

November 2003

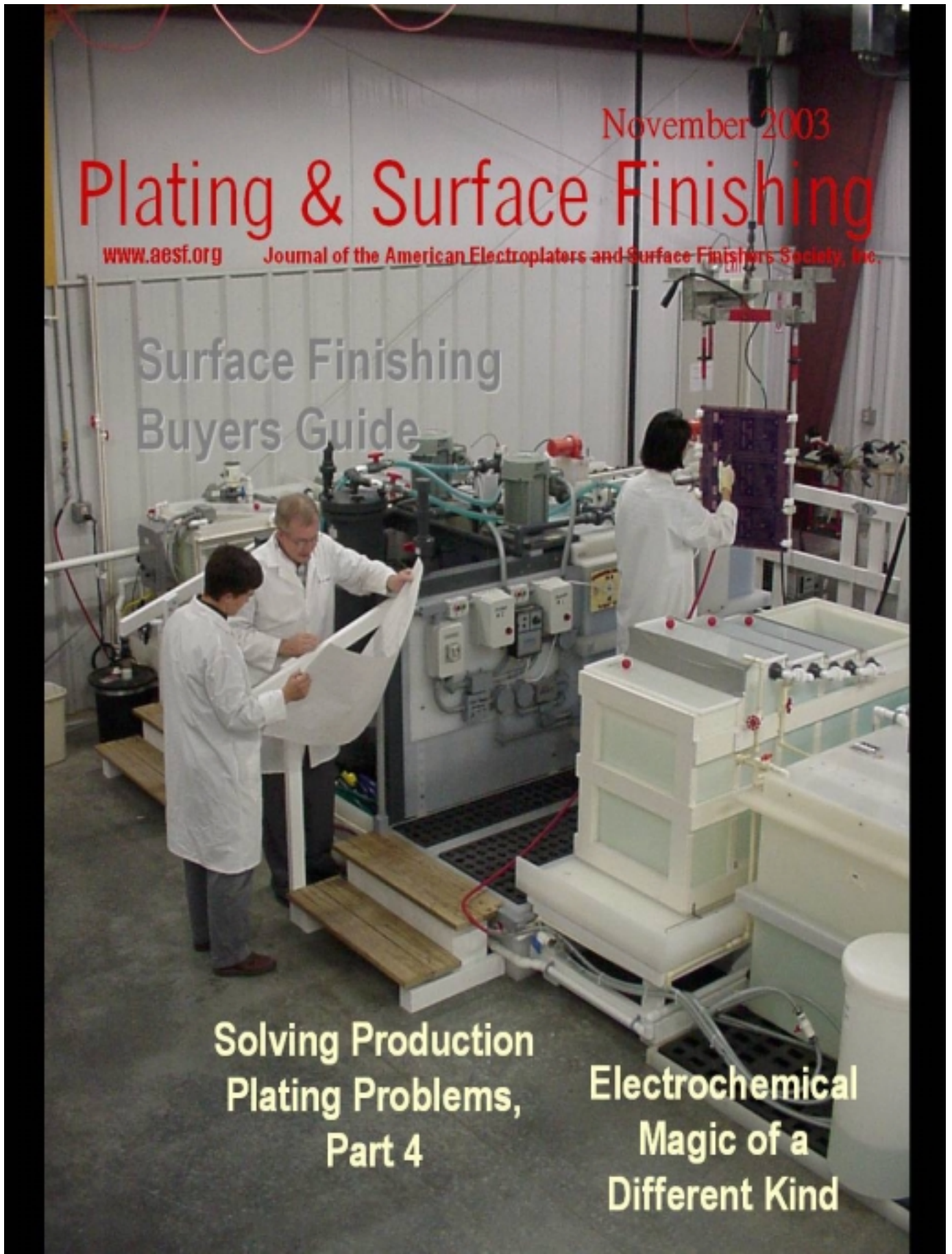
Plating & Surface Finishing

www.aesf.org Journal of the American Electroplaters and Surface Finishers Society, Inc.

Surface Finishing
Buyers Guide

Solving Production
Plating Problems,
Part 4

Electrochemical
Magic of a
Different Kind



Electrochemical Magic of a Different Kind

Most industries adopt standards over time. Things that seem to work best become the norm. Scientists and business owners get used to ideas and they stick to them. Efficiencies and economies of scale are achieved. Manufacturers begin to sit back and accept the status quo as long as the bottom line is positive.

But, what if someone else finds a better way? What if standards are supposed to evolve? What do you do when your competitors begin to challenge the status quo?

Faraday Technology, Inc., Clayton, OH (near Dayton), has demonstrated for the past 10 years that the status quo isn't good enough. Founded on the scientific principles of Michael Faraday—well-known as the father of electrochemistry—Faraday Technology thrives on finding new standards. When something isn't working on the manufacturing line, Faraday can discover a new process to fix it. When innovation is the answer, Faraday can take a solution from the lab bench to the shop floor. When the bottom line isn't positive, Faraday can step in and make a difference.

The truth is, no matter how many standards are created in electrochemistry, there is only one force driving the industry forward. And, that is the market. What works doesn't matter if it can't save money, improve efficiency or solve a manufacturing dilemma. Standards don't last if they can't deliver what customers are demanding or they aren't consistent with new government regulations. That's where Faraday can help.

About the Company

Launched in 1992 by Dr. E. J. Taylor, the company was founded on the belief that scientific discovery should be driven by a commercialization path. Developing and commercializing novel electrochemical technology is the sole motivation for Taylor and the team of diverse employees that make up Faraday Technology, Inc.

The company was founded specifically to exploit what is now known as the flagship proprietary process* of the company. This electrically-mediated approach has four key advantages:

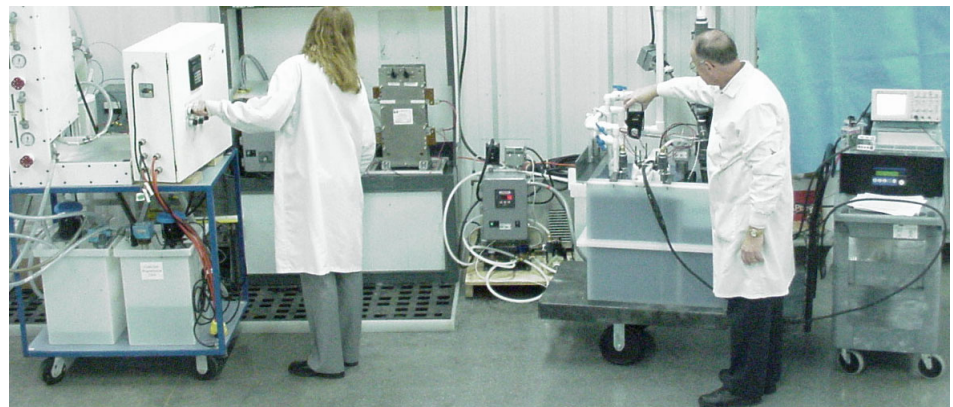


Fig. 1 Faraday's prototype manufacturing equipment includes an electrochemical machining line (top) and a chromium line

1. Robust process control,
2. Enhanced performance,
3. Cost-effectiveness, and
4. A low risk of environmental hazard.

Guiding Faraday Technology's mission and day-to-day corporate strategy is a large patent estate. Faraday has 45 patent actions across four market sectors. Faraday Technology's business model of capitalizing on core research by licensing technology that is protected by patents has created millions of dollars in value for commercial clients. In addition to finding solutions to current manufacturing problems, Faraday can also impart related intellectual property thus adding value to the relationship between Faraday and its clients.

Faraday's facilities - expanded in 2002 - offer customized research, engineering and

light manufacturing capabilities. Faraday hires highly trained technical experts in a variety of fields as well as those who may not have scientific degrees but instead have a wealth of manufacturing experience.

The fact that Faraday's facilities (Fig. 1) are equipped with prototype manufacturing areas allows the company to transition quickly from scientific research to commercial application. Its reputation and past success also allows the company to leverage significant research dollars on behalf of its clients and their particular goals.

The Patented Process

Initiated by Dr. Taylor, Faraday's patented platform technology shifts the focus of an electrochemical process from chemical me-

Faradayic® Process, Faraday Technologies, inc., Clayton, OH

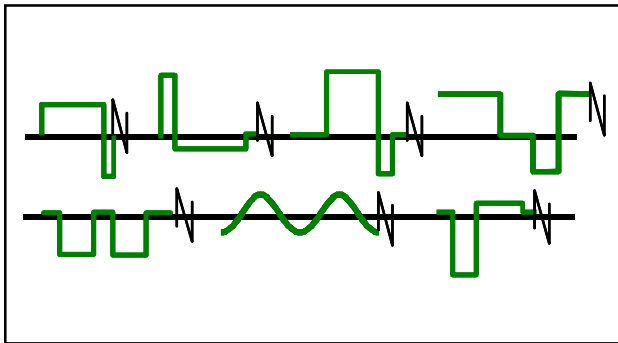


Fig. 2-ECM waveform

diation to electrical mediation, thus shifting process control from “proprietary chemical formulations” to “programmable electric fields.”

An electrically mediated waveform (Fig. 2) is an asymmetric, pulsed waveform characterized by a forward pulse followed by a reverse pulse and/or an off-time depending on the application. The waveform is characterized by the following parameters:

1. Peak forward current, I_{for} ,
2. Forward on-time, t_{for} ,
3. Peak reverse current, I_{rev} ,
4. Reverse on-time, t_{rev} and
5. Off-time, t_{off} .

The sum of the on-times and the off-time is the period of the waveform with the inverse of the period being the frequency of the waveform. The forward, γ_{for} , and reverse, γ_{rev} , duty cycles are the ratios of the respective on-times to the period of the waveform. The average current (I_{avg}) or net deposition rate is given by:

$$I_{avg} = I_{for}\gamma_{for} - I_{rev}\gamma_{rev} \quad (1)$$

Just as there are infinite combinations of height, width and length to obtain a given volume, in electrically-mediated processes there are unlimited combinations of peak currents, duty cycles and frequencies to obtain a given deposition rate. For certain anodic process applications, such as electrochemical etching or polishing, the electric field can be under voltage control.

Unlike direct current (DC) electrolysis, the mass transfer characteristics of electrically-mediated electrolysis are time dependent. Electrically-mediated electrolysis causes concentration fluctuations near the electrode surface and reduces the effective Nernst diffusion layer thickness. Consequently, very high instantaneous limiting current densities can be obtained with electrical-mediation as opposed to DC electrolysis.

Faraday’s electrical mediation technology has become known for its ability to incorporate the advantages of typical electrochemi-

cal processes while addressing the challenges. Other electrochemical techniques have been developed to address these issues but complex chemical “magic” is often used to control the electric field. These complex chemistries are usually proprietary formulations that limit the user’s ability to develop specific applications without relying on chemical suppliers. Faraday Technology’s process simplifies the chemistry and relies on an asymmetric, interrupted square waveform to control the process.

Applying the Process: What Matters is the Market

The evolution of science in this century has been nothing short of fantastic. We are living in an age when discoveries are made at an exponential pace. And, there is plenty of research money out there for a company that wants to discover things.

That is not Faraday Technology’s mission, however. Faraday wants to see the light at the end of the tunnel. Before any research money is brought in-house, a commercialization plan must be clear.

Even though major scientific progress continues at a rapid pace, the only thing that will keep electrochemical companies in business down the pike is the rate at which they can fix what ails their customers. With that in mind, Faraday Technology has developed superior methods not only to push science forward but also to thrive in the company’s three core business areas:

1. Process development,
2. Pilot-scale manufacturing and
3. Intellectual property asset management.

Market Drivers That Motivate— Examples of Success

Regulation of “clean manufacturing:” Replacement of hexavalent chromium— an environmental technology benefit

Hexavalent chromium plating has been used for many years to provide hard, durable coatings with excellent wear and corrosion resistance properties. Due to the toxic nature of the bath and effects on the environment and workers’ health however, chromium baths have come under increasing scrutiny. For a number of years, there has been a concerted effort to find substitutes for hexavalent chromium processes, driven primarily by these

toxicity concerns. Despite many successes, there remain applications for which no suitable substitute for hard chromium has yet been developed, and for which there is no immediate prospect of a replacement.

Hexavalent chromium refers to chromium in the +6 oxidation state, typically associated with processes such as hard chromium electroplating that are intended to provide a mechanically tough, corrosion resistant coating for demanding applications. Chromium is also electroplated using a milder electroplating bath containing chromium in the +3, or trivalent, oxidation state, but such coatings do not typically exhibit the same mechanical properties.

An example is the application of coatings to the insides of long tubes, for which line-of-sight processes are impractical. The persistence of such processes, despite well over a decade of attempts at replacement, have convinced most process engineers that hard chromium plating is going to remain a practical necessity for the foreseeable future. Engineering controls have made workplaces that carry out hard chromium electroplating considerably safer than in the past. Nevertheless, even with the best existing control systems, the health and environmental cost, risk and potential liability associated with the use of hexavalent chromium remains a major concern.

Faraday’s solution: replace chromium with chromium. That is, replace hexavalent chromium electroplating with trivalent chromium electroplating. The technology involves alternating pulses of reverse polarity instead of the usual direct current. Faraday Technology has established intellectual property for controlling these non-steady state electric fields.

The company has found significant advantages result from the use of trivalent chromium. They include:

1. Trivalent chromium is not a known human carcinogen;
2. Trivalent chromium exposure limits are higher than those of hexavalent chromium;
3. Disposal costs are reduced, and sludge regeneration is reduced 10 to 20 times because of reduced chromium content.

Trivalent chromium is also insensitive to current interruptions and the “drag-in: of chloride and sulfate from previous operations is better tolerated.

While DC plating is known to have certain adverse effects (caused by the evolution of hydrogen from water electrolysis



Modern analytical methods help the company to achieve fast results.

at the cathode), including internal porosity, poor adhesion, low corrosion resistance and high internal stresses, electrical-mediation has been proven to:

1. Increase the chromium plating thickness by converting nascent hydrogen gas to H^+ ions, decreasing the pH near the surface;
2. Increase purity, hardness and brightness by eliminating chromic hydroxide precipitation; and
3. Reduce hydrogen embrittlement by converting nascent hydrogen gas to H^+ during the anodic period thus increasing the corrosion resistance of the plating film.

Support for this work has been previously funded by the USEPA to explore:

1. Pulse-reverse current control to allow for thick coatings [250 μm (10 mil) has been demonstrated],
2. Adhesion/cohesion of a trivalent chromium deposit (with thick coatings),
3. Robust trivalent chromium chemistry at a cost comparable to conventional hexavalent chromium chemistry and
4. Microstructure and morphology comparable to hexavalent chromium electroplating.

The process has been further developed by application of state-of-the-art coatings on commercial parts provided by several industrial producers.

Two additional preliminary evaluations have been performed by the Cherry Point Naval Air Depot and by Concurrent Technologies Corporation (CTC). The CTC data is not comprehensive and has not yet been published. The initial Cherry Point evaluation concluded that the Faradayic™ Process was the most promising trivalent chromium coating considered to date, but the current version needed improved hardness to be considered acceptable for military critical applications.

Faraday Technology has therefore struc-

tured a continuation project to address the issue of hardness in conjunction with a commercial manufacturer and two government owned maintenance facilities. The project will be sponsored by the National Center for Manufacturing Sciences (NCMS).

Implementation of "improved manufacturability": Planar metallization for semiconductor wafers — an enabling technology benefit

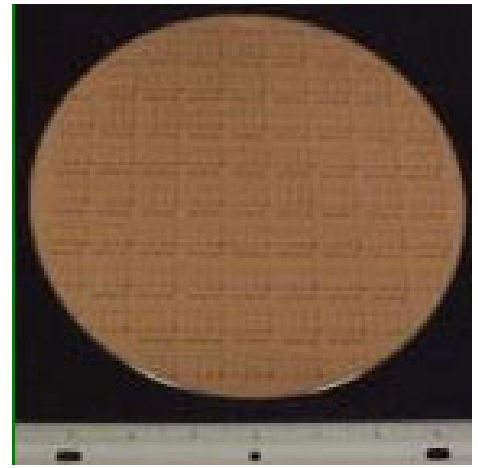
For the past four decades, the semiconductor industry has continued to improve semiconductor devices in order to comply with the market demand for higher performance and cost-effective products. Driving this movement has been the subsequent reduction in feature size, predicted by the Semiconductor Industry Association (SAI) at 30 percent every three years. But, as feature sizes shrink into the submicron region (less than 0.25 μm), the resistance-capacitance (RC) delay associated with the interconnect features becomes the dominant performance-limiting factor. The switch from aluminum to copper for metallization of interconnect features has also resulted in a decrease in electromigration, a phenomenon identified as one of the primary failure mechanisms limiting IC reliability.

Additionally, the main problems associated with electrochemical deposition (ECD) of copper interconnect features are the filling of submicron, high aspect ratio vias and trenches without void or seam formation, and the overfill of copper on the wafer surface.

Faraday Technology has proven these issues can be solved. Improvements have been shown by utilizing the electrical-mediation to demonstrate copper deposition onto 8-in. VLSI wafers. Results such as deposit thickness distribution and uniformity, structure and grain size, as a function of electrically-mediated process parameters, have been studied for feature sizes in the range of 0.25 to 1.0 μm .

Both pulse current (PC) and pulse reverse current (PRC) have the potential to enhance ECD processes significantly by optimizing the associated process parameters, specifically the cathodic (forward) pulse current, the anodic (reverse) pulse current, the cathodic on-time, the anodic on-time and the off-time.

For void-free copper deposition into trenches and vias, the optimum waveform should deposit copper uniformly during the cathodic modulation. Since the thickness of the diffusion layer under conditions of moderate bath agitation is on the order of 75 μm , and the vias and trenches are less than



Faraday has developed technology for planar metallization for semiconductor wafers.

1 μm , the filling of the trenches fits a micro-profile case. To ensure uniform deposition of the copper into trenches and vias, the waveform parameters should be chosen so the microprofile is converted into a macroprofile during the cathodic modulation. This can be achieved by using a high cathodic peak current for a relatively short on-time.

As overfill is a likely problem during ECD, it has also been found that using a pulsed reverse waveform instead of a pulsed waveform reduces overfill and eliminates defects by conformally depositing copper during the cathodic modulation. Further, copper is preferentially etched from the surface, re-entrant and upper sidewalls of the trenches and vias during the anodic modulation. This is achieved by using the high cathodic peak current for a short on-time during deposition and then creating a non-uniform current distribution during the etch process using a low anodic peak current for a relatively long on-time. The final result of this filling profile is a defect-free copper filled trench or a via featuring considerably less overfill as compared to trenches and vias filled under conformal or superfilling profiles.

Additionally, by utilizing the Faradayic™ Process, the elimination of difficult-to-control levelers and brighteners from the plating solution can also be achieved allowing for greatly reduced waste.

Changing "the way we do business": Non-contact polishing — a disruptive technology benefit

What Faraday Technology has discovered has the potential to change the semiconductor industry significantly. Faraday's ability to demonstrate successful semiconductor metallization has been followed by its successful attempts to utilize its electrically mediated platform technology in the planarization process as well.

It is widely known that, as feature sizes get

smaller and smaller, the abrasive nature of chemical mechanical polishing will continue to have damaging effects. There is also a strong movement to replace silicon for substrate wafers. This material is being replaced by low-K dielectric materials thereby creating a constant insulating material impermeable to the flow of electricity.

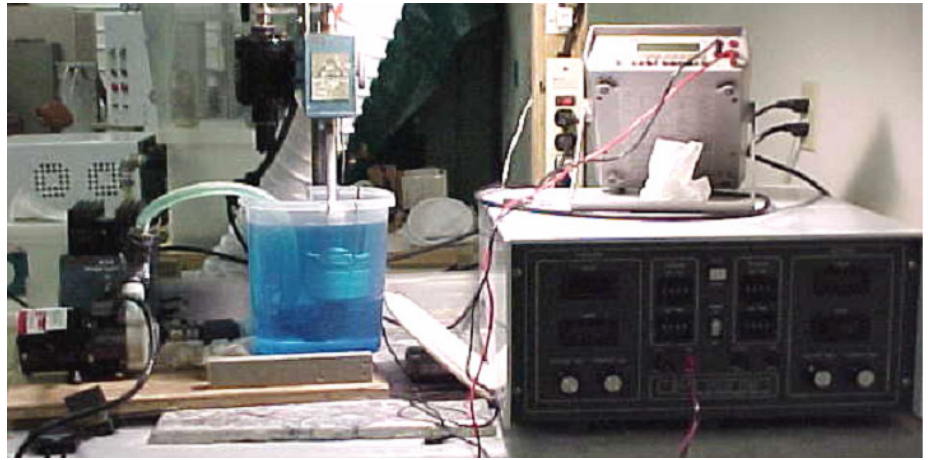
Faraday's significant breakthrough in this area is the application of non-contact polishing. Currently, six patents owned by Faraday Technology support this process, which offers manufacturers a way to achieve a flatter surface at less cost. By applying electrically-mediated current which forces electrons loose, Faraday has shown that copper can be dissolved into a liquid. The non-contact aspect of the process "wipes away" copper even as feature sizes get smaller - and it does so without damaging the substrate.

This is a great example of how technology is truly driving the market. As newer and better manufacturing methods are discovered, companies will have to adopt the faster, most innovative solutions to stay competitive. That means those who are determined not to change the status quo - not to adopt new standards - will be left behind.

Reduced "cost of manufacturing": Edge and surface finishing—a cost-saving benefit

As the use of hard, passive alloys increases in manufacturing, the need to provide edge and surface finishing of these materials is critical. As the design complexity of parts increase, the need for cost-effective, advanced techniques increases as well.

Faraday Technology also has significant knowledge in utilizing high current electro-



Faraday has developed high-current electrochemical processes as a source for edge and surface finishing.

chemical process as a source for edge and surface finishing. These processes have been proven to:

1. Process difficult-to-machine materials,
2. Have removal rates as high as 0.1 to 10 mm/min,
3. Have no tool wear,
4. Successfully finish complex shapes and contours,
5. Eliminate unnecessary manufacturing steps,
6. Use environmentally friendly electrolytes (NaCl and NaNO₃).

Faraday Technology's previously reported work includes the following achievements, which serve as successful commercial applications of the platform technology inspired by Michael Faraday and initiated by Taylor:

1. Edge finishing of cast aluminum alloy wheels
2. Edge and surface finishing of stainless steel valves
3. Surface finishing of titanium and titanium alloys
4. Edge finishing of titanium medical clips
5. Edge finishing of surgical steel blades.

Additionally, many of Faraday's services and applications can come bundled with an in-process recycling system. This novel system has been developed to recycle the spent rinse water back to the rinsing operation. This is done by integrating electrowinning and ion-exchange for the efficient removal of metal contaminants, such as copper. The system utilizes integrated ion-exchange electrodes for the simultaneous removal of

anions and cations in solution. After treatment, heavy metal concentration and total dissolved solids (TDS) are reduced, and the pH is neutralized. Consequently, treated water can be recycled back to the rinse operation. As an added benefit, the cell has the ability to be regenerated *in-situ*.

The Future of Electrochemistry: The Market Shall Rule

While science will continue to be governed by established standards and reliable methods, the market will continue to be the best predictor of business behavior. Consumers will continue to demand better products, manufacturers will continue to scramble to keep up with that demand, and scientists will continue to discover innovative ideas, which can play a role in the race to be the best.

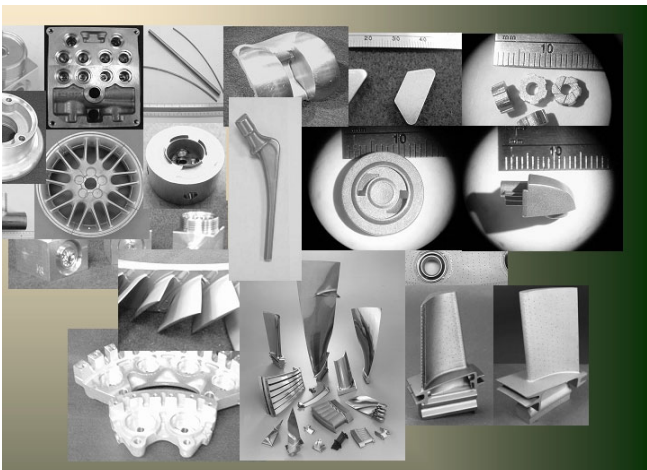
In the end, the companies who respond by taking chances on new ideas will keep pace with the industry's market drivers.

Many corporations have established R&D departments. But, how many of them are spending their days "putting out fires" that break out on the manufacturing line? The answer is most of them are doing exactly that.

That's where Faraday Technology has found its niche - the one that many corporate labs have left behind. Faraday's business model and facilities are set up to be a true R&D environment. Scientists and engineers are not encumbered by maintaining a "manufacturing line." Instead, they can focus their attention on technology development from the bench-scale to the pilot-scale. In return they get to be part of establishing the future of high-risk/high payoff technological innovations for new and emerging markets and methods.

And, what do Faraday's customers get? The chance to be better than everyone else.

P&SF



These electrochemically machined parts include wheels, valves, titanium alloys, medical chips and surgical blades.