MINIMIZING PARTICLE AND METAL ION CONTAMINATION ON FLUID CONTROL COMPONENTS

Semiconductor device manufacturers face many difficult challenges in their quest to adhere to Moore's Law, which states "device complexity doubles every 18 months." Development of new materials and processes at the atomic level, feature size reduction, increased chip size, increased wafer diameter, and ultra-clean processing all have a direct bearing on the quality and cost of semiconductor products. However, the greatest challenge in every semiconductor facility is the avoidance of Moore's second law, which states that "facilities costs increase in semi-log scale" (1)

In June 2008, it was determined that pressure regulators and other fluid control components contributed to significant levels of metal ion contamination and particle shedding, all negatively affecting chip yields in major semiconductor fabs in North America. It was determined that the primary contributors to this 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, deionized (DI) water cleanliness and existing microfiltration methods had already been reduced to a level where they were less influencing to yields, than the metal ion contamination. The level of metal ion contamination was being measured at the surface of the wafer at a molecular level, which had not been done before and 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.

Consequently, the effects of SEMI F-57 (2) were ubiquitous within the fluid controls community and the need to have contaminant levels reduced to SEMI F-57 levels was clearly pressing. The SEMI F-57 Standard addresses 5 separate categories of contaminants: total organic carbon (TOC), 7 ionic contaminants, 16 metallic contaminants, plus particles, and surface roughness. The maximum acceptable levels of these contaminants are expressed in micrograms per square meter ($\mu g/m^2$). It is important to remember in comparing the test values obtained for fluid control components with the markedly lower limits in SEMI F-57, that this standard is in actuality best applied to materials such as perfluoroalkoxy (PFA) and TFM™-grade polytetrafluoroethylene (PTFE), 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.

Thus, we began our research to obtain previously unheard of cleanliness levels (in the parts per billion (ppb) range) for fluid-control devices. Our journey began by searching for best materials and manufacturing processes to minimize, or eliminate any contributing contamination of pressure regulators and other fluid-control devices used within the semiconductor manufacturing process.

Testing—Initial Materials Research

An Ishikawa cause-and-effect diagram was used on assembled valves to isolate all independent variables causing metal ion contamination. We opted against regression analysis, as it gives misleading results when small effects and questions of causality based on observational data are used. The requirements for reliability, sensitivity, and robust regulator performance are all based on strong reliance to elastomers. ethylene propylene dien monomer (EPDM), Viton, and other elastomers. While minimizing creep, they are

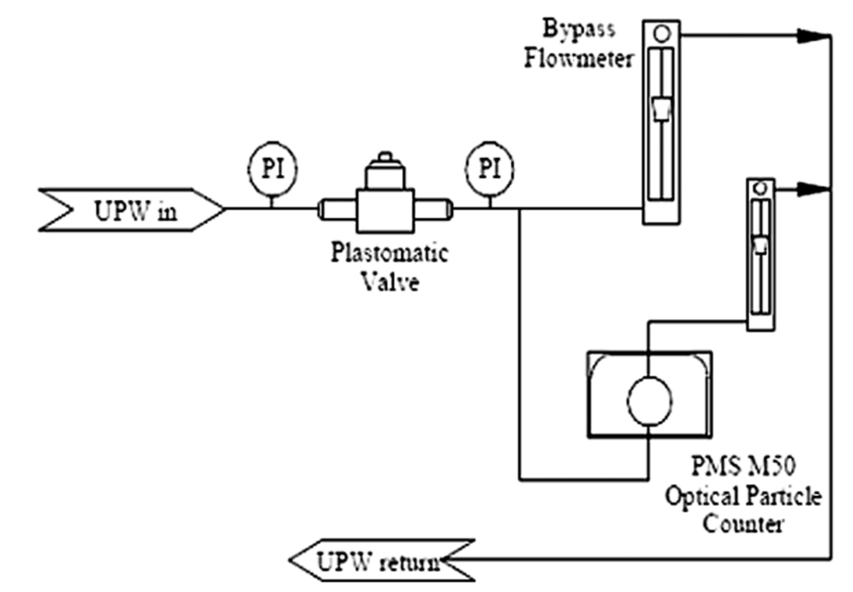

Figure 1. SEMI F-104 test system.

By Ed Cellucci,
and Greg Michalchuk
Plast-O-Matic Valves

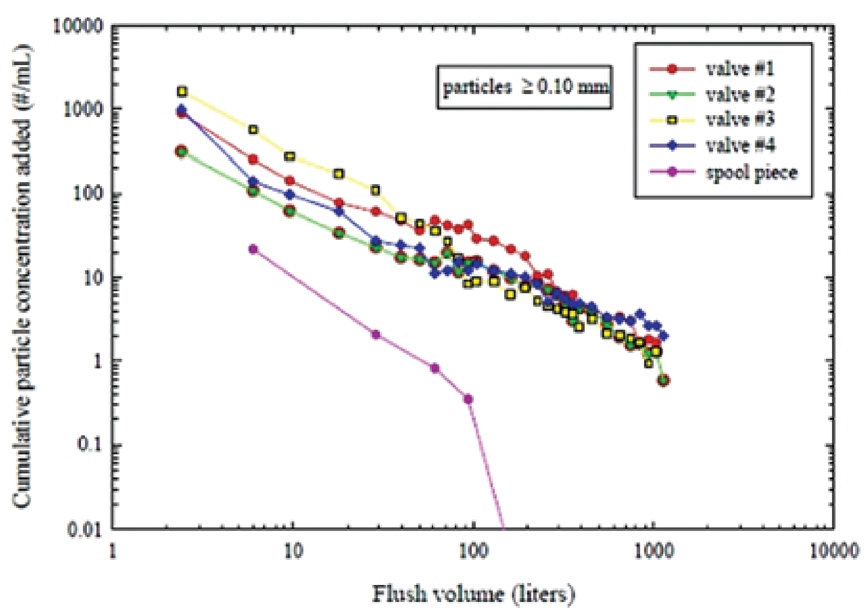

Figure 2. Initial flush data for the pressure-regulating valves Model UPR-PF10.

used for positive shut-off applications, to extend the useful life of fluid control products, and to increase the sensitivity and performance of sensing elements. Elastomers of various durometers and designs, such as U-cups, are excellent seal materials between the valve body, stem, and other moving components used to provide reliable performance, and longevity, while compensating for minor particle contamination.

Zn's elevated level of contamination— because of elastomers being cured with Zn litharge, which improves compression set and acid resistance, was an apparent, initial first major source of contamination. Thus, elastomeric research was conducted first.

Elastomeric research. Here are some of the initial elastomer selection criteria used:

1. Elastomeric properties— memory/durometer maintained.

2. Resistance to aggressive liquids.

3. Resistance to aggressive sterilizing gasses such as ozone.

4. Particle generation.

5. TOC generation.

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

Due to 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.

Elastomer testing nethodology. Here are comments on the testing approach:

1. The elastomer samples were prepared and leached in accordance with SEMI Provisional F57-0301 and SEMI F40-0699.

2. The Elastomers were pre-cleaned by rinsing 10 times with high-purity water with a 2-minute (min) soak in between rinses per Semi F-40.

3. The Samples were agitated manually for 1 min once per day 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 UPW from the same source.

5. The resulted values were blank subtracted.

6. The leach conditions are given in the report (1).

Initial testing proved that our hypotheses to be correct. Based on data from Balazs (3), our initial assumptions regarding EPDM contamination were proven true. Note the Zn contamination levels and other contributing high metal ions (e.g., Al, Fe, Cu, and Ca, among others) contamination.

Knowing the likely source of Zn contamination, we had already begun the process of investigating the availability of other curing methods. It was decided to test peroxide-cured EPDM. It was believed the peroxide-cured EPDM would minimize metal ion contamination levels in positive shut-off regulators. The EPDM seals used and tested were peroxide cured with the results multiplied, based on the surface areas exposed.

The results we obtained were further improved by a proprietary cleaning process, and scavenging of the elastomers prior to testing with a procedure involving:

1. Mixed-acid wash to make the surface amenable to the scavenging of metal ions by the subsequent rinses.

2. Hot DI water rinse for 8 hours.

3. Cold DI water rinse for 8 hours.

The results (4) from July 2008 showed there was a substantial decrease in some of the metal ion contaminants. For example, Zn was reduced by 91%, Pb by 96%, and Al by 62%! The assessment of contamination beyond elastomeric impact was measured after machining, welding, and assembly of pressure regulators. Tables A and B (5) summarize our findings.

Additional testing was done with peroxide-cured material, with proprietary cleaning, including acid washing (hot and cold), and 8-hour DI water rinse up. The effectiveness of our internal, proprietary cleaning process can be seen on Table B.

Having dramatically reduced the metal ion contamination contributed by elastomers in the flow path and knowing better results could be obtained with other non-elastomeric materials (i.e., PTFE, TFM, PFA), we moved to testing body materials.

Body Material Testing

Polyvinylidene fluoride (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 very high strength, superior rigidity, and is very resistant to cold flow.

Table C below illustrates some of the distinct differences between PVDF materials. It is interesting to note the cleaner HP740 PVDF material appears contaminated and with it's milky off-white appearance that is less clean than the Kynar 1000 material. Pure white PVDF is not cleaner, and quite the contrary contaminates more than Kynar 740 (6).

Table D illustrates the author's confirmation of the above material test results with valves and pressure regulator bodies[a]. It can be clearly seen from the data, that the extruding, machining, and welding processes add significant amounts of contaminants in the assembly of valves.

Here is a summary of the findings:

1. Arkema Kynar 700 series PVDF pellet meets the purity requirements of SEMI F-57 for the entire range of referenced contaminants.

2. Arkema Kynar 1000 commercial pellet meets the purity requirements of SEMI F-57 for the entire range of referenced contaminants with the exception of potassium (K) and Sodium (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, the author's have concluded that the Kynar 740 material is cleaner to use as an ultra high-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 in Figure 1 (7) and obtained the much-improved results shown in the final reports. The figure shows a schematic of a test system designed to evaluate valve cleanliness during the initial flush at 1 liter per minute.

A close correlation was found between all four samples tested, as seen in Figure 2 (7). Please note that the spool piece had the greatest particle drop-off in the shortest time because of a minimal surface area. The valve seal material is PFA; 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 represent a huge challenge because of the need to integrate materials with uniquely different properties, and limitations into a device, capable of performing the required function accurately, reliably, and in a cost effective manner.

Static and dynamic elastomers, the flexible 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, whereas particulate contaminants are due to 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-hour 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-hour periods. This process effectively minimizes particulate contamination. Further material improvements can be achieved regarding metal ion contamination by the use of PTFE (albeit with an increase in particle shedding) and the expensive TFM, as the best non-contaminating diaphragm material.

Proper material selection, machine design improvements, and manufacturing process changes with proprietary cleaning methods were all major contributors to the successful outcome in reducing contaminants, while maintaining reliability, outstanding performance, and the highest quality in pressure regulation at a reasonable cost.

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Endnote

[a]The valves and pressure regulator bodies reference to in the text came from Plast-O-Matic Valves Inc., Cedar Grove, N.J.

Author Ed Cellucci is national sales manager with Plast-O-Matic Valves, Inc. He has been with the company 13 years, and has considerable experience with the semiconductor industry. Mr. Cellucci is a member of SEMI, with 25 years experience in high-purity water processes. He previously represented

TABLE A
Pressure Regulator (PRHM) Valve Testing Data

Arkema @ Balazs SEMI F-57 (µ/m²)		PRH075EP-PF	PRH100EP-PF	PRH150EP-PF
Pb	1	ND	ND	ND
Zn	10	140	80	140
Ca	30	920	1,200	770
W	no spec	7	17	5.5

Source: Reference 5

TABLE B
Results from Proprietary Cleaning Process

Ion	PRH150 1.5*	PRH075 0.75*	Metal-Ion-Free Elastomers (*)	
			w/o Clean	w/Clean
Ca	730	550	50	0
Zn	50	90	590	80
Pb	0	27	9	0

*Test performed Nov. 14, 2007 on valves with metal-ion free EPDM elastomers.
Source: Reference 5

Entegris, Parker/Veriflo group and Honeywell while working at Valin Corp. Throughout his career, he has worked with process and high-purity water engineering groups at most of the U.S. semiconductor companies. He holds a B.S. in chemistry and studied at UC Santa Cruz and UC Berkeley.

Coauthor Greg Michalchuk is quality assurance manager at Plast-O-Matic Valves, Inc. He holds a B.S. in biology with a minor in chemistry from Pace University. Mr. Michalchuk has 22 years in the plastics industry, and 42 years industrial experience, which includes employment with Ashland Chemical Corp., Oakite Products, and the Enco division of the American Hoechst Corp.. He is a member of American Society for Quality.

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TABLE C
Kynar PVDF Resin and Extruded Rod High-Purity Water Extraction Tests

	B	C	D	E	F	G	H	I	J	K
1	**Description**		Semi F57	**Kynar 720**	**Kynar 740 5" Rod Outside**	**Kynar 740 5" Rod Inside**	**Kynar 1000**	**Kynar 1000 4 1/2" Rod Outside**	**Kynar 1000 4 1/2" Rod Inside**	**Kynar 1000 3/4 Inch Valve** PRH-075EP-PF
2	**Parameter**	**Units**		**07C6054 720**						
3	(TOC)	(ug/M2)	60,000	7306	19000	17000	9589	21000	20000	110,000
15	**Leachable Anions by IC**									
16	**Parameter**	**Units**								
17	Fluoride (F-)	(ug/M2)	60,000	2922	24000	55000		18000	24000	14,000
18	Chloride (Cl-)	(ug/M2)	3000	3	110	150		99	57	1300
19	Nitrite (NO2-)	(ug/M2)	100	3	4.1			6.3		*
20	Bromide (Br-)	(ug/M2)	100	*						*
21	Nitrate (NO3-)	(ug/M2)	100	3	240	38		500	28	210
22	Phosphate (HPO4=)	(ug/M2)	300	*	14	12		12		510
23	Sulfate (SO4=)	(ug/M2)	300	5	32	46		470	460	450
24										
25	Aluminum (Al)	(ug/M2)	10	0.23	180	130	4	69	38	73
26	Calcium (Ca)	(ug/M2)	30	5.02	250	78	27	140	40	920
27	Copper (Cu)	(ug/M2)		*	20	9.1	1	9.6	5.8	25
28	Iron (Fe)	(ug/M2)	5	*	110	190	1	57	21	88
29	Magnesium (Mg)	(ug/M2)	5	*	61	32	2	29		92
30	Manganese (Mn)	(ug/M2)		*			0		7	2
31	Nickel (Ni)	(ug/M2)	1	*	9.7	3.8	0	7.1	2.4	3.7
32	Potassium (K)	(ug/M2)	15	1.37	130	14	5479	4000	4000	2100
33	Sodium (Na)	(ug/M2)	15	2.47	58	16	279	140	150	810
34	Tungsten (W)	(ug/M2)		0.27	2.2	0.3	5	2.5	0.2	7
35	Zinc (Zn)	(ug/M2)	10	*	140	84	2	220	91	140

TABLE D
Test Results with Valves and Pressure Regulator Bodies

Parameter	*Unit*	*SEMI F57*	*Kynar 1000 Raw Pellet*	*As Extruded Kynar 1000 4.5-in Rod Inside*	*After Machining: Kynar 1000 0.75-in Valve PRH-075EP-PF:*	*After Machining: Kynar 1000 1-in Valve PrH100EP-PF*
(TOC)	$(\mu g/m^2)$	60,000	9,589	20,000	110,000	120,000
Parameter	*Units*					
Fluoride (F^-)	$(\mu g/m^2)$	60,000	--	24,000	14,000	16,000
Chloride (Cl^-)	$(\mu g/m^2)$	3,000	--	57	1,300	1,900
Nitrite (HO_2^-)	$(\mu g/m^2)$	100	--	--	*	*
Bromide (Br^-)	$(\mu g/m^2)$	100	--	--	*	*
Nitrate (NO_3^-)	$(\mu g/m^2)$	100	--	28	210	290
Phosphate (HPO_4^{2-})	$(\mu g/m^2)$	300	--	--	510	890
Sulfate (SO_4^{2-})	$(\mu g/m^2)$	300	--	460	450	820
Aluminum (Al)	$(\mu g/m^2)$	10	4	38	73	120
Calcium (Ca)	$(\mu g/m^2)$	30	27	40	920	1,200
Copper (Cu)	$(\mu g/m^2)$	--	1	58	25	76
Iron (Fe)	$(\mu g/m^2)$	5	1	21	88	80
Magnesium (Mg)	$(\mu g/m^2)$	5	2	--	92	150
Manganese (Mn)	$(\mu g/m^2)$	--	0	7	2	3.6
Nickel (Ni)	$(\mu g/m^2)$	1	0	2.4	3.7	8
Potassium (K)	$(\mu g/m^2)$	15	5,479	4,000	2,100	4,900
Sodium (Na)	$(\mu g/m^2)$	15	279	150	810	1,100
Tungsten (W)	$(\mu g/m^2)$	--	5	0.2	7	17
Zinc (Zn)	$(\mu g/m^2)$	10	2	91	140	80