MATERIALS

MINIMIZING PARTICLE AND METAL ION CONTAMINATION ON FLUID CONTROL COMPONENTS – UPDATE

The semiconductor industry is forecasted to grow at 5.1% Compound Annual Growth Rate (CAGR) in millions of square inches (MSI) of silicon (1) because of a growing middle class in developing countries (2). The main semiconductor market drivers (3, 4) in smart phones, tablets, IPTV set-tops, mobile PCs, and autos will continue to increase, forcing the industry to amplify capacity through advanced technologies.

The International Technology Roadmap for Semiconductors (ITRS) forecasts DRAM (dynamic random access memory) ½-pitch size reductions from 36 nanometers (nm) in 2012 to 28 nm in 2014, with corresponding critical particle size reduction to 18 nm, and critical metal ions from 1,000 parts per trillion (ppt) to 100 ppt by 2014. At the same time, the cost per gate, while constantly decreasing from 2002 (at 90 nm) to 36 nm in 2012, will start to increase to 0.0275 \$/million gates at the 20-nm level, and > 0.278 \$/million gates at the future 14 nm (5). This massive technology shift will have profound impact on wafer cost and yield optimization.

An *ULTRAPURE WATER* article by Cellucci and Michalchuk (6) described new valve design improvements and research dedicated to material optimization to meet the growing demand of an advancing technology in the semiconductor industry. This ongoing and never ending process has led to continuous improvements in valve component and material designs, including adoption of seals that feature TFM™ (a polytetrafluoroethylene [PTFE] derivative) instead of the typical elastomers used such as ethylene propylene diene monomer (EPDM), Viton or Kalrez.

In June 2007, the authors were informed by a major North American fab of their requirement to substantially reduce metal ions, and the impossibility of achieving the needed cleanliness with elastomers exposed to 18 megohm-cm deionized (DI) hot water. The complexity of this was multifaceted with the need to create a regulator without elastomers to achieve the desired reduced metal ion contamination at very high flowrates, with positive shut-off, while minimizing organic and bacteriological growth.

An early portion of the text in Reference 6 notes: "It was determined that the primary contributors to elemental contamination varied by manufacturer, but included particularly high elevated levels of metallic ions: iron (Fe), lead (Pb), calcium (Ca), sodium (Na), potassium (K), and zinc (Zn)."

Particle contamination was also measured; however, based on hot DI water purging and existing microfiltration methods, particle shedding during flow changes with average time to drop back to baseline was reduced to a level that was less influential on yields. The level of metal ion contamination was being measured at the surface of the wafer at a molecular level, which 1. had not been done before; and 2. was not feasible by most industrial, fluid control standard measurement methods (i.e., titration column isolation, and spectroscopy, among others). This is accomplished using mass spectroscopy and prolonged static leach-out tests (6).

It is important to remember in comparing the test values obtained for fluid control components with the markedly lower limits in SEMI F57 (7), that this standard is in actuality best applied to materials such as perfluoroalkoxy (PFA) and TFM, and that very few (if any) fluid-control regulating components are made exclusively of one or both of these materials, as they markedly increase particle shedding.

By limiting the movement of a TFM diaphragm and using polyvinylidene-fluoride (PVDF), and PTFE wetted parts with highly pretreated, microfinished surfaces, the goals of minimizing particle generation, metal ions, and reduction of stabilization time were achieved.

We continued our research to obtain previously unheard of cleanliness levels (in ppt) for fluid control devices. Our extensive journey began by searching for best materials and manufacturing processes to minimize, or eliminate any contributing contamination in pressure regulators and other fluid control devices used within the semiconductor manufacturing process.

Testing-Materials Research

An Ishikawa cause-and-effect diagram clearly demonstrated that elastomers contributed mightily to the contamination levels— more significantly than PFA, HP740 PVDF, and PTFE body materials currently in use for process control components, and in particular, pressure regulators.

Initial elastomer selection criteria included the following:

1. Elastomeric properties— memory/durometer maintained with a positive seal.
2. Resistance to aggressive liquids.
3. Resistance to aggressive sterilizing gases (i.e., ozone).
4. Particle generation.
5. Total organic carbon (TOC) generation.

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Plast-O-Matic Valves

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6. Eliminate metal ion contamination on surface and throughout the material (minimal leaching).

Because of its unique bonding characteristics, Zn litharge has been used to enhance the elastomeric and durability properties of EPDM and other seals for years. Based on knowledge of EPDM curing methods, we surmised it to be the likely source for high Zn contamination in existing EPDM seals in the tested regulating valves.

Elastomeric testing methodology. Here is a summary of the testing approach:

1. The elastomeric samples were prepared and leached in accordance with SEMI Provisional F57-0301 (7) and SEMI F40-0699 (8).

2. The elastomers were pre-cleaned by rinsing 10 x with high-purity water with a 2-minute (min) soak in between rinses (as per SEMI F40).

3. The samples were agitated manually for 1 min once per day as per SEMI F40.

4. Two leach blanks were also prepared, in a polypropylene bottle for anions and a PFA bottle for TOC and metals, and leached under identical conditions to the samples, using high-purity water from the same source.

5. The resulting values were blank subtracted.

6. The leach conditions are given in the report.

Initial testing proved that our hypotheses to be correct. The efficacy of one company's[a] internal, cleaning process is illustrated in Table B of Reference 6 (p. 27).

Subsequent elastomeric research findings. Having dramatically reduced metal ion contamination contributed by elastomers in the flow path, we initiated diaphragm testing with fully fluorinated resins (i.e., PTFE, TFM, and PFA). With the recent high-purity advances to TFM materials, knowing that most non-elastomeric materials would have particle-shedding issues, we selected TFM and began to design a regulator diaphragm that minimizes motion during the stabilization process at flow transition points.

Initial test results showed TFM and PVDF HP740 (see Table C (9) of Reference 5, p. 28) to give excellent results.

Upon subsequent improvements to surface finish and proprietary cleaning processes, tests results were obtained in March 2012 that gave an order of magnitude improvement in cleanliness. These results are shown in Table A (some table data was from Reference 10).

Body Material Testing

PVDF material is used in the semiconductor manufacturing process because of its outstanding mechanical and physical properties: it is easier to work than PTFE, has high strength, superior rigidity, and is very resistant to cold flow. Table C in Reference 6 illustrated some of the distinct differences between PVDF materials. It is interesting to note the cleaner HP740 PVDF material appears contaminated and with its milky, off-white appearance less clean than the Kynar® 1000 material. Pure white PVDF is not cleaner, and quite the contrary, contaminates more than Kynar 740.

Through testing PVDF material in various forms, it was determined the raw pellet material composed of Kynar 740HP has not only the lowest metal ion contamination but in the molding process, typically dependent on breakaway methodology, will have minimal additional hydrocarbon contamination.

The low contribution to contamination by the molding process is quite contrary to the extruding and machining process. Extruding and subsequent machining of bar stock Kynar 740HP, due to the necessity of lubrication, will introduce hydrocarbons at a significant level.

Assembled valves without initial cleaning generated TOC at 110,000 micrograms per square meter (µg/m^2). It was determined the removal of hydrocarbon contamination is not easily removed if the cleaning takes place after assembly. Cleaning after assembly creates the issue of contaminated entrapped areas where, after assembly and after installation with 18 megohm-cm DI water processes, leaching of contaminants will continue to occur.

In a machined component, the necessity of initial cleaning, after machining but before assembly, becomes even more critical to the cleanliness of the final product. The experiential data and processes developed have been able to eliminate any significant levels of TOC and minimize other metal ion contaminants introduced by the extruding, machining, and welding processes.

Summary of Findings:

1. Arkema Kynar 700 series PVDF pellet meets the purity requirements of SEMI F57 for the entire range of referenced contaminants.

2. Arkema Kynar 1000 commercial pellet meets the purity requirements of SEMI F57 for the entire range of referenced contaminants with the exception of K and Na.

3. Kynar 740 rod is contaminated to some degree by the extrusion process.

4. By contrasting the test data for the Kynar rods interior test results with the readings for different size of valves, we have concluded that the Kynar 740 material is cleaner to use as an ultrahigh purity polymer for the body and other fluid-path components.

Final Results

After determination of best PVDF grade material to be used, we focused on the valve interior design to further minimize particle generation with flow path enhancements; such as surface finish, smoothness, and curved surfaces on body and stem, all aimed to provide an easy fluid flow through the inlet and outlet transition areas. We used the test methodology and test stand illustrated below and obtained the much improved results shown in the final reports. Figure 1 in Reference 5 (p. 24) shows the SEMI F104 test system and Figure 2 (Reference 6, p. 26) shows the initial flush data for the pressure regulating valves.

A close correlation was found between all four samples tested. Please note that spool piece had greatest particle drop-off in shortest time because of minimal surface area. The valve seal material is PFA and the body material is Kynar 740.

Conclusions

The design of fluid control devices that provide ultra-low levels of contamination in terms of particulates and undesirable ionic species represents a huge challenge. There is the need to integrate materials with uniquely different properties and limitations into a device capable of performing the required regulating function accurately, reliably, and at a reasonable cost.

Static and dynamic elastomers, the regulating components in fluid control systems, must contribute minimal quantities of metallic ions, yet be extremely durable in terms of cycle life. Elastomers must also conform to the necessary pressure, temperature, and chemical resistance under actual process conditions. Body materials can contribute metallic ions by injection molding, extrusion, machining, welding, and assembly. In contrast, particulate contaminants are because of friction, resulting from mechanical contact between mating parts.

Elastomers are cleaned and rendered as contaminant-free as possible by means of surface scavenging with a proprietary acid system, an initial surface treatment that allows the surface to purge itself of ionic contaminants, followed by an 8-h rinse of 18 megohm-cm DI cold and hot water. Kynar 740, the body stem material of choice for high-purity valves, is purged of ionic contaminants by means of a proprietary pre-cleaning process, followed by sequential rinsing in hot and cold 18-megohm-cm DI high-purity water for 8-h periods.

This process continues to be effective at minimizing particulate contamination. Further material improvements have been achieved regarding metal ion contamination by the use of TFM, as the best non-contaminating diaphragm material.

Material selection, machine design, process improvements, cleaning, and purification methods, all major factors in reducing contaminants, will continue to evolve; maintaining reliability, cleanliness, outstanding performance, and the highest quality in the semiconductor piping components market.❑

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TABLE A
Leach Test Studies[1]

Description	*Comment*	*Units*	*Li*	*Na*	*Mg*	*Cr*	*Fe*	*Ni*	*Cu*	*Zn*	*W*	*Mo*
Company A	~48 h-HPW rinse At < 10 gpm	ng/sample	*	77,000	70,000	*	318	41	97	422	122	58
Company G	New w/4-h HPW rinse	ng/sample	222	5,998	2,000	8	537	60	128	965	95	21
Company G	New w/70-h HPW rinse at >20 gpm	ng/sample	17	2,837	1,004	9	93	36	123	988	113	LDL
Supplier* UPR 2-in	TFM diaphragm, 48-h rinse at 20 gpm	ng/sample	*	457	98	*	114	11	57	190	*	*
Description	*Comment*	*Units*	*Ti*	*Co*	*Ag*	*V*	*Mn*	*Zr*	*Cd*	*Sb*	*Sn*	*High-Risk Metals*
Company A	~48 h-HPW rinse at < 10 gmp	ng/sample	688	*	*	*	*	*	*	*	N/R	560
Company G	New w/ 4-h HPW rinse	ng/sample	180	LDL	LDL	LDL	LDL	LDL	LDL	LDL	N/R	1,053
Company G	New w/70-h HPW rinse at > 20 gpm	ng/sample	LDL	LDL	LDL	LDL	LDL	LDL	LDL	LDL	N/R	1,147
Supplier* UPR 2-in	TFM diaphragm 48-h rinse at 20 gpm	ng/sample	*	*	*	*	*	*	*	*	*	258

[1]At 65°C for 7 hours (h) comparing 2-inch (in) ultra-high-purity pressure regulators.
* = no detection
HPW = high-purity water LDL = low detection limit
Testing dates: 1/16/09 through 3/30/12

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Endnote

*Plast-O-Matic Valves Inc., Cedar Grove, N.J., is the supplier referenced in the text. The UPR 2-inch (in) listed in Table A is a company offering.

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