SEMICONDUCTORS

CRITICAL ULTRAPURE WATER APPLICATIONS FOR THE SEMICONDUCTOR INDUSTRY

Investigating methods for improving the removal of inorganic and organic contaminants, perceived and real, from water, thus producing ultrapure water (UPW[a]) to minimize yield failure concerns, is an ongoing process. As line widths for semiconductor devices become tighter, it has become critical to address not only particulate and ionic contaminants, but also specific organic issues. A service company[b] has developed processes that specifically address the total organic carbon (TOC) levels coming from elements such as chloroform, urea, isopropyl alcohol (IPA), and others to reduce them to sub part-per-billion (ppb) levels. This has been shown to have significant benefits in integrated chip (IC) manufacturing, and improved life cycle costs of critical process equipment components.

This article will explain the process and the benefits where TOC excursions and critical UPW process parameters are maintained for the manufacturing process.

Background

Moore's Law continues to play a defining role in integrated circuit (IC) manufacturing; "the law," simply said, is that the number of transistors in a single microprocessor will double every 18 months in order to keep up with leading edge technology in the industry. In order to meet the technology requirements, circuits are to be packed into a microprocessor at 22 nanometers (nm) and below. The common microchip is also being packaged into smaller devices and applications, presenting a number of challenges for manufacturers, including providing critical UPW.

By Alan Knapp
and Gareth Thomas
Siemens Water Technologies

ISSN:0747-8291.

COPYRIGHT (C) Tall Oaks Publishing, Inc. Reproduction in whole, or in part, including by electronic means, without permission of publisher is prohibited. Those registered with the Copyright Clearance Center (*www.copyright.com*) may photocopy this article for a flat fee per copy.

The International Technology Roadmap for Semiconductor (ITRS) indicates a continuing need for the following to reduce the risk of yield problems, especially in the area of logic chip manufacturing:

1. Further reduction in organic and inorganic contaminants.
2. Further reduction in the amount of water consumed in terms of liters per cubic centimeter (L/cm^2) of wafer.
3. An increasing recovery of used water in terms of UPW recycled (reuse after treatment or reclaimed including extracting useful components from waste).

The latest version of ITRS issued in 2009 with certain updates planned in 2010 shows a continuation of this trend.

One of the key elements in this direction is to constantly seek ways to reduce TOC levels. This can be stated to be the quantity of carbon bound up in an organic compound. Most analyses measure the total carbon levels and deduct the inorganic levels to arrive at the organic value.

TOC typically comes from decaying natural organic matter such as humic acid, fulvic acid, amines, in addition to urea from fertilizers, animals and some chemical processes. The synthetic chemical sources may come from incompletely treated industrial and domestic waste streams such as detergents, pesticides, and herbicides. The impact of these organics on semiconductor facilities can be directly attributed to seasonal changes and agricultural activities in most regions. In many municipal water feed streams, the combination of chlorine and the organics produces trihalomethanes (THMs), such as chloroform.

The impact on TOC of 1.0 part per billion (ppb) of chloroform is approximately 0.1 ppb. The impact on TOC of 1.0 ppb of bromoform is approximately 0.047 ppb. Therefore, removing chloroform, or preventing its introduction is very important in minimizing TOC levels.

The primary methods of removing

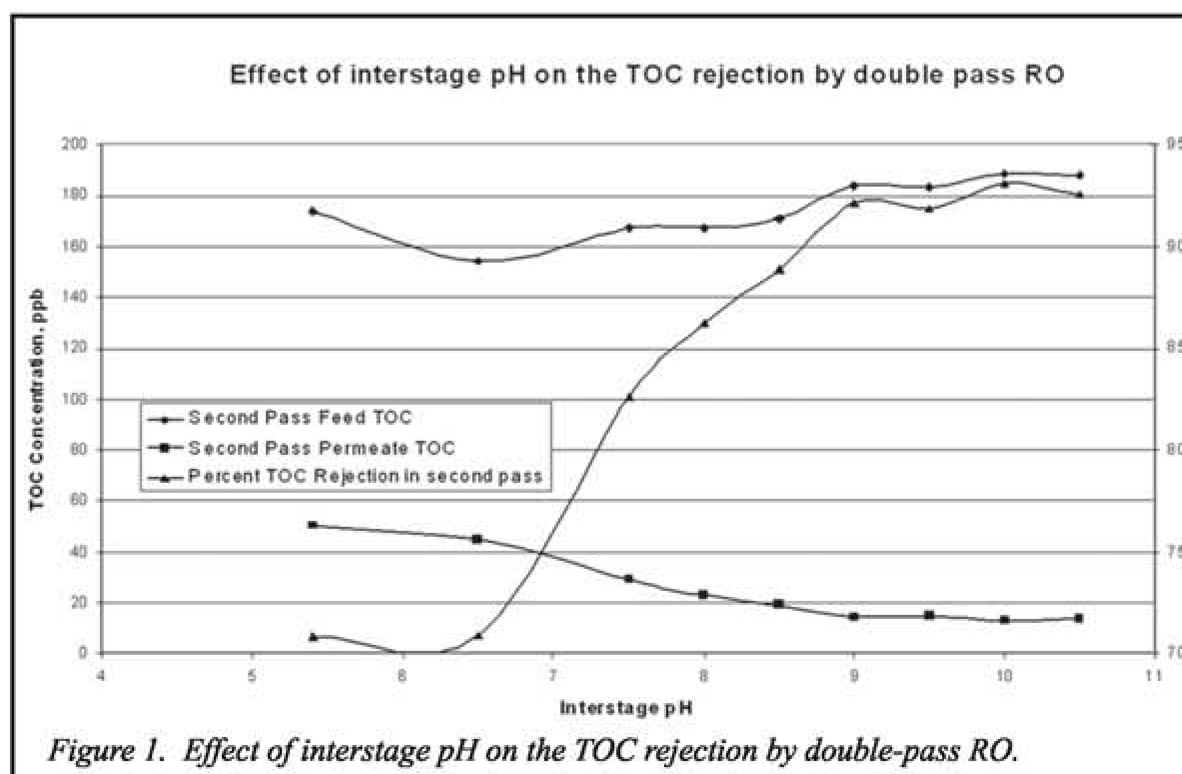

Figure 1. Effect of interstage pH on the TOC rejection by double-pass RO.

Figure 2. A typical UPW UV system.

Figure 3. A typical UPW membrane degasification system.

TOC are through the use of activated carbon absorption and the use of hyperfiltration (typically reverse osmosis [RO]). Increasing the pH of the liquid takes advantage of the hydration impact on the organics to increase the molecular weight and therefore improve the rejection rate, as shown in Figure 1. Increasing the pH above 9 has an additional benefit of also improving the rejection of boron by the RO membrane. THMs are removed readily by activated carbon. However, the absorption capacity of the carbon is limited, and TOC spikes associated with THMs are common where the carbon process is designed for chlorine removal or is infrequently changed.

The other main method of reducing the residual level of TOC is through applying heat, especially combustion and ultraviolet (UV) irradiation, with or without a chemical oxidizer such as persulfate or iron and hydrogen peroxide (Fenton's reaction), or with the use of a catalyst such as platinum or titanium dioxide.

In a January 2003 article in *ULTRAPURE WATER*, Thomas and Dey (1) described a process using 185-nm wavelength UV to reduce THMs from high-purity water, especially chloroform. It showed that, subject to the energy input level, at least 40% of the THMs could be removed. Figure 2 shows a typical UPW UV treatment system.

Brominated hydrocarbons (e.g., bromoform [$CHBr_3$]) break down easily in the presence of 254-nm wavelength UV light into carbon dioxide and bromide ions. However, chlorinated hydrocarbons such as chloroform ($CHCl_3$) do not break down easily. The use of heat changes the bond strength of the organic structure of chloroform. The change enables the gas transfer membrane to extract the now volatile organics, thus reducing the residual TOC levels (2). Figure 3 shows a typical UPW membrane degasification system.

Sodium bromide and ozone, together with UV for oxidation and ozone destrucyion have been used to reduce urea levels. This approach has been developed to address what was believed to be the natural decomposition of urea into ammonia. The concern was that this decomposition would adversely affect the acid catalyzed chemical amplified photoresists that are used with DUV (deep ultraviolet) lithography.

Advanced Oxidation

For certain complex organics, especially non-degradable and volatile organics, there has been a move towards advanced oxidation commonly referred to as the "advanced oxidation process" (AOP). There have been a number of different methods such as:

- Hydrogen peroxide and UV irradiation.
- Ozone and UV irradiation.
- Ozone and hydrogen peroxide and UV irradiation.
- Fenton's reagent (ferrous sulfate and hydrogen peroxide) and UV irradia-

tion.

- Persulfate and UV irradiation.
- Caro's acid (peroxymonosulfuric acid) and UV irradiation

Where IPA (C_3H_8O) is present, the use of UV irradiation changes it into acetone. The problem with acetone as an organic is that it is so close in molecular weight to water that it is virtually impossible to completely break it down; therefore, an additional process is needed to completely reduce IPA.

Oxidants and UV has been used in the semiconductor industry for some time, but is not always a successful TOC reduction process. The use of persulfate previously had been limited in its scope because of the impact of contaminants such as sulfate, which is known to aid in the breeding of bacteria and is an ionic contaminant.

The persulfate/UV process has now been refined with critical improvements in the reactor design, allowing for reduction in power and capital costs along with reduction in chemical utilization.

One equipment maker[b] has recently introduced its own advanced oxidation system[c] (AOS), which has a patent pending, to reduce and control THMs, urea, and IPA, in addition to controlling other critical process parameters. These are the primary organics that can require a more elaborate treatment and cause potential risk to an IC manufacturing facility.

This AOS technology has been successfully applied at semiconductor fabs in point-of-use (POU) applications, in which the TOC level is normally low but the customer experiences TOC excursions in the UPW polishing loop throughout the year.

The system is designed as a POU system and provides the best solution for removal of target trace organics with an expected positive effect on yield. It also provides a more effective destruction of IPA and other organic compounds than traditional ozone and peroxide/UV systems, in typical reuse and reclaim designs.

Figure 4 shows data that represents the impact of a TOC elevation in the feedwater that worked itself through the complete UPW system. The primary organic in the system during the TOC elevation shown here is urea.

The UPW system is fed to the POU AOS to maintain a TOC level below 1.0 ppb, typically 0.5 ppb, with up to 18 ppb in the feedwater (polish loop quality). Note: Both TOC analyzers were calibrated parts-per-trillion (ppt) analyzers.

In applications using medium pressure UV, the generation of hydroxyl ions and hydrogen peroxide is well understood. However, once the water enters the mixed bed, there is a catalytic effect whereby the dissolved oxygen is released. There

MEMBRANES INTERNATIONAL INC.

Ion Exchange Membranes for Electrodeionization

219 Margaret King Avenue, Ringwood, NJ 07456 USA
Tel 973.998.5530 Fax 973.998.5529

email:customerservice@membranesinternational.com
www.membranesinternational.com

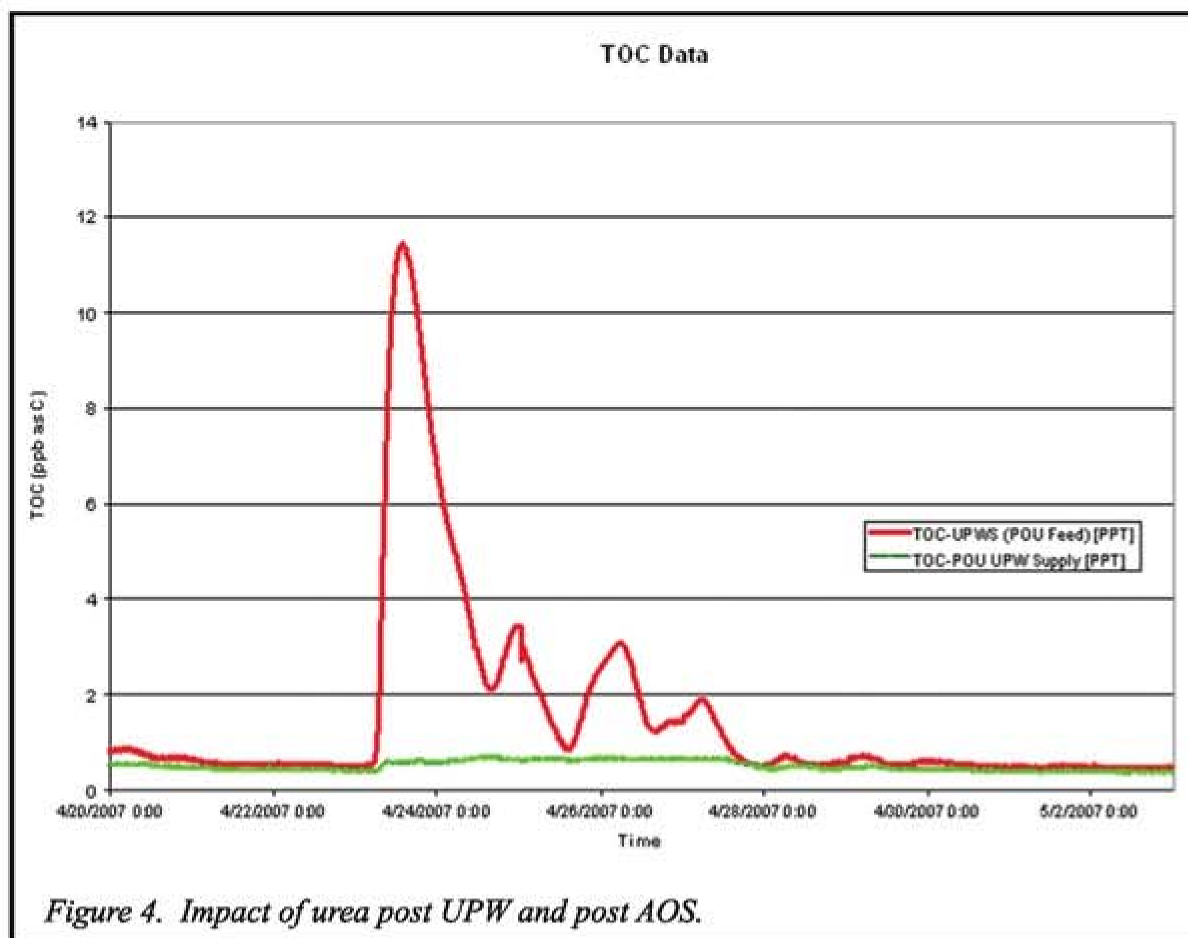

Figure 4. Impact of urea post UPW and post AOS.

is typically a trade off of TOC reduction versus an oxygen increase in many applications. The AOS process includes the use of the membrane vacuum degasifiers to remove the generated dissolved oxygen. Ammonia from the urea and carbon dioxide from the breakdown of the organics is removed in a mixed-bed ion exchange (IX).

The equipment company has developed a process that purifies ion-exchange resin to close to equilibrium values, so that the product quality for residual metals is reduced to sub-ppt levels. Specialty IX resins[d] are part of the process with the AOS so that any trace metals and ionic contaminants are consistently removed. The residual metals levels are below 1.0 ppt.

The goal is to provide consistent process control to critical fab tools. So far, our experience with the AOS has shown that the quantity of residual particles is consistently less than 100 particles per liter (p/L) at 0.05 micron.

The heat exchanger control is also carefully monitored so that the temperature variability is maintained within ± 0.1°C. This helps ensure that there is minimal variability in the feedwater condition, and maximizes the effectiveness of the UPW when it is used by the fab tools.

Summary

UPW continues to play a critical role in the manufacture of integrated circuits, while at the same time, environmental conditions and the desire to reduce water use in today's semiconductor facilities drive the need for new process technology. The purpose of the AOS equipment described in this article is to maintain consistent POU product quality during excursions from the feed or reuse water sources for critical manufacturing processes such as found in a semiconductor plant.❑

Ultrapure Water® on CD

Digital editions of ULTRAPURE WATER® journal or previous issues of 2009 and 2008 are now available on CD.

Issues are complete as published and available as Adobe Acrobat PDF files.

Only $60 each.

Order your copy now at:

www.ultrapurewater.com/zencart

References

1. Thomas, G.; Dey, A. "Removal of Trihalomethanes from RO Product Water Using UV 185-nm Technology", *ULTRAPURE WATER 20(1)* pp. 18-24 (January 2003).
2. Thomas, G.; Dey, A. "Method of Removing Organic Impurities from Water", U.S. Patent No. 6,858,145 (Feb. 22, 2005).

Endnotes

[a]In the text, the term UPW refers to semiconductor-grade water produced in microelectronics facilities. Its quality parameters are defined under the International Technology Roadmap for Semiconductors (ITRS).

[b]Siemens Water Technologies Corp., based in Warrendale, Pa., is the equipment company referred to in the text.

[c]Vanox™ is the advanced oxidation system referred to in the text that has been introduced by Siemens Water Technologies.

[d]NR-30 MEG Nano is a specialty ion-exchange resin manufactured by Siemens Water Technologies.

Author Alan Knapp is marketing director of semiconductor and solar marketing for Siemens Water Technologies. He has been active in the water industry since 1984, with a focus on semiconductor applications since 1995. He can be reached at alan.knapp@siemens.com.

Coauthor Gareth Thomas was employed for several years as technology manager of semiconductor and solar for Siemens Water Technologies in Asia. Before that, he was managing director of Chemitreat from 1988 to 2008. He holds patents that focus on the production of ultrapure water. Mr. Thomas was employed by Siemens Water Technologies when this article was written.

This paper was presented at ULTRAPURE WATER Micro 2009, which was conducted Nov. 4 and 5 in Portland, Ore.

Key words: ION EXCHANGE, ORGANICS, PARTICLES, SEMICONDUCTORS, STANDARDS, TOC