

AN EFFECTIVE METHOD FOR PHOTORESIST REMOVAL USING MICROWAVE PLASMA ASHING

PROBLEM

As semiconductor device size shrinks deeper into the nanometer scale, surface topography becomes increasingly complex. This complexity creates significant challenges in device fabrication, not the least of which is the effective removal of photoresist residue (ashing) following an etch or implant step. Extreme topographies can cause problems with the uniform distribution of reactive radicals in occluded areas on a substrate surface leading to poor penetration in deep trenches or structures exhibiting re-entrant angles. The material and chemical characteristics of resist residues may vary across a substrate resulting in poor resist removal rate uniformity. The presence of such factors means that the equipment characteristics and operating parameter values for an ashing process must be application specific, with

optimized reactive gas transport to the substrate surface and customized settings for independent process variables such as the power level, wafer and chamber temperatures, total gas flow, and process pressure. With up to two dozen lithography cycles in modern device fabrication, optimization of each ashing step in a production line is critically important for device yields.

BACKGROUND

Photoresist ashing using a chemically reactive species comprised of radicals or ions produced by a microwave frequency or microwave plasma discharge is referred to as "plasma ashing". In the plasma ashing process, reactive radicals produced in the plasma are transported to the substrate surface where they react with any residual

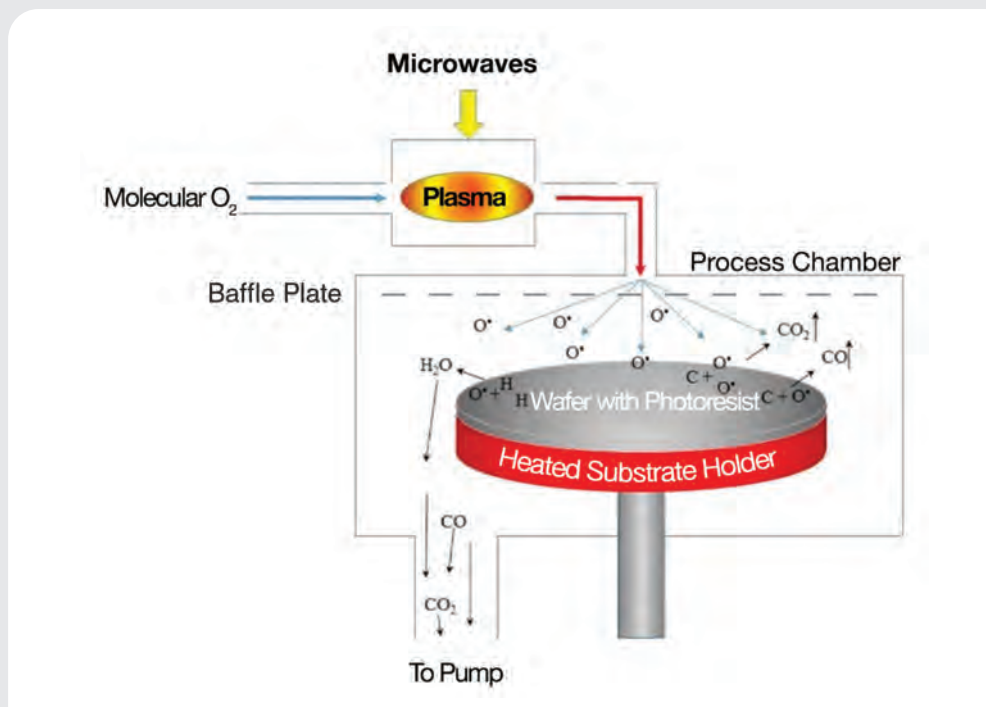
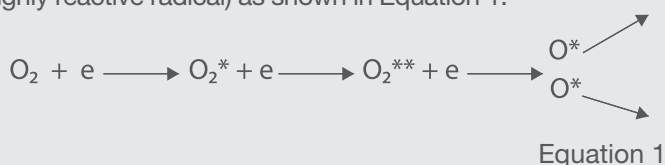


Figure 1 - Schematic of a typical photoresist O₂ plasma ashing tool.

photoresist, producing volatile products that can be pumped away by the vacuum system. The most effective plasma ashing processes are designed to maximize the concentration of neutral reactive radicals transported to a substrate surface while minimizing the production of ionic species. Reactive radicals remove photoresist without damaging the substrate which happens when ions are present.

Diatomic nitrogen and oxygen molecules, N_2 and O_2 , break down into monatomic nitrogen and oxygen radicals or ions in a plasma. Similarly, hydrazine (N_2H_2), generates monatomic nitrogen and hydrogen radicals. In a microwave plasma process using molecular oxygen (O_2), the molecule is split into two monatomic O^* radicals (here $*$ is used to denote a highly reactive radical) as shown in Equation 1:



In a typical O_2 plasma ashing process, O^* radicals are generated in a 2.45 GHz microwave plasma source and transported to the substrate where they react with photoresist to produce volatile products such as CO , CO_2 , H_2O , OH , and $CxHy$ fragments. Microwave excitation is preferred over RF excitation since it produces higher concentrations of neutral reactive radicals and lower concentrations of ionic species. In a downstream plasma asher, as shown in Figure 1, the reactive gas flows into the process chamber through a gas distribution plate or baffle and is maintained at an electrical potential (bias) suitable to extract residual ions from the gas stream, reducing damage to the substrate from ion impact effects. After the application-specific equipment characteristics and process temperature have been defined, other process variables like microwave power, substrate temperature, total gas flow and pressure are optimized. All of these variables affect the ashing rate and uniformity of photoresist removal across the substrate surface.

Three factors determine the efficiency of a plasma ashing process: the chemical reaction rate of the ashing agent with the resist (ashing rate); the generation rate of the ashing agent; and loss of the ashing agent prior to reaction with the photoresist.

- The ashing rate of the photoresist can be described quantitatively using an Arrhenius Equation as shown in Equation 2:

$$AR = c \langle R^* \rangle^{-E_a/k_B T} \quad \text{Equation 2}$$

where

AR = Ashing rate

c = Reaction coefficient (Tool dependent)

$\langle R^* \rangle$ = Concentration of ashing agent, R^* , at the photoresist surface, where

$\langle R^* \rangle = f$ (generation, losses, transport)

E_a = Activation energy of the ashing process (most chemistry dependent)

k_B = Boltzman constant

T = Photoresist temperature (K)

- The efficiency of generation of the reactive ashing agent depends on:
 - The degree of plasma dissociation of the molecular precursor gas
 - f (microwave power, total gas pressure and gas phase additives)
- The degree of loss of reactive ashing agent between generation and reaction with photoresist depends on:
 - Gas phase recombination
 - Surface recombination
 - f (gas pressure, gas and surface temperatures and "wetted" surface characteristics where "wetted" surfaces are those surfaces in direct contact with the gas containing the ashing agent)

SOLUTION

The MKS High Power Microwave Plasma System as shown in Figure 2, equipped with the MKS High Power Microwave Plasma Source, has demonstrated improvements in plasma uniformity and thermal management compared with other microwave plasma sources. These improvements increase the life expectancy of the plasma source, allow higher power operation, and produce a 20% decrease in peak temperature within the plasma source under multiple

power conditions. Lower peak temperatures are especially advantageous since they allow the plasma source to achieve the highest dissociation and lowest recombination rates with molecular precursors such as O_2 , N_2 , Forming Gas (N_2H_2 , 3-5% H_2/N_2), and CF_4 .

The MKS High Power Microwave Plasma System delivers high concentrations of reactive radicals at a low electron temperature, making it an ideal reactive radical source for many applications ranging from front end processes such as radical-assisted deposition using O_2 or N_2 and photoresist ashing for surface conditioning in back end processing. Plasma ashing tools that incorporate the MKS High Power Microwave Plasma System in proprietary downstream designs can achieve photoresist removal rates with the lowest substrate damage and contamination levels in the industry.

The MKS High Power Microwave Plasma System consists of a 6kW microwave generator with isolator, the MKS High Power Microwave Plasma Source and an auto-tuning system that integrates the MKS Precision Power Detector with a SmartMatch® advanced microwave matching unit. It ignites a variety of process gases in seconds and under a wide range of process conditions ensuring maximum throughput in the most demanding applications. Its advanced closed loop power control exhibits <1% variation in output accuracy providing wafer-to-wafer repeatability in a fully optimized ashing process and other applications. The System includes enhancements to the resonant cavity and thermal management system resulting in longer uptime by reducing non-uniform wear in the plasma tube. Enhanced power and control electronics and optimized monitoring and self-diagnostics give the System the highest level of operational reliability. The MKS High Power Microwave Plasma System is available with either quartz or sapphire plasma tubes to suit your specific application and chemistry requirement.



Figure 2 - MKS High Power Microwave Plasma Source (applicator)

The MKS High Power Plasma Source operates at 20% lower peak temperatures than other plasma sources. Figure 3(a) shows a comparison of the peak temperatures observed in

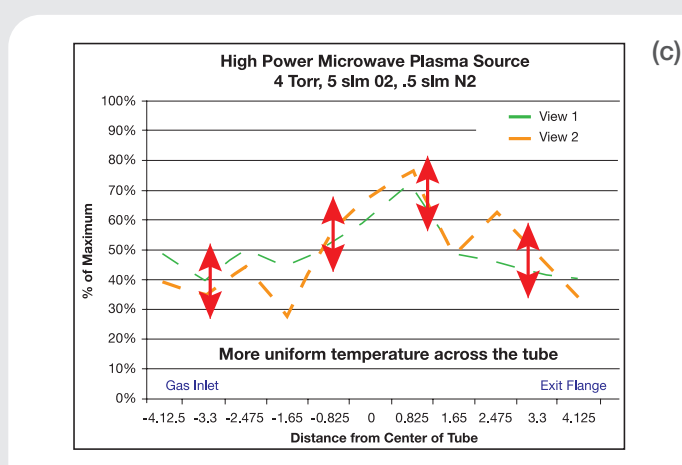
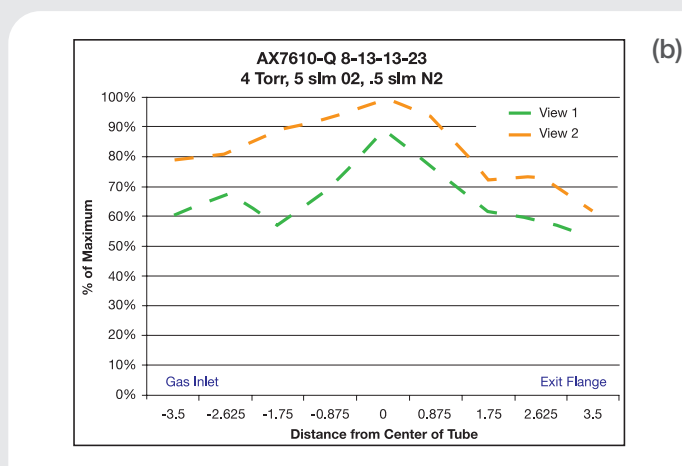
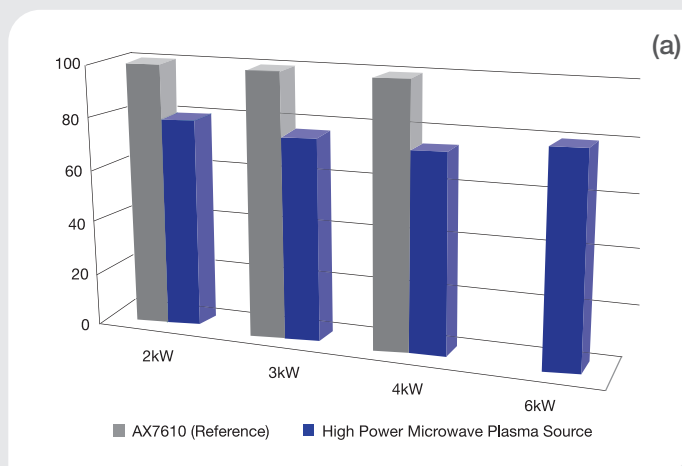
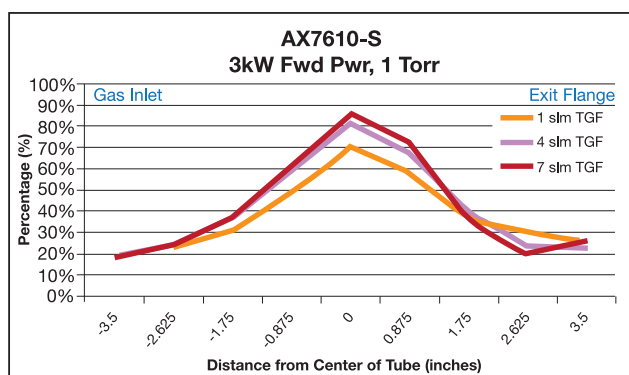


Figure 3 - Operational characteristics of the MKS High Power Plasma Source (a), (b), and (c).

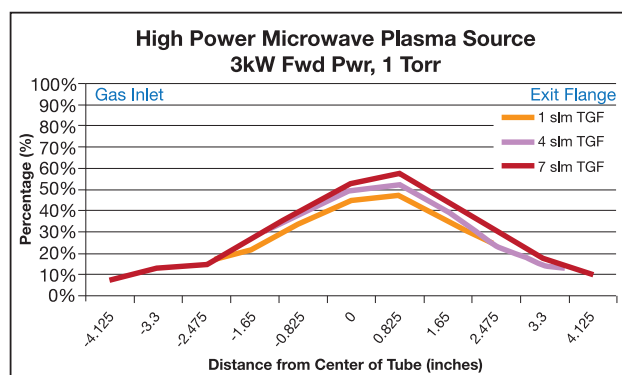
the plasma source at different power levels with those observed in a reference plasma source under O₂ plasma ashing conditions. The temperatures were determined at a process pressure of 4 Torr and a total gas flow of 5500 sccm (1:10 N₂:O₂). Similar peak temperature results are observed when forming gas is used as the plasma gas. As noted, this 20% reduction in peak temperatures vs. other plasma sources yields longer life expectancy and reduced maintenance requirements for the High Power Microwave Plasma Source. Additionally, it expands the process window for the ashing process since higher powers can be used without damaging the plasma source.

The improved thermal management design in the High Power Microwave Plasma Source creates a more uniform plasma distribution within the source as shown by the comparison of temperature profiles from the gas inlet to exit (shown for

O₂ plasma ashing) in Figures 3(b) and (c). Similar results are observed with forming gas. This reduction in peak and profile temperatures minimizes the effects of thermals and allows increased total gas flow (TGF) through the source. A comparison of how flow affects the temperatures in the applicator of the High Power Microwave Plasma Source and that of a reference plasma source is shown in Figure 4. As well, improved thermal management as demonstrated by the comparison of peak temperatures at different pressures shown in Figure 5 allows the High Power Microwave Plasma Source to operate at higher pressures before peak temperatures become damaging to the plasma source. Table 1 shows a comparison of the operational characteristics possible for ashing processes using O₂ and forming gas with the High Power Microwave Plasma Source vs. a reference plasma source.

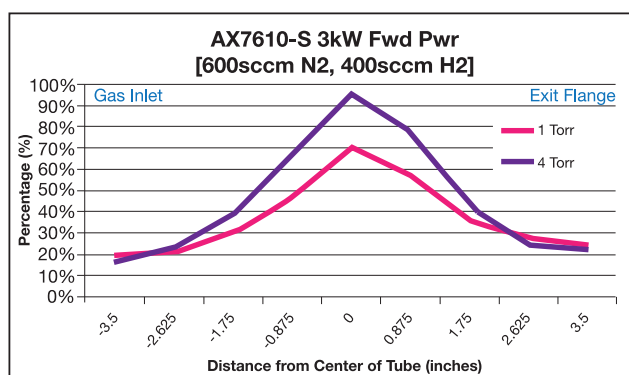


(a)

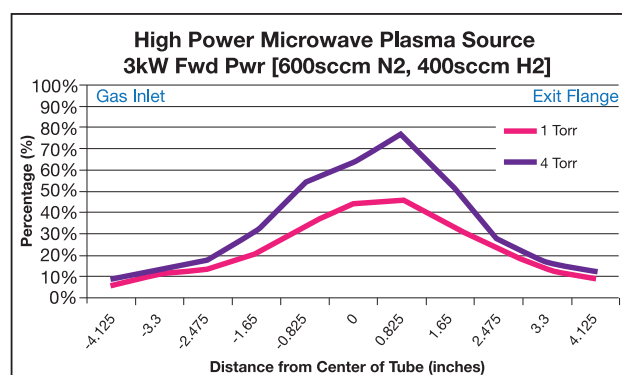


(b)

Figure 4 - A comparison of the impact of changing total gas flow (TGF) on the temperature profile (plasma profile) across the plasma source in a reference plasma source (a) and in the High Power Microwave Plasma Source (b).



(a)



(b)

Figure 5 - A comparison of the effect of pressure on peak temperature (plasma profile) in a reference plasma source (a) as compared with the High Power Microwave Plasma Source (b).

Specifications	O* Process		Forming Gas (up to 40% H ₂)	
	High Power	Reference	High Power	Reference
Operating Frequency (MHz)	2450-2470	2450-2470	2450-2470	2450-2470
Maximum Rated Power (kW)*	≤6	≤3	≤5	—
Ignition Space	In process gas	In process gas	—	—
Gas Compatibility*	Standard Ashing: O ₂ :N ₂ (ratio 90-10)	Not specified	Enhanced Ashing: Compatible to N ₂ :H ₂ with 40% H ₂	Will fail
Total Gas Flow (SLM)	1-10	1-5	1-7	N/A
Operating Pressure* (Torr)	1-8	2-8	1-4	N/A
Plasma Tube Material	Quartz	Quartz, Sapphire	Quartz, Sapphire (planned)	

* Lifetime of applicator dependent on process conditions

Table 1 - O₂ and forming gas ashing process comparison for the High Power Microwave Plasma Source and a reference plasma source.

Process Development for Plasma Ashing

In this Application Note, we will not consider process chamber and in-chamber gas delivery system design since these are fixed within a given ashing tool. However, it is important to note that process chamber design strongly influences the success of plasma ashing. Surface recombination that deactivates the ashing agent in a reactive gas transport system, uniformity of gas distribution and temperature control and uniformity at the substrate surface all impact the success of ashing processes. These factors are directly controlled by hardware characteristics such as chamber component surface treatments, mechanical design of baffle plate assemblies, and temperature control uniformity in the substrate holder. This Application Note deals only with the optimization of the independent process variables, assuming process chamber gas flow and temperature control have been optimized.

The independent variables in the ashing process include gas and substrate temperature, process pressure and total gas flow and gas composition. The process settings for these variables that produce an optimized ashing process are highly application-specific since the chemical and physical interactions between the ashing agent, the photoresist, and the substrate surface are strongly influenced by prior process history and by the unique surface characteristics of the device (i.e., topographical features such as trench

aspect ratios, the presence of re-entrant geometries, etc.). Consequently, every photoresist ashing step in a process sequence requires a unique process development protocol to determine the best combination of temperature, pressure, total gas flows, gas mixture composition, etc. for resist removal.

We will use O₂ plasma ashing to demonstrate process trends since it is the dominant plasma ashing process. Consider the terms in the ashing rate equation adapted for the O₂ ashing process as shown in Equation 3:

$$AR = c \langle O^* \rangle^{-E_a/k_B T} \quad \text{Equation 3}$$

We will not consider c , the reaction coefficient, since it is mainly determined by the hardware configuration. O^* , the concentration of the ashing agent O^* at the photoresist surface, is determined by the degree of conversion of molecular oxygen to O^* in the microwave plasma tube minus the loss of O^* due to gas phase and surface recombination of O^* between generation in the plasma tube and reaction on the substrate. The degree of conversion of O₂ to O^* in the plasma is determined by the microwave power and the gas pressure, along with the impact of additive gases such as nitrogen and hydrogen. Figure 6(a) shows the relationship between input microwave power, pressure and the conversion efficiency in a microwave plasma. Increasing the microwave power to the plasma increases the concentration of O^* radicals, with the trend being more pronounced at lower pressures.

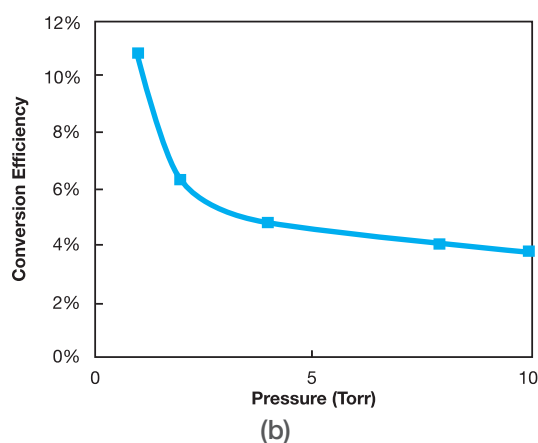
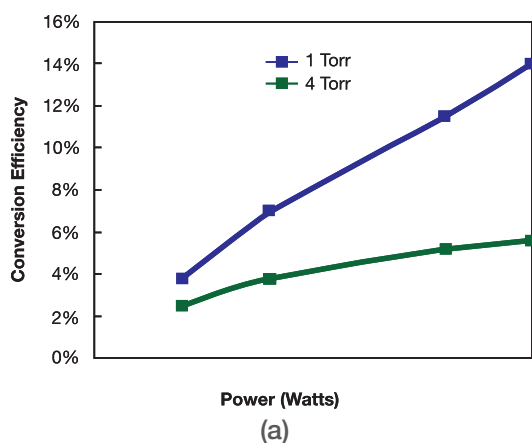
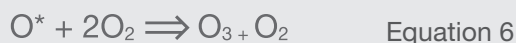
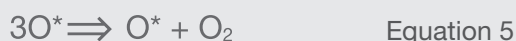


Figure 6 - The relationship between input microwave power, pressure and the efficiency of conversion of molecular oxygen to O^* monatomic radicals in a microwave plasma (a); The relationship between plasma and the conversion of molecular oxygen to O^* monatomic radicals in a microwave plasma (b).

The effect of pressure on the conversion of O_2 is shown more clearly in Figure 6(b) with conversion frequency dropping significantly as pressure increases. The presence of additive gases can also influence the concentration of O^* in and downstream of the plasma. Figure 7 shows the impact of the addition of nitrogen and hydrogen on the generation of O^* in a microwave plasma.

The trends apparent in Figure 6(a) and (b) are due to two phenomena within the plasma. First, when microwave power increases, the available free electrons gain additional energy and create more free electrons by ancillary processes. This increases the production of O^* according to Equation 1. Secondly, any gains in conversion efficiency due to increased power input are reduced as the pressure rises. This is because at higher pressures, collisional processes such as those illustrated in Equations 4, 5, and 6, are statistically more probable and result in a reduced O^* concentration.



The conversion of $O_2 \Rightarrow O^*$ is an inefficient process with approximately 10% initially converted.

Gas additives can:

- Increase generation efficiency
- Decrease surface recombination
- Decrease photoresist action activation energy

N_2 in the O_2+N_2 plasma is used to increase the generation of atomic oxygen. The addition of N_2 beyond the optimum value decreases atomic oxygen concentration due to the dilution of oxygen.

H_2 in the O_2+H_2 plasma increases the atomic oxygen percentage by lowering the activation energy required to generate atomic oxygen.

The addition of H_2 beyond the optimum value decreases atomic oxygen concentration due to the dilution of oxygen and new recombination reactions, forming water vapor over atomic oxygen.

The underlying causes for the trends due to additives, as shown in Figure 7, are poorly understood and undoubtedly complex. It may be that chemical stabilization of O^* occurs in the presence of small quantities of N^* and/or H^* or that N^* and H^* function to inhibit surface recombination of O^* on the wetted surfaces between the plasma chamber and the substrate. A detailed discussion of the source of the trends shown in Figure 7 is beyond the scope of this paper.

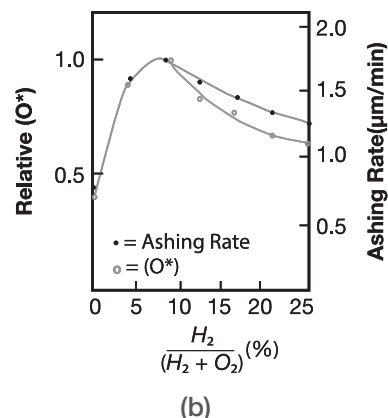
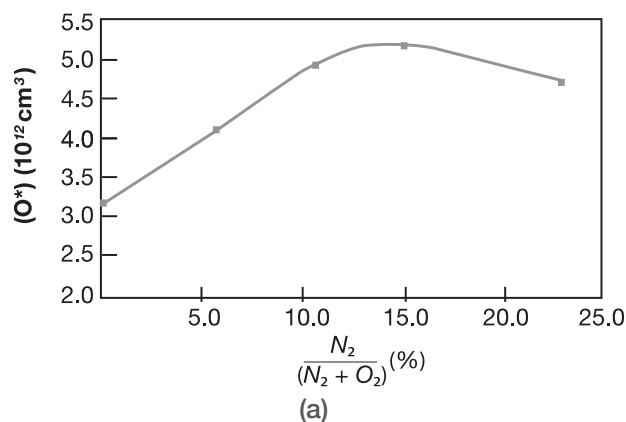


Figure 7 - The relationship between input microwave power, pressure and the efficiency of conversion of molecular oxygen to O^* monatomic radicals in a microwave plasma (a); The relationship between plasma and the conversion of molecular oxygen to O^* monatomic radicals in a microwave plasma (b).

The exponential factor in Equation 3, $\frac{-E_a}{k_B T}$, includes the constants E_a and k_B and the independent process variable temperature (actually substrate temperature). E_a is the chemical activation energy for the photoresist oxidation reaction which is constant for a given chemical formulation of the resist and a given ashing agent such as O^* . k_B is the Boltzmann constant that relates the kinetic energy of a particle with its temperature.

The variation of ashing rate with substrate temperature as shown in Figure 8 demonstrates a first order dependence between temperature and ashing rate.

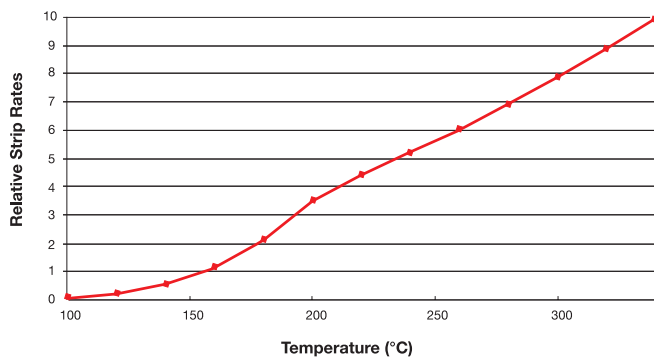


Figure 8 - The variation of photoresist ashing rate with substrate temperature.

Before beginning process development for an O_2 plasma ashing process step, the process goals must be defined. While these are unique to the device and process sequence, there are common process characteristics that usually require optimization:

- Ash rate:
 - Ash rate is normally maximized
- Ash rate non-uniformity, across wafer and wafer-to-wafer:
 - Non-uniformity of photoresist removal is minimized
- Throughput:
 - The step time is minimized to maximize throughput
- Cleanliness:
 - Photoresist removal must be complete and contamination due to the ashing process minimized
- Substrate damage:
 - Substrate damage must be minimal or preferably non-existent

Once the desired process results are defined, it is necessary to identify the different process and substrate factors that influence these results. These include:

- Substrate size:
 - Impacts ash rate uniformity
 - Determines the size of the process chamber, pressure, and ancillary chamber equipment such as substrate holders, gas baffles, etc.

- Physical properties of the photoresist like thickness, density and surface area:
 - Influences the ashing time which impacts throughput
 - Impacts process temperature
- Chemical properties of the photoresist like chemical composition or carbonization:
 - Influences ashing time (throughput)
 - Determines microwave power O* requirements
- Post ash residues:
 - Influences throughput (over-ash % (total ashing time))
- Physical issues with the substrate like contamination, substrate loss/growth or dopant loss:
 - Influences yield losses due to substrate damage

Once the unique goals and influencing factors are identified, the process engineer can use this knowledge to create a process recipe for the O₂ ashing process step. Ashing process recipes are defined in terms of the controllable process variables that include settings such as:

- Process step time
- Over-ash % (time)
- Substrate temperature
- Process pressure
- Total gas flow
- Plasma power

O₂ ashing process recipes are typically categorized according to photoresist chemical type and mix.

Experimental Methodology

This section describes a representative approach to developing a baseline O₂ ashing process. The approach employs bare silicon wafers coated with photoresist having the same thickness, chemical formulation and density as is expected for the process step.

Use an available algorithm for Design of Experiments (DOE) to create an experimental test matrix based on input microwave power, process pressure and total gas flow, as an example. Gas composition is fixed in this example but it can be a variable. The test values for the factors

should be selected using certain rules of thumb common for ashing process development. For microwave power, tests are conducted with a low factor value for the power input of approximately 1000 watts and a high value set at the maximum capability of the generator in use. TGF values depend on the substrate size. For 150 mm substrates, the center point for a design should be around 2000 slm; for 200 mm substrates around 4000 slm; and for 300 mm substrates the center point should be around 7000 slm. The values used for pressure should be uniformly low to ensure the best etch rates.

Always confirm that pressure control is independent of the gas flow (i.e., the vacuum system must have sufficient pumping capacity to guarantee that the low factor value for pressure is truly a controlled variable and not limited by the lowest pressure achievable at any of the design gas flow settings). Once the factor levels have been defined, carry out the experimental matrix using a two-step procedure for each ashing test as shown in Table 2. In the first step, allow the substrate temperature and the gas flow to stabilize without plasma present (microwave power is OFF). Once gas flow and temperature are stable, turn on the microwave power to create the plasma and perform the ashing test. The ashing step time should be chosen so that approximately half of the resist thickness is removed to ensure that the rate is measured without over-ashing.

Step	Time	Temperature	Power	Pressure	O ₂	N ₂ (or N ₂ H ₂)
1	20	250	OFF	C	85% off TGF	15% off TGF
2	20	250	B	C	85% off TGF	15% off TGF

Table 2 - Representative two step test procedure for each experimental point in a test matrix.

Use the results of the DOE matrix of experiments to create a graphical representation of the process window such as the one shown in Figure 9. Other measured results from the tests in the experimental matrix can be used to define the process window in terms of different process needs, e.g., throughput, non-uniformity, cleanliness and substrate damage. This methodology can be easily generalized for different ashing process step development projects.

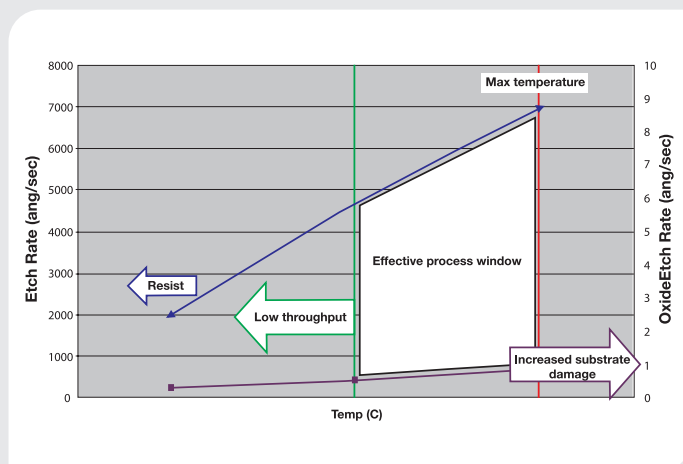


Figure 9 - A representative Process Window for an O₂ ashing process.

CONCLUSION

Photoresist removal is one of the most important process steps in modern device fabrication and plasma ashing is proven to be the most effective way to accomplish this critical step. Of the available plasma ashing processes, O₂ microwave plasma ashing is preferred since it produces relatively more neutral radical species in the plasma source than other methods, minimizing substrate surface damage due to lower ion bombardment. The operational characteristics and process data in this Application Note clearly show that the MKS High Power Microwave Plasma System using the High Power Microwave Plasma Source provides superior performance in the production of reactive radicals in both O₂ and N₂/H₂ plasma ashing processes. The reduced peak temperatures and advanced thermal characteristics of the High Power Microwave Plasma Source allow the process engineer to operate plasma ashing processes within a significantly expanded process window as compared with systems using other plasma sources. The expanded process window produces a more stable ashing process, reducing yield loss through better process control.