

## ASTRON® Remote Plasma Source for Thin-Film Photovoltaic Process Chamber Cleaning

### PROBLEM

The layers in a thin film photovoltaic (TFPV) device are deposited using deposition techniques, some of which have been adapted from semiconductor device fabrication. For example, antireflective coatings are fabricated using plasma-assisted chemical vapor deposition (CVD) processes that produce thin films of silicon dioxide or silicon nitride. These CVD processes are performed in sealed process chambers, normally under vacuum conditions. The films deposit not only on the substrate surface, but also on all surfaces within the chamber during the process. If allowed to accumulate, the wall deposits can produce contamination or particles on the substrates that are unacceptable. In addition, wall deposits can adversely affect the deposition process or in-situ metrology of the process results.

### BACKGROUND

The development and application of thin film photovoltaics (TFPVs) has grown rapidly over the past decade. Silicon solar cells are made from silicon wafers, either mono- or multi-crystalline, with a protective, anti-reflective layer deposited on the side that will be exposed to the sun (typically silicon nitride, and conductive pastes that act as the conduction path to the outside world. TFPVs all have the same basic multilayered structure, either built upon a support layer/substrate (built from back to front), or built on the glass that will act as the front side of the finished module (built from front to back). (Figure 1). Transparent conductive layers form the front and back of the cell. The side exposed to the incident light must also have antireflective properties, while the one behind the cell must allow unabsorbed light to be reflected back from the highly reflective backside of the cell. The antireflective layer may also be patterned to create a topology that further enhances light trapping in the active layers below. The CVD processes used to deposit these various layers indiscriminately deposit thin film material on all surfaces in the process chamber. Therefore, these chambers must be periodically cleaned in order to minimize contamination of the substrates which can impact process results or in-situ metrology methods.

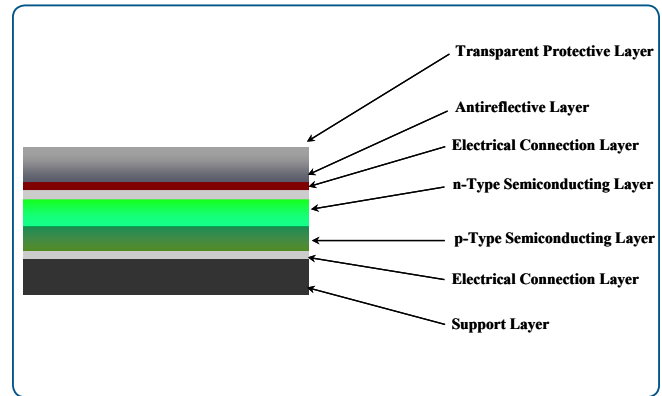


Figure 1 - A schematic showing the typical multi-layered structure of a photovoltaic cell.

### Transition From Manual Cleaning Processes to In-Situ Plasma Cleans

Initially, chamber cleans used wet chemistry to remove thin film deposits; to do so, the process tools were often disassembled and the chambers taken off site to be cleaned using liquid solvents such as aqueous hydrofluoric acid solution. This approach produced excessive system downtime and incurred high labor costs and serious workplace safety risks. For these reasons, in-situ cleaning methods were developed that avoided dismantling the equipment and exposing workers to corrosive solutions. The in-situ cleans used in TFPV manufacture normally employ fluorine chemistries in which a molecule containing fluorine (a precursor) is dissociated to produce molecular fragments that react with the wall deposits, converting them to gaseous compounds that can be pumped away. In some thin-film processes (i.e. thermal CVD) chamber cleaning precursors can be dissociated thermally in the process chamber, creating species that react and remove deposits. However, the thin-film processing equipment used for the oxide and nitride AR films in TFPV manufacturing cannot tolerate the high temperatures required for thermal deposition and cleaning. In these cases, the CVD tools employ  $\mu$ wave or RF-excitation in low temperature plasma assisted deposition processes for  $\text{SiO}_2$  and  $\text{Si}_3\text{N}_4$  thin films as well as for any etching steps involved in the TFPV process. In-situ plasma cleaning methods were therefore developed as a logical extension of these plasma deposition tools. These cleaning methods use the available plasma excitation to produce reactive species from molecular precursors. The combination of plasma-assisted deposition processes with in-situ plasma cleaning proved a significant advance in semiconductor and TFPV manufacturing, resulting

in valuable reductions in system downtime and much reduced labor costs as compared with wet cleaning.

Modern plasma-assisted cleaning systems use a variety of chemistries to create ionic species and reactive radicals. The choice of chemistry will depend on a mixture of considerations that encompass the nature of the reactive chemistry, the risks incurred in storage and use of the reactive precursor and environmental issues. Depending upon the elemental composition of the deposits to be removed, either fluorine or chlorine radical species may be desired. For example, the deposition chambers used for AR thin-film processes are cleaned using fluorine radicals as the reactive species. Fluorine radicals are produced by the dissociation of different compounds, including  $F_2$ ,  $NF_3$ ,  $ClF_3$ , and  $SF_6$ .  $NF_3$  is the most commonly used feed gas for chamber clean applications, because it can be handled safely and it dissociates relatively easily.

Even though chamber cleaning with an in-situ generated plasma may appear to be simpler, that method can also produce serious problems for thin film device manufacturers. These same problems do not result when cleaning is done with reactive gases generated in a remote plasma source. Cleaning with plasma generated in the process chamber (in-situ cleaning) can cause ion bombardment of the chamber walls and other components inside the process chamber wherever there is direct exposure of a surface to the plasma environment. This exposure degrades device performance, reduces yield, and damages the internal components of the process chamber. Furthermore, a cleaning process using in-situ generated plasma may be slower due to lower dissociation efficiency.

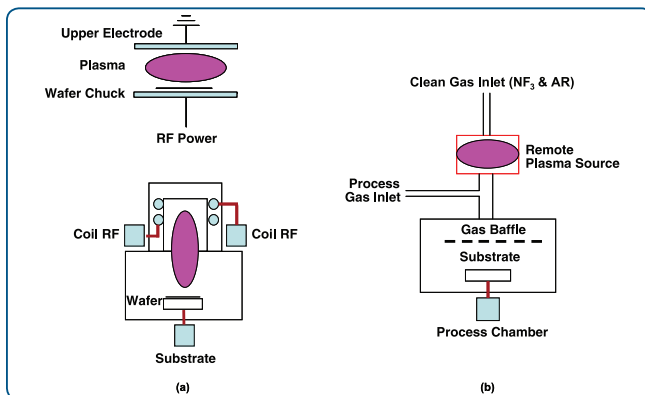


Figure 2 - (a) Two configurations that are typical of plasma process deposition tools that use in-situ plasma exposure; (b) A chamber configuration using remote plasma deposition and cleaning.

	Remote Plasma Source	In-Situ RF	Manual
Dissociation Efficiency	Excellent	Fair	N/A
Cleaning Uniformity	Good to Excellent	Fair	Fair
Cleaning Efficiency	Good to Excellent	Fair	Poor
Damage to Parts of the Process Chamber	None	Yes, due to ion bombardments	Yes, due to bead blasting, and etc.
Impact to Deposition or Process RF set-up	None	Need increased power for clean	Yes, chamber components must be easily removable
Impact to Deposition or Process RF Matching	None	Need wide range RF match for clean	Yes
Other Impact	Add interface on deposition or process chamber	May need $NF_3$ abatement in exhaust	Life time of the process chamber
COO	Good	Fair	Poor in General

Table 1 - Relative characteristics of a remote plasma source for chamber cleaning as compared to in-situ RF plasma generation or manual cleaning methods.

## SOLUTION

The development of remote plasma technology for deposition, etch and cleaning has effectively addressed the problem of ion-bombardment induced damage during these processes. Figure 2 shows schematics for conventional in-situ plasma systems (2a) as compared with remote plasma sources (2b). Using remote plasma sources it is possible to eliminate the presence of electric fields and ionic species within the process chamber. These sources use plasma excitation in a chamber that is physically removed from the process chamber to generate reactive ionic and radical species. The reactive gas stream is then passed through an ion filter that removes any ionic species.

These remote sources thus deliver only neutral excited-state (i.e. radical) species to the substrate and chamber surfaces where they either react to form the growing film, or, when cleaning chemistries are employed, etch the deposited material away. More recently, this technology has been adapted to employ RF excitation in a move to lower the cost and to increase the flexibility of these plasma sources. Table 1, below, compares different characteristics of manual wet cleaning, in-situ RF plasma cleaning, and remote source plasma cleaning of CVD process chambers.

## SOLUTION (CONT.)

### A Flexible Remote Plasma Source

The ASTRON remote plasma source from MKS Instruments Inc. is an economical, reliable remote plasma system for generating reactive radical streams that can be used in TFPV chamber cleaning applications. The ASTRON source is shown in Figure 3a. It is packaged such that control, power and plasma generation are all contained in a single unit of near desktop dimensions. The plasma source technology is based on a transformer in which the primary circuit is powered by an RF power supply and the plasma is enclosed in a loop (a toroid), as can be seen from the schematic shown in Figure 3b. Current driven in the primary coil induces a current in the plasma (secondary) in the opposite direction by Faraday's induction law. A ferrite core confines the electromagnetic fields to improve magnetic field coupling and reduce stray RF fields. Typically, this electric field is 4-8 V/cm. Since the electric fields within the plasma are maintained at such low levels, sputtering of the source chamber walls is avoided. Within the source, the plasma is contained within a 2.5-cm diameter plasma channel. In operation the ASTRON plasma source dissociates a precursor gas, typically  $\text{NF}_3$ , in the plasma toroid producing atomic fluorine for the downstream chamber clean. For large scale processing as required in some TFPV applications, gas flows of up to 30 SLM  $\text{NF}_3$  may be used. The power input to the plasma is dependent on the gas flow and pressure in the plasma chamber, and it can range between 300 W and 20 kW, depending upon the application requirements.

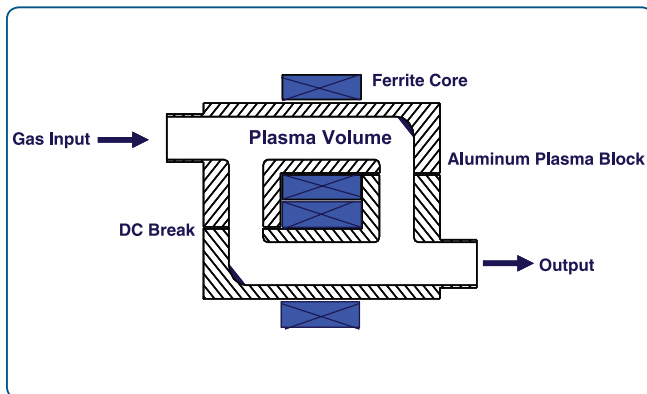


Figure 3 - Schematic layout of the ASTRON® source chamber

Typically, ASTRON sources produce >95% dissociation of  $\text{NF}_3$  precursor over the system operating flow and pressure range. This characteristic has obvious relevance to the suitability of the ASTRON source in cleaning applications. The effectiveness of the ASTRON in dissociating molecular species enables more latitude in the selection of the precursor gas used in cleaning applications. As noted above, there are concerns for the use of  $\text{NF}_3$  as a fluorine radical source owing to the impact that  $\text{NF}_3$  releases can have on GHG emissions. Indeed, GHG considerations have led to increased interest in the use of much more hazardous source gases such as molecular fluorine,  $\text{F}_2$  and anhydrous hydrofluoric acid, HF. However, the ASTRON source nearly completely dissociates  $\text{NF}_3$  (EPA reports suggest >99% dissociation). When this observation is combined with the low recombination rates in the ASTRON plasma source and transfer lines, it becomes apparent that the risk of GHG emissions when using  $\text{NF}_3$  source gas is minimized. The EPA estimates that  $\text{NF}_3$  source gases, when used in a remote plasma cleaning application, can produce a reduction of 5,500 metric tons of carbon equivalent (TCE) as compared with conventional chamber cleaning approaches.

The ASTRON source produces very high concentrations of neutral radical species and delivers these high concentrations to the process chamber. Since radical species have limited lifetimes, measured in 10's of milliseconds, recombination reactions on the plasma chamber and transport line walls must be minimized. This is accomplished in the ASTRON source through the appropriate selection of materials of construction. The ASTRON employs anodized aluminum for all of the wetted metal surfaces, since the recombination rate of fluorine radicals on aluminum oxide is very low relative to other material choices such as quartz or stainless steel. The ASTRON system also maintains the concentration of reactive species delivered to the process chamber through its ability to process relatively high gas flow rates and through admixture of Ar with the reactive gas precursor stream. High gas flow rates and fast pumping speeds increase the gas velocity through the ASTRON source and the gas transport lines, thereby reducing the residence time of the reactive species in these system components. As well, the high gas velocities force the flow of reactive species to surfaces once in the process chamber (i.e. transport of reactive species to the walls is flow driven rather than diffusion driven) and this further improves the delivery of

## SOLUTION (CONT.)

high concentrations of reactive species to those surfaces needing cleaning. Process chamber temperatures are maintained at relatively high levels during cleaning since remote plasma reactions are driven by purely thermal mechanisms and reaction rates follow an exponential dependence on surface temperature. Cleaning rates are proportional to the partial pressure of reactive gases for similar reasons.

## Best Practice For Chamber Cleaning Using The ASTRON® Source

The best chamber cleaning sequence using the ASTRON remote plasma source in TFPV tools involves a five step process. Once the reaction chamber has been brought to temperature, Ar gas is flowed through the system for up to 10 seconds to purge any residual gases due to previous processes. When the chamber purge is complete, the plasma is ignited using the purge Ar and the plasma allowed to stabilize for up to 10 seconds. Following the ignition step, the Ar flow is maintained while NF<sub>3</sub> gas flow is introduced into the system in two transitional steps, the first using 1/5th of the planned total NF<sub>3</sub> flow for 5 seconds, and the second increasing the NF<sub>3</sub> flow to 2/3 of the total value over another 5 second period. Following these transition steps, the NF<sub>3</sub> flow is increased to its full value and the chamber clean is allowed to proceed for a pre-determined time that has been shown to produce clean chamber walls. Finally, at the end of the cleaning step, the reactor is purged with an Ar/N<sub>2</sub> mixture for 10 or more seconds. Figure 5 shows typical results for a silicon dioxide residue clean using the ASTRON remote plasma source. Faster oxide etch rates (up to ~10 μm/min) are possible at higher process pressures (up to 10 Torr), and there is an optimum pressure for cleaning rates as is shown for SiO<sub>2</sub> in Figure 6. Process chambers that have been used to deposit other films for TFPV manufacturing can likewise be cleaned using the ASTRON remote source. Figure 7 shows data for the etch rate of silicon nitride at different temperatures and pressures.

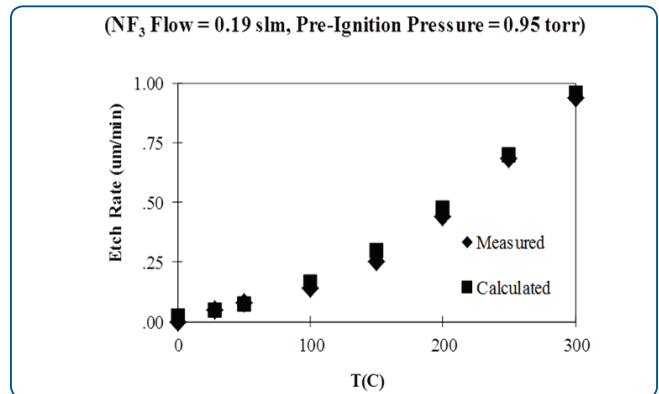


Figure 5 - Silicon dioxide etch rates as a function of temperature in a typical chamber clean using the ASTRON remote plasma source.

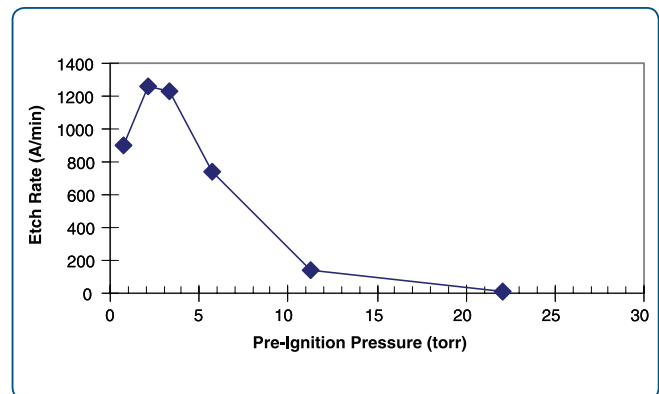


Figure 6 - Etch rate as a function of chamber pressure for SiO<sub>2</sub> using an ASTRON source to dissociate NF<sub>3</sub>; T=150 °C, NF<sub>3</sub> flow of 150 sccm and Ar flow of 750 sccm.

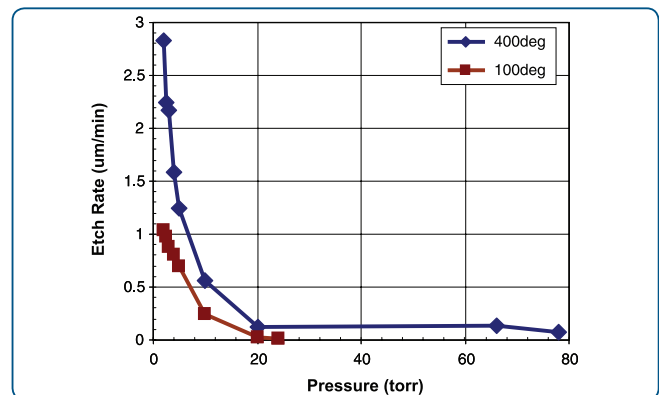


Figure 7 - Etch rate as a function of chamber pressure and temperature for Si<sub>3</sub>N<sub>4</sub> using an ASTRON source to dissociate NF<sub>3</sub>; T=150 °C, NF<sub>3</sub> flow of 150 sccm and Ar flow of 750 sccm.

## CONCLUSION

Remote plasma cleaning has distinct advantages over the other available technologies for removing wall deposits and other contaminants from the surfaces of thin-film process chambers. Etch rates for oxides and nitrides are significantly greater than those achievable with in-situ thermal or plasma cleaning. High process temperatures and ion bombardment are avoided, eliminating damage to internal process chamber components. By selecting a safe yet reactive precursor gas such as  $\text{NF}_3$ , it is possible to achieve the benefits of improved yield and reduced cleaning downtime while maximizing workplace safety. While  $\text{NF}_3$  is itself a potent greenhouse gas, the nearly complete dissociation of  $\text{NF}_3$  in the remote plasma source results in overall reductions in industry GHG emissions. The ASTRON remote plasma source when coupled with the selection of an inherently safe source gas can thus provide the safest, most cost effective chamber cleaning solution for semiconductor and photovoltaic chambers. For these reasons, solar equipment makers are replacing manual cleaning methods with ASTRON remote plasma sources for chamber cleans. Remote plasma cleans are being deployed for many solar photovoltaic manufacturing processes, especially for silicon nitride, silicon oxide, and amorphous silicon deposition chambers.

## REFERENCES

Plasma Sources Line Card  
ASTRON® G7 datasheet

For further information, call your local MKS Sales Engineer or contact the MKS Applications Engineering Group at 800-227-8766. ASTRON® is a registered trademark of MKS Instruments, Inc., Andover, MA.