

Dynamics of Surface Treatments and Pre-Cleans for High Volume Wafer Manufacturing

J. Crites¹, W. Snodgrass², and L. Luu³

¹Skyworks Solutions, Inc. 20 Sylvan Road, Woburn, MA 01801 Phone: 781-376-3191, E-mail: jim.crites@skyworksinc.com

²Avago Technologies 4380 Ziegler Road, Fort Collins, CO 80525 Phone: 970-288-1171, E-mail: william.snodgrass@avagotech.com

³Global Communications Semiconductor, LLC 23155 Kashiwa Ct, Torrance, CA 90505 Phone: 310-530-7274, E-mail: lluu@gcsincorp.com

Abstract

The importance of surface treatments and pre-cleans within the semiconductor industry is well known. In order to assure good thin film adhesions and low resistance of metal-semiconductor contacts, certain solvent or plasma cleans followed by acid or base treatments are essential for removing organic residues and surface oxides. A variety of etchants are known to be effective for the removal of native GaAs oxides. There is, however, little standardization within the industry on what treatment is used at a particular processing step and what concentration and processing time is needed to achieve effective results. Furthermore, the costs associated with preparing a particular etch chemistry and the effective lifetime of the chemistries involved has not previously been carefully explored. This collaborative paper will review general practices for wet oxide removal etches within several high volume manufacturing organizations and studies of the effectiveness of these practices.

INTRODUCTION:

As part of the manufacturing process, all semiconductor manufacturing sites use acids, bases, solvents, and plasma cleans to remove oxides, resist scum, or GaAs and related epitaxial compounds. As an example, patterning a photoresist opening may require a plasma clean to remove residual resist that remains after a develop step, and this is frequently followed by an oxide removal to assure good adhesion of an evaporated film. Similarly, a surface clean may be required to prepare the wafer surface for the next layer of photolithography or a dielectric deposition. In the case of wet processing, the chemistry may be available as a bath in a fume hood or dispensed from a wafer track or other automated single-wafer processing tool. It is the responsibility of engineering to determine what bath to use, what concentration to employ, and what the effective bath life should be. This paper provides examples of those choices and discusses how these processing steps are utilized at some of the major manufacturing sites in the U.S.

DETERMINATION OF OXIDE REMOVAL EFFECTIVENESS

To explore the effectiveness of different oxide removal chemistries, bare GaAs mechanical wafers were deliberately oxidized in a downstream plasma etch tool. The wafers were then submitted to a variety of common agents and concentrations. XPS and spectroscopic ellipsometry and reflectometry were used to characterize the oxide thickness and surface composition resulting from the initial oxidation and the different oxide removal treatments. After the intentional oxidation step, the wafers were measured on a Nanometrics Nanospec 9300 spectroscopic ellipsometry and reflectometry tool and the measured oxide thickness was found to be in the 26-29Å (2.6-2.9nm) range. Wafers were then processed through 4 different oxide removal chemistries: A 1:5 HCl:DIW solution prepared from 37% HCl, a 1:50 NH₄OH:DIW solution prepared

from 29% NH₄OH, a 1:1600 HF solution, and 0.26N TMAH developer. For the HCl and NH₄OH treatments, the solutions were prepared in a tank and wafers were immersed for 25s with manual agitation followed by a 20s overflow rinse and 1 cycle quick dump rinse. Wafers were then spun dry in a heated N₂ environment. For the HF and TMAH solutions, wafers were processed through production single-wafer spray tools with in-situ rinse and spin dry. After the oxide removal treatments and within 1 hour of processing, oxide thickness was again measured by ellipsometry. The post-etch results were quite consistent independent of what chemistry was employed; the measured oxide thickness after wet treatment ranged from 8.5-11 Å. Figure 1 summarizes the ellipsometry measurement results, including a control group of wafers which received no wet treatment. The samples were then stored in a typical production cleanroom environment in a standard process cassette and box. Oxide thickness was remeasured at periods of 24hrs, 48hrs, and 72hrs after initial oxide removal. The results of these measurements are shown in Figure 1, showing a very gradual regrowth of native oxide over the time period studied.

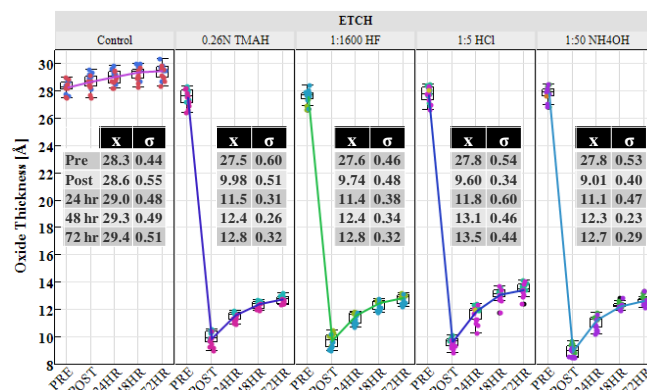


Figure 1: Oxide thickness of etched samples as measured by ellipsometry prior to etch, within 1 hour of etch, and at 24 hour intervals.

HYDROGEN CHLORIDE SOLUTIONS FOR OXIDE REMOVAL

A dilution of HCl is often used as an agent for removing a surface oxide prior to film deposition. The most widely used starting concentration of HCl is commonly referred to as 37% HCl, which more accurately means an 11 to 12 Normal solution of hydrogen chloride packaged with a label indicating 36 to 38% HCl. Full strength 37% HCl is rarely used for wafer cleans with 1:1 HCl:DIW (18% HCl) or 1:5 HCl:DIW (6% HCl) being much more common. Although many facilities refer to a bath concentration by dilution ratio, this presents an opportunity for confusion if the starting HCl concentration is not consistent from site to site. Skyworks has etch baths that are stocked from multiple starting concentrations of HCl ranging from 18% to 36%. In this section,

concentration will be described in terms of hydrogen chloride percentage instead of dilution ratio.

In recognition of the importance of effectively cleaning the oxide from the surface prior to next step, most facilities act conservatively and use strong solutions with short bath life; typically 12 hours per bath fill. In order to explore the requirements for effective oxide removal using HCl, a series of bare GaAs mechanical wafers were prepared by deliberately oxidizing the wafer surface in a downstream oxygen plasma etch tool. Samples were evaluated against bath age and bath strength.

Since 18% HCl and 6% HCl are most common, concentrations of 12% and 3% HCl were evaluated as alternatives. Using the oxidized GaAs mechanical wafers, tests were done comparing normal bath to dilute bath as shown in Table 1.

Table 1: Oxide Removal vs. HCl Conc.

HCl Conc.	Dip Time	Initial Oxide Thickness	Final Oxide Thickness
18%	15s	24.0 Å	9.5 Å
12%	15s	25.1 Å	10.3 Å
6%	30s	25.5 Å	10.3 Å
3%	30s	31.3 Å	10.4 Å

For the standard concentration, the evaluation samples were run at the end of bath life when the solution had been used for a substantial number of production lots. For the more dilute concentrations the bath was prepared and a limited number of dummy runs were made to approximate bath utilization. There was no significant difference in the measured final oxide thickness.

An effort was also made to evaluate bath lifetime by performing an oxide removal test with a bath that was used longer than standard lifetime. At the Skyworks site in Woburn MA there are several 6% HCl baths that have a 12 hour utilization time before the bath must be replaced, and a couple tanks that have a 24 hour effective lifetime. Comparing runs made at end of life for both 12h and 24h tanks showed no difference in oxide removal ability. All tests showed the previously demonstrated reduction from ~25Å initial oxide thickness to about 10Å after treatment. In one special case an 18% HCl bath that sat idled for over two weeks was checked. In this particular case the bath was not heavily utilized as the tank was not a manufacturing tool and only a limited number of wafers were cycled through the bath for an unrelated experiment. Nevertheless, this chemistry performed well, with the measured post dip oxide thickness in the 10-12Å range.

This raises the question of what HCl concentration is really necessary in order to remove an oxide layer and how long a dilute solution may be considered effective; does the bath really need to be changed every 12 hours? Given that some of the more sophisticated chemical stations can monitor the bath conductivity and spike the bath with fresh chemistry in order to maintain bath strength, there seems to be an opportunity to extend bath lifetimes and reduce chemical consumption. At a cost of approximately \$10/gal for 37% HCl, a typical wet station bath with a five gallon tank using an 18% solution therefore costs roughly \$25 per fill. Using 3000 wafer starts per week and a process requiring five evaporation steps, this would correspond to about 1000 wafers cleans per 12 hour shift. For a facility using five HCl clean stations, this corresponds to 200 wafers per tank fill, and thus about \$0.13 per processing step. There is also a corresponding cost required to pH neutralize that amount of acid before it can be discharged as wastewater. These costs could be substantially reduced if 6% HCl could be effectively utilized instead of 18% HCl or if the bath lifetime could be extended.

OTHER CHEMISTRIES FOR OXIDE REMOVAL

A dilute solution of aqueous HF is another effective wet treatment for the removal of GaAs native oxides. At Avago Technologies in Fort Collins CO, a 1:1600 dilution of 49% HF:DIW is used to remove surface oxide prior to thin film deposition. The solution is prepared from 49% HF (28.2 N), which is first diluted to 1:10 HF:DIW (2.56 N or 5.3% wt) in an automated blend system. The blend system is fed from a chemical tote and utilizes conductivity measurement to control dilution. After blending, the 1:10 HF solution is transferred to a distribution tank where the conductivity is continuously monitored by a recirculation loop. The 1:10 HF distribution tank feeds a bulk chemical distribution system that delivers the chemical to the wet process tools. The tools used for GaAs oxide removal are dry-in, dry-out single-wafer spray tools with internal reservoirs. It is in these reservoirs that the 1:10 HF solution fed to the tool is further diluted to 1:1600 HF:DIW (0.0176 N or 0.035% wt) by metering the volume of 1:10 HF and DIW dispensed. A typical oxide removal sequence consumes approximately 125 mL of the 1:1600 solution for each wafer. At a cost of less than \$20 per gallon for the 49% HF feedstock, the raw material cost of this oxide removal approach amounts to about 1/25th of 1 cent or about \$0.01 for every 25 wafers processed. Oxide removal by 1:1600 HF:DIW is typically preceded by some form of oxygen plasma descum, and followed by thin film deposition such as metal evaporation or PECVD dielectric deposition. A 1 hour time limit between oxide removal and the start of the subsequent deposition is imposed to minimize native oxide regrowth.

TMAH is a strong base that is readily available in pre-diluted form in most wafer fabs, where it is used as photoresist developer. These diluted solutions of TMAH may also be used to remove surface oxide from GaAs. Oxide removal is necessary to ensure good adhesion of some photoresists to a GaAs surface, and since the diluted TMAH solutions are available on the same tools that perform the photoresist coating, it can be convenient to use them as the oxide removal chemistry of choice for this application. A typical developer solution is 2.4% TMAH (0.26 N). With a dispense volume of approximately 60 mL, the chemical cost of this process is approximately \$0.05 per wafer.

Dilute solutions of NH₄OH have also been utilized for surface pre-cleans at a variety of processing steps. They are most commonly employed prior to photolithography steps and nitride depositions, and in some cases prior to metallizations. Usage of NH₄OH for surface clean is preferable over HF and HCl in some cases. HF can attack PR-GaAs interfaces and HCl will attack any exposed Ni. At Global Communications Semiconductor, a 1:50 dilution NH₄OH(29%):DIW is typically used for surface pre-cleans. The cleaning process uses baths of 3060ml at room temperature for 5-30sec dips followed by DIW rinse and spin dry. Each bath is mixed within 5mins before use and is only used once for up to 25wafers. At a cost of less than \$20/gal, each wafer costs about \$0.01 of chemical to clean. The time from pre-clean to the subsequent processing is limited to 15-60mins to prevent oxide regrowth.

XPS STUDY OF GAAS OXIDES

To further examine the effects of the different wet oxide removal treatments, the surface chemistry of the as-etched wafers was characterized by XPS. Analysis was carried out over a 100µm diameter spot at 45° take-off angle, using a Physical Electronics Instruments Quantum 2000 system with monochromatic Al K_α radiation source. Samples were placed under vacuum in the XPS tool within 2 hours after completion of the oxide removal processes to minimize the opportunity for oxide regrowth. Survey scans were performed on each sample to check for contamination prior to performing high-resolution scans. Only Ga, As, and O were de-

ected on all samples. High resolution XPS spectra were acquired using a pass energy of 11.75eV and energy interval of 0.1eV/step.

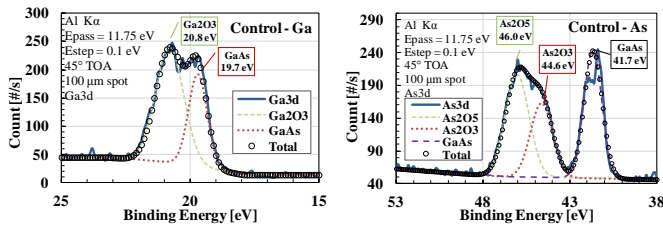


Figure 2: Ga-3d (left) and As-3d (right) XPS spectra of un-etched control sample with total spectra curves modeled as a sum of peaks representing the different Ga and As compounds.

Figure 2 shows the measured data from high resolution scans of the Ga 3d and As 3d binding energy spectra taken on a control sample that was intentionally oxidized but received no wet oxide removal treatment. The spectra can be modeled as the sum of two or more normal distributions centered at different binding energies representing different Ga and As-containing compounds. Figure 2 illustrates how the Ga 3d spectrum can be modeled as the sum of two distributions representing Ga_2O_3 and GaAs, while the As 3d spectrum is modeled using three distributions representing As_2O_5 , As_2O_3 , and GaAs. The area of the modeled distribution representing each compound is compared to the total area of the Ga or As spectrum to determine the relative concentration of each compound. The surface chemistry of each sample was extracted using the XPS spectra deconvolution technique illustrated in Figure 2, combined with survey scan data that provides the relative atomic concentrations of Ga, As, and O. The resulting surface compositions are summarized in Table 2. The data indicate that the surface volume of the intentionally oxidized sample is approximately equally partitioned between Ga oxide, As oxides, and unreacted GaAs. The compositions of the etched samples are consistent with one another, and show little oxide remaining. The oxides that do remain are primarily Ga_2O_3 and As_2O_3 . This is consistent with some earlier reports^[1], while others have found only As oxides remaining after wet treatment^[2]. The data may suggest that the acidic HCl and HF solutions may be less effective at removing As_2O_3 , as a higher concentration remains on these samples than on those treated with NH_4OH or TMAH. However, as the data for each treatment comes from a single site and single wafer, it is not known whether or not this observation is significant or merely the result of non-systematic variation. All samples were found to be As-rich, with ratios of the integrated areas of As to Ga peaks^[3] in the range of 1.6-1.7.

Table 2: Surface composition of etched samples

	Ga_2O_3	As_2O_5	As_2O_3	GaAs
Control	35%	17%	12%	35%
1:5 HCl	5.9%	0.23%	8.8%	85%
1:50 NH_4OH	5.0%	0.24%	7.2%	87%
1:1600 HF	5.3%	0.10%	8.1%	87%
0.26N TMAH	6.5%	0.51%	6.9%	86%

The complete set of high resolution XPS spectra measured on the 5 different samples is shown in Figures 3 and 4. From examination of these spectra, it is clear that no new Ga or As containing compounds are formed after the wet treatments and that all of the chemistries studied produce a similar final surface composition. To characterize the relative oxide thickness across the set of samples, the in-situ Ar-ion sputtering capability of the XPS tool was employed to produce a depth profile of oxygen content. A sputtering process that is calibrated to remove SiO_2 at the rate of $20\text{\AA}/\text{min}$ was run for 10 second intervals and high resolution scans of the Ga, As,

and O binding energies were captured after each interval up to 40s total sputtering time. Figure 4 plots the atomic concentration of oxygen extracted from these scans versus sputtering time. The initial oxygen concentration of the etched samples is 23-24% and falls to less than 1% after 40s of sputtering, while for the unetched sample the initial concentration is 53% and this falls to 27% after 40s of sputtering. If a comparable sputtering rate is assumed for SiO_2 and GaAs/GaAs oxides, then the oxide thickness estimated from the XPS depth profiling is approximately 12\AA for the etched samples and 27\AA for the unetched control. This is consistent with the values obtained by ellipsometry as reported in Figure 1.

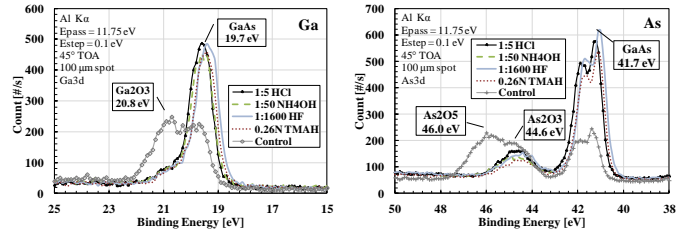


Figure 3: Ga (left) and As (right) XPS spectra of etched samples.

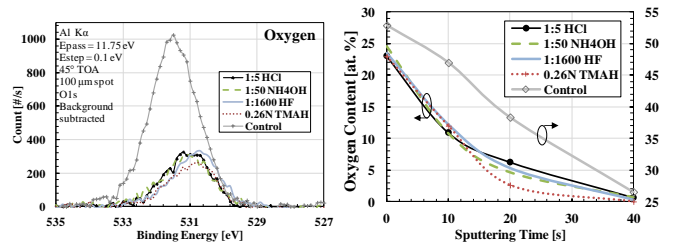


Figure 4: O XPS spectra (left). Surface atomic percent oxygen content of etched samples as determined by XPS analysis vs. in-situ sputtering time (right). Sputter rate is calibrated to remove SiO_2 at a rate of $20\text{\AA}/\text{min}$.

PROCESS UNDERCUT EVALUATIONS

One way GCS characterizes the effectiveness of a chemical preparation step is by checking the adhesion of the cleaned surface to photo resist or SiN ^[4]. Wafers are cleaned in various chemistries and concentrations for 20sec then rinsed in DIW for 5mins and then dried in a heated N_2 environment. For GaAs- SiN_x adhesion check, the cleaned wafers are passivated with PECVD SiN within 30mins and then patterned with photo resist. The patterned wafers are processed through dry etch to remove the SiN outside of the PR pattern. For GaAs-PR adhesion check, the cleaned wafers are coated with PR within 30mins with no other surface adhesion promoter or pre-bakes.

To create the wet etch undercut, wafers are then processed through GaAs wet etch to remove $8000 \pm 300\text{\AA}$ in height. The etch chemistry used is 1:1:20 $H_3PO_4(85\%):H_2O_2(35\%):DIW$. No agitation is performed during the wet etch in order to emphasize the undercutting from the adhesion between the two layers. The distance from the top edge of the wet etched feature to the SiN bottom edge or PR bottom edge is measured to characterize the quality of the GaAs surface clean; this technique is illustrated in Figure 5.

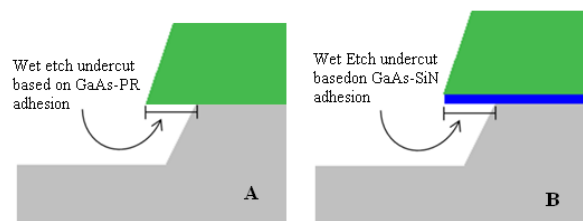


Figure 5: Block Figure of the undercut check and measurement. A) GaAs-PR check. B) GaAs- SiN check

The wet etch undercut of a GaAs wafer with only DIW rinse as the pre-clean serves as the baseline to compare the oxide removal of the different chemical cleans. For GaAs-SiN_x adhesion, wafers cleaned with HCl and NH₄OH has similar undercuts as the baseline wafer. Wafers cleaned with HF have improved adhesion and have about 25% less wet etch undercut than other pre-clean methods. This adhesion improvement is likely due to another effect of the HF exposure other than oxide removal. There is no significant difference between the two dilutions of each clean chemistry. For GaAs-PR adhesion, all chemical cleans yielded worse adhesion than the baseline wafers. To conclude if there is a difference between each clean condition, more data is needed because there is too much variation in the undercut of each condition.

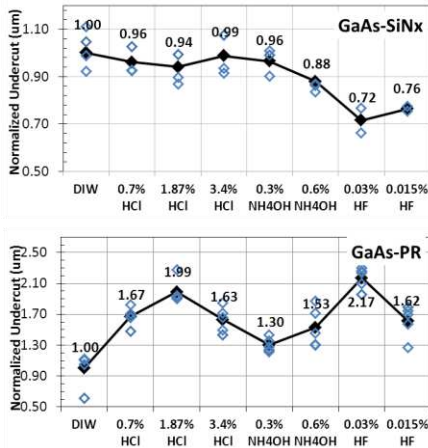


Figure 6: GaAs wet etch undercut after various wet cleans before SiN passivation and before PR coating.

Similarly, the effect of bath life can also be evaluated using the GaAs-PR undercut check. We expect that as the solution is used up, the cleaning will behave more like the DIW cleaning only and yield lower wet etch undercuts. The bath volume was 3300ml for the 3.4% HCl solution and was 3060ml for the 0.3% NH₄OH solution. Each solution was “consumed” by cleaning GaAs wafers that have been oxidized in an O₂ plasma. One bath is mixed for each chemistry. A test wafer is cleaned in the bath and then 50 oxidized GaAs wafers are cleaned in the bath. Another test wafer is cleaned followed by another 50 GaAs wafer cleaning. This cycle is repeated until 200 GaAs wafers have been cleaned. From the wet etch undercut results, each bath can be used for up to 200 wafers without affecting the adhesion.

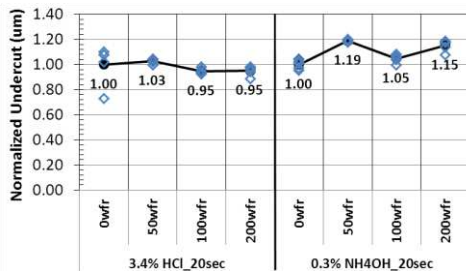


Figure 7: GaAs-PR undercut vs. bath usage of wet cleans SiN passivation and before PR coating.

The same undercut evaluation method can be used to compare the effectiveness of clean times. Clean times of 20sec to 5mins were evaluated. Each clean time used a fresh bath. For both GaAs-SiN and GaAs-PR adhesion, no significant change in etch undercut was observed for wafers cleaned for longer times except

for the wafers cleaned in more concentrated HCl. The 6.2% HCl clean for 2mins and 5mins seems to increase the SiN adhesion to GaAs. Since GaAs-SiN adhesion is unaffected by HCl clean while GaAs-PR adhesion tends to decrease with clean, the similar trend in undercut vs. clean time supports that for higher concentration, clean time is a factor to be considered.

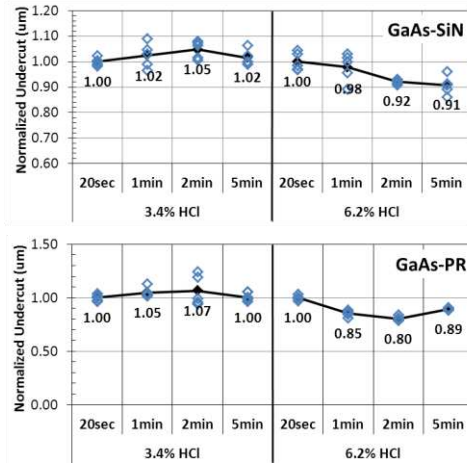


Figure 8: GaAs wet etch undercut after varying time of wet cleans before SiN passivation and before PR coating.

SUMMARY

Several different common chemistries are employed by GaAs wafer manufacturers in the U.S. for the purpose of etching GaAs oxides. The efficacy of each of these was evaluated. With respect to oxide thickness, each chemistry achieved approximately equivalent results. For the case of HCl, little or no dependence on concentration or bath life on the as-etched remaining oxide thickness was found. XPS analysis of samples etched using different chemistries confirmed that each produces a similar final surface composition and residual oxide thickness. The influence of etch chemistry on thin film adhesion to GaAs was evaluated by measurements of GaAs wet etch undercut of SiN and photoresist masks deposited following different oxide removal treatments. Some dependence of undercut on oxide removal chemistry was found when using a SiN etch mask, while results with a photoresist mask were inconclusive. No bath consumption or loading effects were observed for HCl and NH₄OH baths up through 200 wafers usage.

REFERENCES

- [1] T. Mirandi, D.J. Carlson, The Effects of Chemical Treatment and Storage Time on the Surface Chemistry of Semi-Insulating Gallium Arsenide, 2009 CS MANTECH Technical Digest, May 2009.
- [2] M. Rei Vilar et.al., Characterization of wet-etched GaAs (100) surfaces, Surf. Interface Anal. 37, 2005
- [3] A. Chanda et. Al., Etching of GaAs substrates to create As-rich surface, Bull. Mater. Sci. 50, 2007
- [4] A.J. Grine et. al., Pre-photolithographic GaAs surface treatment for Improved Photoresist Adhesion During Wet Chemical Etching and Improved Wet Etch Profiles, 2010 CS ManTech Technical Digest, May 2010

ACRONYMS:

- TMAH: Tetramethylammonium hydroxide
- XPS: X-ray photoelectron spectroscopy