40.68 MHz compared to 13.56 MHz through ohmic heating. Though the plasmas are compared for the same power, not the same voltage, for higher frequencies more power can be coupled into the plasma before arcing and hence produce more reactive species, possibly explaining the perceived advantage of using 40.68 MHz.

Measurements of atomic oxygen show a linear increase with input power and atomic oxygen density [11, 23]. This is exhibited in the etch rates in figure 3, where etch rates improve with higher input power, once again reflecting the higher O density. Equation 1 shows that higher flow rates will be linked to higher etch rates if n_x is not reduced dramatically as v_x increases. Figure 4 shows a positive increase in etch rate with flow rate, and so the flux must be increasing to elevate etch rates.

Though increasing the flux of reactive species to the surface will increase chemical etch rates, by increasing the gas flow through the device, the residence time of the plasma is also decreased, possibly leading to a trade off between O density and flux. Previous TALIF measurements [11] of the core plasma show a time required for the atomic oxygen density to saturate is 0.6 ms at 1 slm He and 0.5% O_2 . At flows of 3 slm and above the flow speed is great enough that this criteria is no longer met in the core. TALIF measurements of atomic oxygen density made at <0.5 mm above the photoresist surface in figure 6 highlights the effect the reduction in residence time has on atomic oxygen density between 1–5 slm at 13.56 MHz at low input powers.

TALIF [23, 24], optical emission spectroscopy [12] (OES), and modelling [21] of the effluent region show that O density drops off rapidly with increased distance from the exit, which was also observed as a reduction in etch rate during preliminary testing. However this rapid decay in species density is offset as the species are reaching further into the open air due to faster flow rates. This is seen as an apparent increase in atomic oxygen density to begin with in figure 6. However, the decreased residence time begins to outcompete the gains made by increasing the flow rate, hence a peak density seen at around 2 slm. The total effect is that the resultant O flux increases despite any reduction in n_x.

Furthermore, TALIF and actinometry can shed light on the observed two orders of magnitude increase in etch rate to that of low pressure systems. The atomic oxygen density for a low pressure oxygen plasma [19] is on the order of 10^{18} m^{-3}, whereas though molecular oxygen is only a small fraction of the neutral gas in the atmospheric case, the atomic oxygen density [11, 26] is of the order 10^{21} m^{-3}. The APPJ has an atomic oxygen density roughly three orders of magnitude higher than the low pressure case.

Power measurements of the APPJ indicate that plasma power is on the order of ∼5 W, whereas the power reported is from the generator with significant losses into a Pi-matching network. This results in a power per treated area similar to that of a traditional ICP, however the etch rate is 2 orders of magnitude faster than that of a traditional ICP.

Moreover, the APPJ uses less power and less gas consumed for equivalent area than other atmospheric photoresist removal devices [5–7]. The tailoring of atomic oxygen gives the unique combination of efficient high etch rates, without undesired plasma contact with the substrate that can cause sheath induced damage. Although this study provides promising results, further investigations are needed before our method can be adopted by the semiconductor industry. In particular, the efficacy of completely removing PR from substrates with industry relevant substrate architectures needs to be assessed,

as well as confirm if damage or roughening of the substrate occurs through other mechanisms besides ion bombardment.

In this feasibility study, we demonstrate that the neutral effluent of the atmospheric pressure plasma jet can remove photoresist. The etch rate of photoresist ashing is heavily dependant on atomic oxygen flux to the treatment surface, as well as the temperature of the substrate. We achieved a maximum etch rate of 10 μm min^{-1} when operating at 40.68 MHz with a gas flow of helium with 0.5% oxygen admixture at 7 slm, while producing a quality of removal expected in industry. These high etch rates are twinned with the unique advantages of not using vacuum equipment and no damaging effects that are associated with sheath formation at the substrate surface. The etch rate achieved requires less input power and less gas compared to other atmospheric pressure plasma treatments for the same treatment area of 300 mm^2 and provides a local ashing rate two orders of magnitude faster than low pressure alternatives.

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