Development of Fluoride-Containing Solvent-Based Strippers

In the early days of the semiconductor industry, mixtures of sulfuric acid and hydrogen peroxide were used to strip photoresist from wet-etched wafers (1). The photoresist removal mechanism involved oxidation of the organic polymer. These mixtures were strong oxidizers and due to safety issues, solvent mixtures that were considerably safer were developed and commercialized. As each new generation of product was developed it retained the benefits of the previous generation, addressed problems, and added new capabilities. The semiconductor stripper and cleaner market is now dominated by a few classes of solvent-based products; amine-based, amide-based, and fluoride-containing solvent-based strippers.

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Evolution of Solvent-Based Strippers

First and Second Generation Solvent-Based Strippers

Many of the first generation solvent-based strippers, introduced in the mid-1970s, were phenol-based (e.g., J-100). Phenol-based products were operated at or above their boiling point (>120°C) which raised concerns regarding safety and potential health problems. Consequently, product modifications incorporated safer solvents that operated at lower temperatures. These modified strippers (e.g., Ashland-ACT's ACT® 1 and ACT® CMI strippers) introduced in the early 1980s remained solvent-based, designed to again primarily remove photoresist, and to operate below the boiling point at 75 to 80ºC. ACT CMI stripper, which consisted of an amide, an alkanolamine, and a complexing agent, was the first commercially available product to contain a corrosion inhibitor to protect exposed metals. New competitive stripper products included some form of corrosion inhibition technology in reaction to the precedent set by ACT CMI stripper and the ever shrinking critical dimension (CD) variation tolerance for post-etch cleaning. As these strippers did not contain oxidizing or reducing agents, the photoresist removal mechanism involved penetration by solvent, swelling of the polymer, and dissolution[3].

Third Generation Amine-Based Strippers

During the 1980s, there was a transition from wet etching of semiconductor metal and via levels to less isotropic etching using plasma processes which introduced another type of residue. As dry etching processes evolved, it became necessary to remove etch residue and photoresist during the post-etch cleaning process. Etch residue was purposely generated during the dry etch process, by physically sputtering material from the substrate, to produce an in situ etch mask on the sidewall and improve the anisotropy of the plasma etching process[3,4]. Some amides are quite polar and can dissolve inorganic etch residue; however, other more polar organic solvents were better for removing typical etch residue and were also able to remove photoresist. Other requirements included the customers' need for strippers that operated at lower temperatures due to safety concerns, had a longer bath life, and met operating temperature limitations of some process tools. Customers also desired multiple suppliers for the stripper components to minimize risk if a sole supplier had delivery problems or limited capacity.

In the early 1990s, the next generation of amine-based products was introduced, most of which contained several amines (e.g., hydroxylamine and a primary alkanolamine like ethanolamine), a corrosion inhibitor (e.g., catechol), and water. These Amine-based strippers are typically operated at 65 to 75ºC to work efficiently, which could limit the product's bath life due to component loss.

Alkanolamines had been used in paint strippers for years and were effective in removing novolak-based photoresist. Examples of third generation products include Ashland-ACT's ACT® 935 stripper and EKC-265. These products contain both oxidizing agents (e.g., hydroxylamine) and reducing agents (e.g., hydroxylamine and catechol). Figures 1 and 2 contain scanning electron micrographs (SEMs) of aluminum lines and oxide vias, respectively, before and after cleaning with ACT 935 stripper at 75ºC. Another third generation amine-based product is Ashland ACT® 690C, which does not contain HA, but does contain catechol.

One process challenge that has been observed is that primary and secondary amines in the presence of water undergo protonation and produce hydroxide in situ which aids in cleaning, but can also facilitate corrosion of metal lines. Thus, it became necessary to include a corrosion inhibitor in these semi-aqueous, amine-based products. Much like resist removal, the mechanism to remove etch residue is generally thought to involve penetration, swelling, and dissolution[3]. The reducing capabilities of hydroxylamine may play a role in solublizing some metal salts in the etch residue. Typically, for metals with multiple stable oxidation states, lower oxidation states form compounds that are more soluble than those formed from higher oxidation states. Hydroxylamine can reduce metals from their M^{3+} oxidation state to their M^{2+} or M^{1+} oxidation states that typically form more soluble compounds.

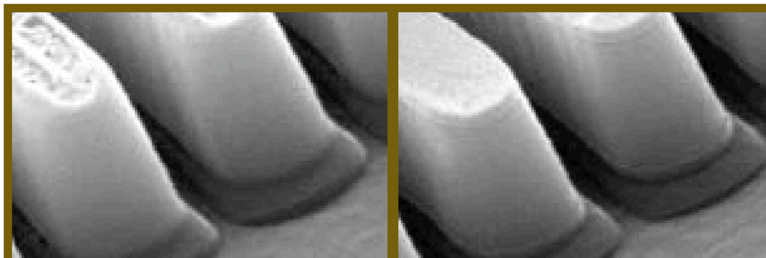

Figure 1. ACT 935 Stripper. Process: Strip (75ºC, 20min.) ➔ DI Rinse(23C, 3min.) ➔ dry.

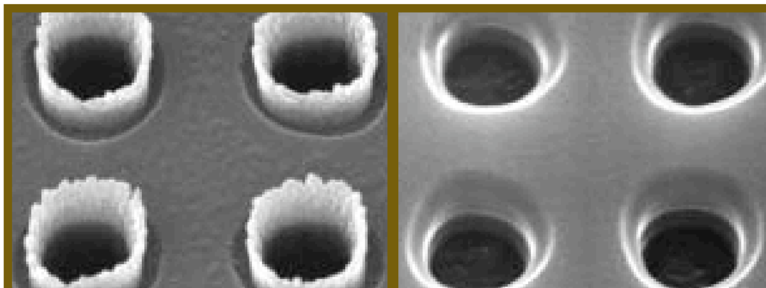

Figure 2. ACT 935 Stripper. Process: Strip (75ºC, 30min.) ➔ DI Rinse(23C, 3min.) ➔ dry.

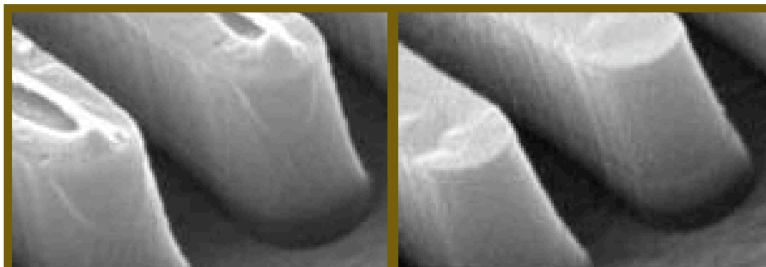

Figure 3. Process: Strip (70ºC, 20 min.) DI Rinse (23ºC, 3 min.) dry.

Fourth Generation Amine-Based Strippers

As the post-etch stripping process became more critical in ensuring appropriate high device yields, semiconductor manufacturers became sensitive to the presence of single-sourced components in stripper products. The worldwide Hydroxylamine crisis highlighted supply chain risk in single-sourced raw materials, and prompted a development effort to eliminate HA from advanced strippers. Examples of fourth generation amine-based products include Ashland-ACT's ACT® 970 and ACT® AS-65 strippers. These products typically operate at temperatures of 50 to 75ºC. ACT 970 stripper is the first commercially available amine-based stripper that was compatible with copper, aluminum, and many low-k dielectrics and is used in manufacture for both aluminum gap-fill and copper-Damascene technologies. Figures 3 and 4 contain SEMs of aluminum lines and vias in oxide before and after cleaning with ACT 970 stripper at 70ºC and 75ºC, respectively. Figure 4 also shows removal of bulk photoresist. ACT AS-65 stripper is an improved version of ACT 970 stripper with enhanced cleaning capabilities. Figures 5 and 6 contain SEMs of aluminum lines and oxide vias before and after cleaning with ACT AS-65 stripper processed at 65ºC.

Evolution of Fluoride Containing Strippers

Fifth Generation Fluoride-Containing Strippers

The next series of post-etch strippers are a departure from past development efforts as they include a new cleaning agent (i.e., fluoride), operated at or near room temperature, and do not include an amine as a principal solvent. Fluoride-containing strippers have some unique characteristics not attributed to amine-based strippers. The residue removal mechanism for fluoride-containing strippers appears different than that for amine-based strippers. In addition, fluoride-containing strippers skim the SiO_2 surface whereas amine-based strippers typically do not. In addition, fluoride-containing fifth generation strippers operate at lower temperatures (i.e., 20 to 40ºC).

The semiconductor industry has used fluoride for silicon cleaning applications since its inception[1,2]. Initially, hydrofluoric acid (HF) was used with a glycol for front end of line (FEOL) cleaning of silicon wafers and etching of silicon dioxide. As the industry evolved, buffered oxide etchants (BOE) were developed by including an HF salt (e.g., NH_4F) along with HF in a glycol or dilute aqueous solution. In the mid-1990s, fluoride-containing strippers were introduced for back end of line (BEOL) applications to remove etch residue. These products include ATMI NOE, ST-200 series, and Ashland-ACT's ACT® NE-12 stripper.

Fluoride-containing strippers are capable of skimming the exposed SiO_2 which can reduce the trace metal contamination level by several orders of magnitude, improving both device yield and reliability. Some speculation exists as to the exact fluoride species responsible for etching[1,5,6]. However, dielectric etch rates scale linearly with the total fluoride concentration which allows tailoring strippers for various applications. It is unlikely that the fluoride species produced in a dilute aqueous solution from a mixture of HF and NH_4F are the same as that produced in an anhydrous mixture of organic solvent and NH_4F. Some fluoride species commonality may exist in semi-aqueous HF salt solutions compared to aqueous solutions. The etch residue removal process for fluoride-containing solvent-based strippers may include several mechanisms. The solvents can penetrate, swell, and dissolve. Controlled, light substrate etching can result in an under cut and lift off mechanism. Lastly, fluoride may react with a typically water insoluble etch residue and convert it into a water soluble residue as shown in Figure 7. Aluminum hydroxide ($Al(OH)_3$) is usually found in etch residue after aluminum etching. NH_4F can react with $Al(OH)_3$ to form ammonium aluminum fluoride (NH_4AlF_4). $Al(OH)_3$ is insoluble in water whereas NH_4AlF_4 is highly soluble in water. Consequently, the converted etch residue dissolves in a semi-aqueous stripper and/or during the water rinse cycle whereas the original residue would not[7].

Several problems were encountered with some of these fluoride-containing strippers.

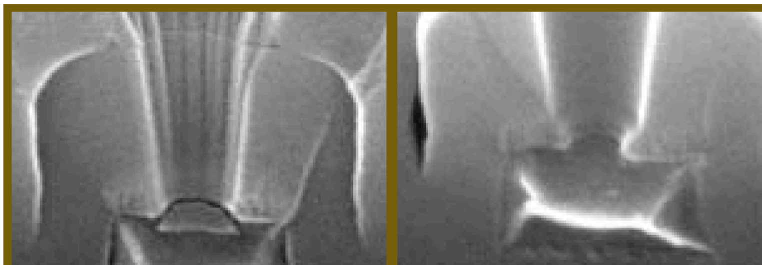

Figure 4. Process: Strip (75°C, 40 min.) DI Rinse (23°C, 3 min.) dry.

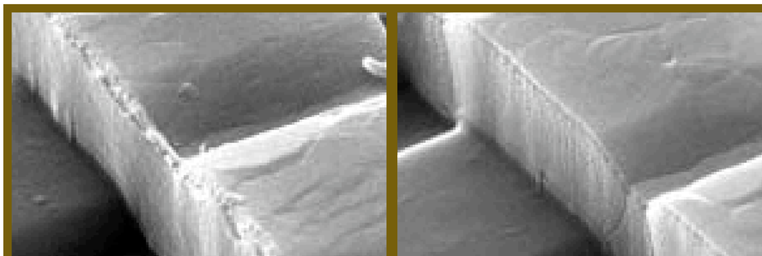

Figure 5. Process: Strip (65°C, 30 min.) DI Rinse (23°C, 3 min.) dry.

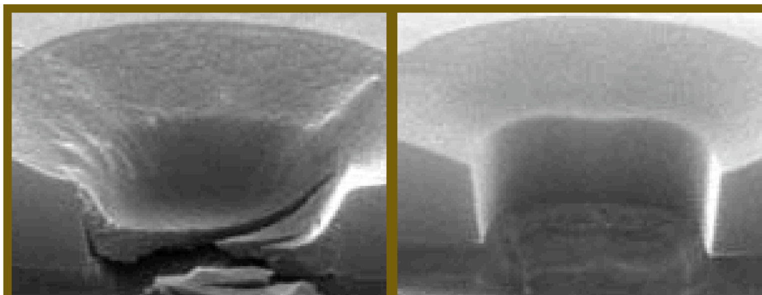

Figure 6. Process: Strip (65°C, 15 min.) DI Rinse (23°C, 3 min.) Æ dry.

First, high viscosity stripper formulations resulted in fab operational problems with pumping and recirculation processes in chemical delivery systems and process tools. Next, these strippers could not remove photoresist; however, in situ oxygen ashing of photoresist had become quite popular in many wafer etching tools, and wet stripping operations were typically not required to remove photoresist. Ashing processes cannot remove inorganic etch residue, so wet cleaning was used in addition to a dry clean or ash. Finally, these fluoride-containing strippers did not provide stable SiO_2 etch rates. Addition of a few % of water to anhydrous glycol-based fluoride-containing strippers resulted in increases in SiO_2 etch rates of about 200-300%.

Sixth Generation Buffered Fluoride-Containing Strippers

Instability of the SiO_2 etch rates led to the development of pH-buffered strippers to set and maintain a certain pH. Ashland developed acidic, buffered fluoride-containing products (e.g., Ashland-ACTs ACT® NE-series strippers) in the mid- to late-1990s to address some of the weaknesses of the early glycol-based fluoride-containing strippers. These strippers are amide-based, which allowed them to remove some novolak photoresists, even when operated at ambient temperature. As low-k dielectrics are introduced into semiconductor device manufacturing, there is a trend to eliminate oxidative or reductive ashing, which may damage the dielectric, and to return to the requirement to strip bulk photoresist during the post-etch clean process. These buffered fluoride strippers have low viscosity, which eliminates chemical delivery system pumping and process tool re-circulation problems. Introduction of pH buffering allows us to tailor the pH of the stripper to minimize metal etch rates and, to control dielectric etch rates. By examining stability diagrams (i.e., Pourbaix diagrams) for various metals and determining regions of passivation, one could find a pH common to the passivation regions for several metals[7]. Introducing a pH buffer to set the pH to a predetermined value then acts like a corrosion inhibitor since the metals will passivate and not corrode.

The buffer also maintains the pH of the stripper over its bath life and minimizes pH changes which would alter its performance. The pH of unbuffered strippers may change due to absorption of atmospheric contaminants (e.g., CO_2, NH_3, etc.), loss of volatile components (e.g., NH_3), dissolution of acidic or basic etch residues, and dissolution of an acidic photoresist. Figure 8 contains pH data for an ACT BNE series product which is stable for more than 7 days and a non-buffered stripper which is unstable. Finally buffered, fluoride-containing strippers are capable of being configured to operate in a batch wafer processing tool, where process times may be 20 to 30 minutes, or in a single-wafer tool, where process times of 1 minute or less are required to achieve a throughput of at least 60 wafers per hour. As an example, Ashland-ACTs ACT® NE-14 and ACT® NE-28 strippers are used for batch processing in immersion tools and spray tools (see aluminum lines and vias SEMs for ACT NE-28 in Figures 9 and 10) while ACT® NE-89 stripper is used on single wafer tools (see SEMs of aluminum lines in Figure 11). One can scale the aggressiveness of fluoride-containing strippers to match the process tool requirements. This degree of freedom was not available in amine-based strippers, partly due to the different residue removal mechanisms operable for fluoride-containing strippers. Fluoride-containing solvent-based strippers are used in post-etch cleaning for a wide range of technologies which include; aluminum gap-fill, copper-Damascene, microelectromechanical systems (MEMS), and surface acoustic wave (SAW) devices. However, these fluoride-containing acidic strippers had a problem. The etch rates for silicon-based oxides and some low-k dielectrics were too high.

Seventh Generation Fluoride-Containing Strippers

The high silicon oxide and low-k dielectric etch rates are eliminated in the current generation of fluoride-containing strippers. There is an extensive history of metal corrosion inhibition in other industries. Materials used for corrosion inhibition of

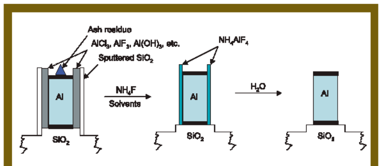

Figure 7. Residue Removal with Fluoride.

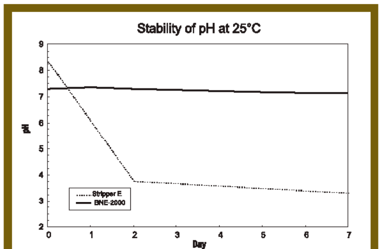

Figure 8. Stability of pH at 25°C.

metals in semiconductor applications (e.g., catechol) have also been used to prevent corrosion in water cooling and boiler systems for many years[8]. This history has been exploited for ideas for semiconductor post-etch stripper products. The art or science of controlling dielectric etch rates is relatively new and appears to be a problem unique to the semiconductor industry. As the feature size decreases, the available tolerance for critical dimension (CD) variations for the post-etch strip process is virtually zero. Other upstream processes like mask making, photolithography, and etching consume nearly the entire CD variation tolerance for advanced device technologies. Damascene processing is used with copper due to the inability to produce readily volatile copper dry etch products. Consequently, an additive process must be used instead of a subtractive process like that for aluminum gap-fill technologies. The metal line size is controlled by the pattern width in the dielectric for a Damascene process. In order to produce the correct line size, and to achieve the correct semiconductor device parameters, it is necessary to control the dielectric feature size.

The dielectric etch rate is pH dependent; therefore the pH for fluoride-containing strippers may be changed to tailor the dielectric etch rate within a wide range of values by selecting an appropriate buffer.

As one goes from slightly acidic (i.e., pH < 7) to slightly basic (i.e., pH > 7), the etch rate for silicon-based dielectrics (e.g., SiO_2, TEOS, etc.) typically decreases. Figure 12 contains etch rate data for three types of TEOS as a function of pH for ACT NE-28 stripper formulations with different pH buffers. As can be seen, the TEOS etch rate decreases as the pH increases. This may be due to the fluoride species present at various pH values. Also, if the dielectric etch process requires H+, a decrease of several orders of magnitude in H+ concentration can significantly reduce the reaction rate. This was the concept utilized during development of these new, basic, fluoride-containing strippers in the late-1990s and early-2000. The primary goal was to increase the pH to a value > 7 to control dielectric etch rates. Examples of these strippers are Ashland-ACT's ACT® BNE-series strippers, EKC-600 series, and ATMI ST-250 series. Figure 13 contains SEMs of aluminum lines before and after processing in ACT BNE-8500 stripper at 27°C for one minute. The ACT BNE-series strippers use a pH buffer, while the other products mentioned use a solvent base to increase and set the pH to a value above neutral.

Fortunately, the etch residue removal process seems to be very weakly dependent on pH since acidic and basic fluoride-containing strippers typically perform equally as well if they use the same solvent matrix. The use of buffers provides the flexibility to tailor products to have specific dielectric etch rates by setting and controlling the pH, just as we saw for metals. In addition, additives have been discovered which allow controlling the etch rate for specific dielectrics without a general muting of the fluoride activity.

Summary

The last thirty years has seen many generations of strippers developed for the semiconductor industry. Unlike semiconductor devices which are predicted by Moore's law to change generations every 18 to 24 months, post-etch strippers have averaged more than four years between generations. By retaining some attributes of previous generations of strippers, new products introduced into the market may be used on both new device technologies as well as on older device technologies. Customer requirements for safer operation, better performance, lower toxicity, and higher device yield are principal drivers in post-etch solvent-based stripper development. The introduction of new materials (e.g., metals, dielectrics, antireflective coatings, and photoresist), as well as changes in processing technology (e.g., introduction of single-wafer cleaning, elimination of ashing of photoresist, etc.) are also drivers for post-etch stripper development where solvent-based products are the most prominent type of post-etch stripper used by the semiconductor industry.

Fluoride-containing, solvent-based strippers were the focus of development for several stripper manufacturers during the mid- to late-1990s and are expected to become the dominant stripper technology as semiconductor technology continues to develop. The ability to adapt products for selectivity allows for removing Al of organic-based residues from organic-based dielectrics without damaging the dielectric. The larger number of degrees of freedom for fluoride-containing, solvent-based strippers allows an ability to adjust performance to match most any semiconductor application. Simple, inorganic acid mixtures may not offer the adaptability, selectivity, wide process latitude, or wide range of applications that can be obtained from a multi-component, fluoride-containing, solvent-based stripper. The stripper development process has been one of evolution rather than revolution. The inclusion of corrosion inhibition technologies for metals and dielectrics, incorporation of fluoride as an active cleaning species, and use of pH buffering to tailor the product's performance characteristics were notable technology gains that have occurred along the development path.

As a Responsible Care* company, Ashland is committed to developing products which are less toxic and better for the environment. Several of the ACT BNE-series strippers also utilize new, safer solvents. Next generation products are always under development when the latest stripper is introduced and commercialized. New generation fluoride-containing solvent-based products that strip DUV photoresist, bottom antireflective coatings (BARC), and remove etch residue

Figure 9. Process: Strip (20°C, 10 min.) DI Rinse (20°C, 3 min.) dry.

from porous and non-porous low-k dielectrics are under development and in beta-testing. In addition, fluoride-containing strippers for use with supercritical CO_2 ($SCCO_2$) processing are also under development and in beta testing. The post-etch stripper development paths over the past thirty years have been interesting, leading to multiple chemistries to solve challenging wafer processing requirements.

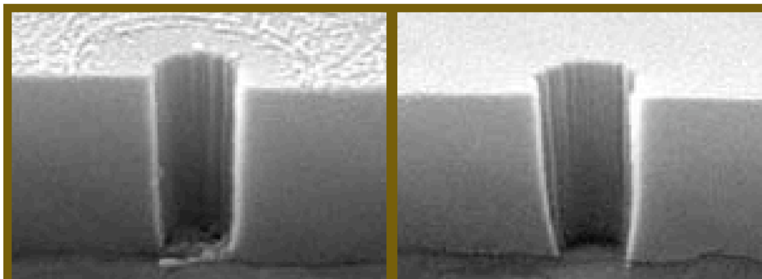

Figure 10. Process: Strip (20°C, 10 min.) DI Rinse (20°C, 3 min.) dry.

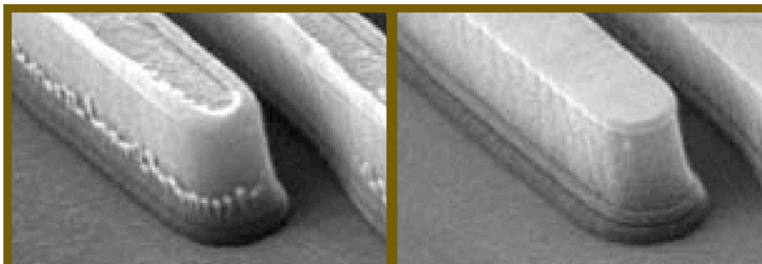

Figure 11. Process: Strip (24°C, 1 min.) DI Rinse (24°C, 30 sec.) dry.

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References

[1] Wayne M. Moreau, "Semiconductor Lithography Principles, Practices, and Materials", Plenum Press, New York (1989).

[2] David J. Elliott, "Integrated Circuit Fabrication Technology", 2nd Ed., McGraw-Hill, New York (1989).

[3] Yaw S. Obeng and R. S. Raghavan, "'Back End' Chemical Cleaning in Integrated Circuit Fabrication: A Tutorial", MRS Symposium Proceedings, 477 (1997).

[4] S. M. Sze, "VLSI Technology", 2nd Ed, McGraw-Hill, New York (1988).

[5] D. M. Knotter, J. Am. Chem. Soc., 122, 4345 (2000).

[6] Christopher P. Wade and Christopher E. D. Chidsey, "Preparation of Pit-Free Hydrogen-Terminated Si(111) in Deoxygenated Ammonium Fluoride", MRS Symposium Proceedings, 477 (1977).

[7] D. W. Peters, et al, "Corrosion Inhibition Technologies for Post-Etch Strippers", International Sematech Wafer Cleaning and Surface Preparation Workshop (2002).

[8] "Principles of Industrial Water Treatment", Drew Industrial Division, Boonton, NJ (1994).

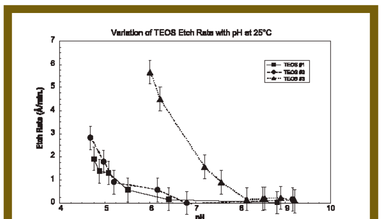

Figure 12. Variation of TEOS Etch Rate with pH at 25°C.

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Biographies

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Darryl has over 20 years' experience in the semiconductor industry in various engineering and management roles. He earned his B.S. in Chemistry from San Diego State University and earned his Ph.D. in Physical Chemistry from Ohio State University. Before joining Ashland-ACT he held various technical positions in lithography, deep UV stepper development and multi-photon processes.

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Over the past four years Rob has worked as a Development Chemist and Applications Engineer at Ashland-ACT. In addition to the Semiconductor industry, he has also worked in the Biotechnology and Pharmaceutical industries. He holds a Ph.D. in Synthetic Organic Chemistry from Temple University.

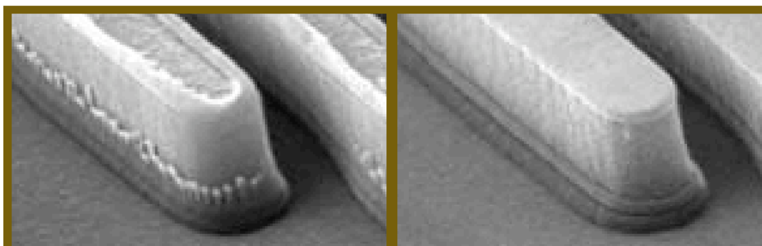

Figure 13. Process: Strip (27°C, 1 min.) DI Rinse (27°C, 30 sec.) dry.