PROBLEM
The internal surfaces of plasma blocks used in remote plasma reactive gas sources are subjected to a highly reactive plasma environment. As a consequence, surface erosion occurs that can shorten block lifetime and produce unacceptable particle levels in the processes in which the source is being used. Employing a hard anodized surface treatment prolongs block lifetimes and maintains acceptable particle levels, however advances in device and process specifications have produced an on-going need for further improvements in these equipment characteristics.

BACKGROUND
Paragon, the eighth generation ASTRON® remote plasma source, was developed with the following design objectives:
• Increased reliability
• Improved performance
• Improved ignition times
• Increased block-lifetime
• Reduced particles
• Improved power control

Improvements in block-lifetime and particle performance were achieved through the combination of advances in the physical design of the plasma block with advances in surface treatments that dramatically reduce the rate and extent of erosion of the internal surfaces in the plasma block.

Figure 1 shows the plasma block employed in the Paragon remote plasma source. The physical design of the block is optimized to reduce erosion and particles. Tight radius corners have been eliminated from the internal plasma channel and the plasma channel length and diameter have been increased over earlier designs to reduce the heat flux within the block. Reductions in heat flux translate directly to reduced erosion rates in the highly reactive plasma environment. Also, direct impingement of reactive gases on the internal surfaces is limited to further reduce erosion and consequent particulates.

While the physical design of the plasma block is critical for limiting erosion and subsequent particle generation, of equal impact is the physico-chemical inertness of the interior block surfaces that are wetted by the reactive plasma gas. Plasma blocks for the ASTRON family are fabricated out of aluminum. Aluminum artifacts are typified by the presence of a thin, coherent native aluminum oxide that protects the surface from routine corrosion. This native oxide film, however, is inadequate for the protection of the interior surfaces of a plasma block since these are exposed to the highly reactive chemical species produced in the ASTRON reactive gas source. For this reason, the surfaces of the plasma block in ASTRON sources are treated to produce a protective hard anodized surface.

Hard anodization of aluminum is an electrochemical process, performed in acidic solution that produces a very hard and corrosion resistant surface film of aluminum oxide. This film is much thicker and more chemically inert than native aluminum oxide. The use of this surface treatment enabled earlier generations of ASTRON sources to achieve particle performance commensurate with or better than existing device manufacturing process requirements. However, device design rules continue to shrink and this results in ever more stringent limits on the number of particles added by individual processes. As a consequence, MKS Instruments has developed a proprietary new surface treatment, plasma electrolytic oxidation (PEO), for the Paragon plasma block that significantly improves on the performance of the earlier hard anodization surface treatments. This note describes the new plasma block surface treatment and process results achieved with its use.

SOLUTION
HA vs. PEO Surface Treatments
Hard Anodization (HA) and Plasma Electrolytic Oxidation (PEO) processes produce hard, thick aluminum oxide surfaces on aluminum substrates. These processes do not deposit the oxide on the surface, but rather convert the aluminum substrate directly into the oxide, resulting in a much denser, more compliant film than can be achieved by deposition.
Hard anodization is usually carried out at high voltage using sulfuric acid, which produces a porous, amorphous, columnar oxide layer, typically more porous than mild anodized surface films. Figure 2 shows an electron micrograph which reveals the porous nature of HA surfaces. HA coatings typically exceed 10 µm and can be as much as 100 µm in thickness. HA surface treatments provide significant protection against both mechanical wear and chemical corrosion.

Plasma Electrolytic Oxidation produces a thick aluminum oxide film that does not exhibit the inherent porosity of HA films. The lack of porosity produces an aluminum oxide film with significant improvements over HA in terms of hardness and resistance to chemical erosion. Like the HA process, the PEO process initially forms a porous, amorphous and columnar aluminum oxide on the metal surface by anodic processes. However, the PEO process differs from the HA process in that it employs a combination of anodic oxide film formation, dissolution and dielectric breakdown to create a much denser, non-columnar film. The non-columnar structure of PEO is advantageous in applications in which the surface treatment must be applied to complex shapes such as plasma blocks with many sharp angular transitions or tight corners, like those found on the earlier ASTRON models. The columnar nature of HA allows the formation of cracks that penetrate the entire film thickness at such transition points (Figure 3). These cracks can serve as sites for enhanced erosion of the protective oxide and allow penetration of the oxide film by reactive chemical species. The non-columnar nature of PEO avoids the potential for forming such defects and thus provides much superior protection in structures such as the Paragon plasma block.

The films produced by HA and PEO processing are chemically identical. Figure 4 shows EDX scans for HA vs. PEO films. Both films are clearly aluminum oxide with essentially identical stoichiometries. The only difference apparent in the EDX spectra of the two films is the presence of a small amount of oxygen.
sulfur peak in the scan of the HA film. This is residue from the sulfuric acid electrolyte used in HA processing. A small, additional spectral artifact is apparent in both scans which is due to the gold plating used in EDX work.

The chemical equivalence of the two films is reflected in the fact that both HA and PEO films are stable at high temperatures of up to 900°C without structural or chemical change. (The ASTRON and Paragon remote plasma source blocks are directly water cooled and are kept well below this temperature.)

**Plasma Block Surface Erosion**

The non-columnar microstructure, greater density and higher dielectric strength of PEO films produce a superior protective coating. PEO films have greater resistance to physical and chemical erosion than do HA films, and this translates into increased plasma block lifetimes and reduced particle levels in plasma processes. This has been demonstrated experimentally through testing within MKS using either test coupons or an ASTRON ex plasma block.

Figure 5 shows electron micrographs that record the thickness reductions observed in side-by-side testing of flat coupons having either HA or PEO films. An accelerated plasma life test was conducted to qualitatively compare the erosion rate differences between HA and PEO films. Table 1 shows the loss rate data for the films on these coupons following 50 hours of exposure in accelerated NF$_3$ testing. Overall, the plasma etching rate for new PEO films, measured at multiple locations was only 20-30% of the etch rate observed for HA films. Similar results were observed in 1000-hour tests conducted using ASTRON ex plasma blocks. The most serious erosion in the blocks was observed next to the injection nozzle, and erosion was present in both HA-treated and PEO-treated plasma blocks. However, the erosion spot observed for the HA-treated block was 1.8 x 5.5 mm, over 10x the size of the spot observed for the PEO-treated block after a 1000-hour life test.

![Figure 5](image)

*Figure 5 - Electron micrographs measuring thickness reductions on flat sample areas following identical accelerated NF$_3$ plasma exposure. Total exposure time: 50 hours (approximately equivalent to 1000 RF production hours).*
Particle Testing

The reduction in erosion observed for PEO films in the accelerated etching and life tests resulted in concomitant reductions in particle levels in process. ASTRON ex blocks with HA and PEO surface treatments were compared using the following test sequence:

1. Mechanical transfer
   - Check chamber background
2. 1st 20 cycle run
3. 2nd 20 cycle run
4. Mechanical transfer
   - Check chamber background
5. Single cycle
6. 3rd 20 cycle run
7. Overnight run (205 cycles total)
8. Evaluate on-wafer metal concentration using VPD-ICP-MS

The results of the particle tests for the second 20 cycle series of tests are shown in Figure 6. It can be seen that the particle level per process cycle is more than an order of magnitude lower in ASTRON ex blocks that have a PEO film as compared with blocks having an HA film. Note that some application-specific variations in particle results may be expected.

**CONCLUSION**

This Application Note describes testing for MKS’ proprietary Plasma Electrolytic Oxidation (PEO) plasma block surface treatments used in the ASTRON and Paragon Remote Plasma Sources. The PEO surface treatment significantly extends the block life in ASTRON sources. The overall plasma etch rate of internal block surfaces with PEO treatment was only 20-30% of the rate observed in blocks with existing HA surface treatments. This reduction in erosion rates produced an accompanying reduction in particle levels in systems with PEO treated plasma blocks. The measured particle levels for PEO treated systems were an order of magnitude lower than those observed in systems employing plasma blocks having existing HA surface treatment. Particle test results outside the lab will vary based on process conditions, chamber configurations, chamber conditioning and application usages.

For more information on MKS Instruments remote plasma sources, visit:
For a general catalog of MKS plasma sources, visit:
http://www.mksinst.com/docs/UR/PlasmaSources-DS.pdf