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Reducing ESD in semiconductor fluoropolymer fluid handling systems while maintaining chemical purity

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Fluoropolymer Electrostatic Discharge (ESD) tubing reduces electrostatic charge to levels below the ignition energy of flammable semiconductor chemicals and maintains chemical purity, ensuring safety and improving process yields.

Semiconductor processes, such as photolithography and wet etch and clean, have become more metal sensitive at advanced process nodes. As a result, extracted metals from chemical delivery systems can cause critical wafer defects that negatively impact process yields. To counter this negative yield impact, fabs have converted many of their stainless steel fluid handling systems that had been traditionally selected for use with flammable solvents to fluoropolymer systems. The change to fluoropolymers resulted in reduced extracted metals in the process chemicals.

However, the increased use of fluoropolymer systems creates new concerns with ESD in components such as PFA tubing. Solvents used in the semiconductor industry have low-conductivity, which enables them to generate and hold electrical charge. When these solvents are transported in fluoropolymer systems there is a significantly greater risk of static charge generation and discharge due to the nonconductive nature of the fluoropolymer materials and the low conductivity properties of the solvents. ESD events generated in fluoropolymer systems that are transferring flammable solvents can create leak paths through the tubing and possible ignition of the surrounding, potentially flammable, solvent-rich environment. An example of an ESD-created leak path through PFA tubing is shown in **FIGURE 1**.

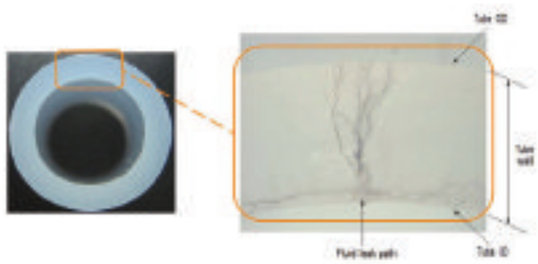

FIGURE 1. Example of electrical discharge through the PFA tubing wall (0.062″ diameter wall thickness).

Factors influencing static charge accumulation

Low-conductivity fluid flowing in nonconductive tubing can cause charge separation at the fluid- tube wall boundary as shown in **FIGURE 2**. This separation of charge is similar to what happens when two materials move with respect to each other and transfer charge as shown in **FIGURE**

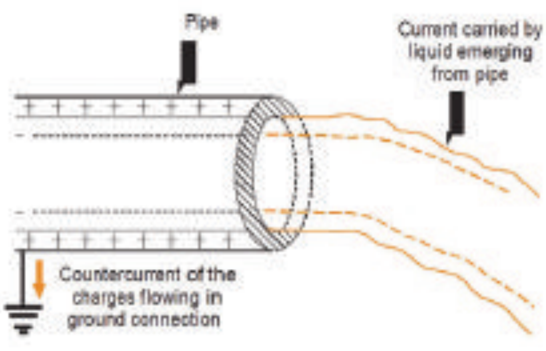

FIGURE 2. Charge separation at the fluid-tube wall boundary [1].

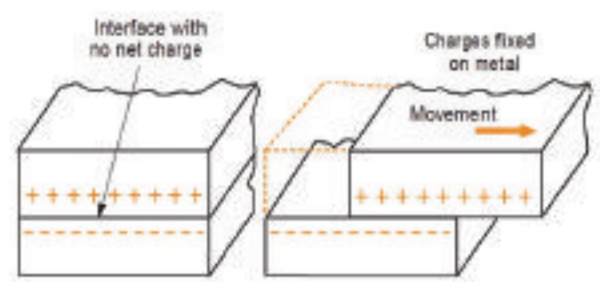

FIGURE 3. Charge transfer caused by movement .1

3. A charge is created as a result of the transfer of electrons and is similar to the charge that develops by walking across a carpet in dry conditions.

Tubing characteristics affecting charge generation

Table 1 lists the tubing characteristics that are factors for charge generation and accumulation. For each characteristic, the effect on the electric field strength is noted. As an example, as the inner diameter of the tube increases there is more surface area for charge generation, resulting in increased charge and electric field strength.

Tube Characteristic	Static Charge Generation or Accumulation
Inside diameter increases	Increases
Conductivity of the tube material increases	Decreases
Tube length increases	Increases
Resistance per unit length of tube increases	Increases
Dielectric constant of the tube wall material increases	Increases
Volume resistivity of the tube wall material increases	Increases
Surface resistivity of the tube wall material increases	Increases

TABLE 1. Tube characteristics affecting the charge that develops on the tube

The overall mechanism of charge generation and accumulation in fluid handling systems is highly complex. A model for this charge generation and accumulation mechanism is described in Walmsley, H. L. (1996).[2] This model describes the factors influencing static charge generation and accumulation as a result of fluid flow in fluid handling systems.

Fluid properties and conditions affecting charge generation

Table 2 lists the fluid characteristics that affect charge generation and accumulation. National Fire Protection Association (NFPA®) 77 9.3.3.1 reads, "In grounded systems, the conductivity of the liquid phase has the most effect on the accumulation of charge in the liquid or on materials suspended in it." [3]

Liquid Properties	Static Charge Generation or Accumulation
Conductivity increases	Decreases
Flow velocity increases	Increases
Dielectric constant increases	Increases
Relaxation time constant increases	Increases

TABLE 2. Fluid properties affecting the amount of charge generated or accumulated

Table 3 lists some low-conductivity chemistries used in the industry.

Gas or Vapor	Conductivity Pico Siemen/Meter (pS/m)
nBA	4300
PGMEA	3×10^4
nMP	2×10^6
Water – DI 18 mega-ohm-cm	5.5×10^6
Acetone	6×10^6
IPA	6×10^6
Cyclohexanone	10.9×10^6
Methanol	4.4×10^7
Ethyl Lactate	1×10^8
Water – Air Distilled	1×10^9

Increasing Conductivity

TABLE 3. Conductivity of fluids commonly used in semiconductor processes

An example of a high-flow velocity ESD event in a non-solvent application

In the process of cleaning a newly installed PFA chemical line, dilute chemistry is introduced into the line followed by a nitrogen purge then ultrapure DI water. Before fully concentrated chemical can be introduced into the bulk delivery line, the water must be removed. To remove the final DI rinse water, high-purity dry nitrogen is forced through the lines at high velocities. The high-purity nitro- gen, along with the water droplets that cling to the inside diameter of the tube, can generate and hold significant static charge. These flow conditions can result in ESD events causing pinholes in tubing and fluid handling components. The same mechanism of charge generation and accumulation may also occur when processing with high-purity steam.

PFA systems for solvent chemical distribution could also go through a DI water flush and nitrogen purge sequence. However, it is far more common to perform only a nitrogen purge, which, when introduced, can cause an ESD event.

Potential effects of ESD on fluoropolymer fluid handling systems

Dielectric strength is the measure of a material's insulating strength. NFPA 77 defines the dielectric strength as "the maximum electrical field the material can withstand without electrical breakdown". [3]

Dielectric strength is usually specified in volts/mm of thickness. As wall thickness and dielectric strength increase the tubing becomes more resistant to electrical breakdown and discharge through the tubing wall.

Standard fluoropolymer tubing, such as PFA, is a very good insulator with high dielectric strength. PFA's insulating properties make it difficult to ground and also contribute to charge generation and storage in tubing systems. There have been field instances where the generated charge was able to create a discharge path through the tubing wall and cause a leak. After the electrical discharge creates the first fluid leak path, it is likely that subsequent static generation will discharge through that same leak path at lower charge levels.

A spark from the outside of the tube to ground may ignite a solvent-laden environment

Two conditions that must be present to start a fire or explosion are an electrical discharge of sufficient energy and a flammable or combustible environment. A flammable solvent leak caused by discharge through the tubing wall or a discharge from the out- side of the tube to ground could cause an explosion.

The energy of a spark and its ability to ignite a flammable fluid or gas is directly related to the square of the voltage level of the discharge as shown in Equation 1. [3] As voltage increases, the energy available to cause ignition in a flammable environment increases.

$$W = \tfrac{1}{2} CV^2$$

Where:

W = energy (joules)
C = capacitance (farads)
V = potential difference (volts)

To assess whether the electrical discharge energy is sufficient to cause ignition, the Minimum Ignition Energy (MIE) value of the fluid or vapor is considered. **Table 4** lists MIE's of commonly used semiconductor fluids

Gas or Vapor	MIE Millijoules (mJ)
Methanol	0.14
Acetone	0.19
IPA	0.21

Less flammable

TABLE 4. Mie of fluids commonly used in semiconductor processes

ESD tubing: proposed solution for mitigating electrostatic discharge

NFPA 77 lists several strategies for mitigating the amount of charge accumulation in electrically nonconductive pipes as a result of electrically nonconductive fluid flow. [4] Several of these are:

1. Reduce flow velocity
2. Reduce wall resistivity to less than 10^8 ohm-m
3. Increase the breakdown strength of the pipe wall material by:
   a. Increasing thickness
   b. Changing material to one with higher breakdown strength
4. Increase conductivity of fluids. (Unlike other industries this is rarely a possibility in the semiconductor process industry where any added particles, especially conductive, are not permitted.)
5. Incorporating an external grounded conductive layer on the piping

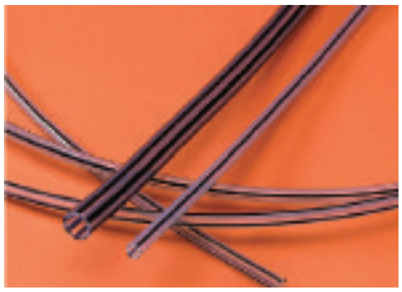

FIGURE 4. Entegris FluoroLine ESD tubing minimizes potential issues related to electrostatic discharge in the fab.

Entegris has chosen strategy #5 and has developed FluoroLine® tubing with static dissipative PFA stripes on the outside of the tubing that can be connected to ground (see **FIGURE 4**). Charge accumulation that develops on the outside of the tube as a result of fluid flow is redirected to external ground paths (**FIGURE 5**). This approach is consistent with the NFPA 77 observation that, "Carbon black can be added to some plastics or rubbers to increase conductivity." [3] Carbon-filled plastics and rubber particles are sometimes sufficiently conductive to be grounded like metal objects.

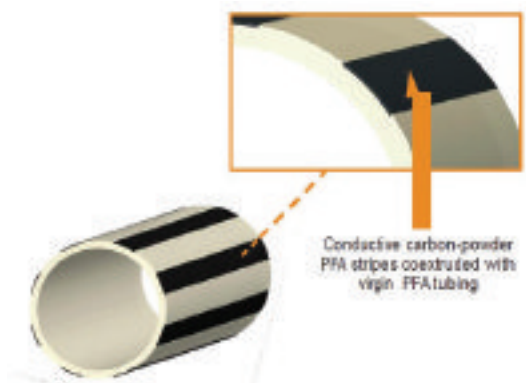

FIGURE 5. 1/2" FluoroLine Electrostatic Dissipative tubing.

FIGURE 6. Test setup of four-foot and 28-foot tube lengths.

The purpose of having coextruded, PFA carbon stripes only on the outer diameter is to preserve the cleanliness of the tubing's pure PFA inner layer. Stripes were also used so the fluid can be seen inside the tubing.

Test assemblies were made to hold four-foot and 28-foot long samples of tubing that simulate how customers would use this tubing (**FIGURE 6**). The tube ends were attached to PFA fittings, the same fittings customers use, so that charge would not be discharged through the end connections.

To simulate a common flow condition used by customers during the commissioning of their systems, an alternating flow of non-conducting 18 Mohm Deionized (DI) water and Extreme Clean Dry Air (XCDA® purge gas) was used. **Table 5** lists the flow ranges of XCDA and DI water along with the corresponding pressures at the tube inlet.

Flow Rate	XCDA Inlet Pressure	XCDA Flow Rate	DI Water Flow Rate
100%	72 psi	200 SCFH	1.2 gal/min
75%	36 psi	150 SCFH	0.9 gal/min
50%	16 psi	100 SCFH	0.6 gal/min
25%	5 psi	50 SCFH	0.3 gal/min

Ambient temperature: 20°C–22.4°C (68°F–72.4°F)
% RH: 19–25%
DI water resistance: 16.9–17.9 m ohm
DI water conductivity: 5.91×10^5–5.59×10^5 pS/m

TABLE 5. Pressure and flow conditions

Tube Tested	Material	OD	Wall Thickness	28' Length	4' Length
Entegris FluoroLine ESD tube, EPLAT-04	PFA, ESD PFA stripes	0.25"	0.039"	X	X
Entegris XKT250-047	PFA	0.25"	0.047"	X	X
¼" tube	304 stainless steel	0.25"	0.098"		X

TABLE 6. Tube and materials tested for electrostatic discharge

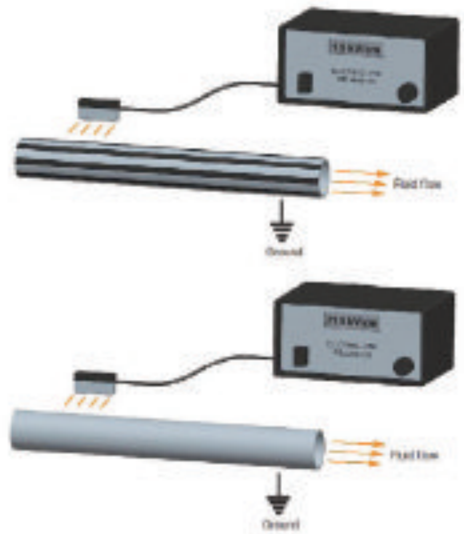

FIGURE 7. Monroe Electronics 257C-1, 20 KV to 20 KV electrostatic field meter testing ESD charge.

The 100% flow rate was the maximum flow through the tube that could be achieved with the test setup. Reduced flow rates were tested to determine the effect of flow rate on the level of charge generated.

A Monroe Electronics 257C-1, 20 KV to -20 KV electrostatic field meter was used to measure the charge level 1 cm from the outside of the tube (**FIGURE 7**). A resistivity meter was used to monitor the resistance of the DI water during the tests.

Note: Clean nitrogen and XCDA, because of their extreme cleanliness, are good insulators and thus possess the ability to create and hold large electrical potential.

Test procedure

- Tube was cut to length and installed in the fixtures with nonconductive PFA polymer fittings at each end. Tube samples, fittings and probe tips were wiped down with IPA after installation.
- DI water resistance was measured and monitored throughout the test.
- The electrostatic voltage field meter was placed with the probe at 1 cm distance from the tube OD.
- Alternating flows of DI water and XCDA were introduced to the tube and the field strength was measured at three different locations along the length of the tube. Each tube was subjected to this flow condition with and without a conductive ground strap connecting the tube to ground. In addition, the flow rate was reduced to 75%, 50% and 25% of the maximum flow rate to determine how the level of charge was affected.

Test conclusions

1. Grounding standard PFA tubing does not reduce the field voltage on the outside of the tube that is produced by flowing XCDA and DI water on the inside. Up to 20 KV field voltage was measured with the XCDA/DI water delivery system (Figure 8).

2. Grounding ESD PFA tubing and stainless steel does significantly reduce the field voltage on the outside of the tube that is produced by flowing XCDA and DI water flowing on the inside (**FIGURE 8**).

3. The field voltage developed along four- and 28-foot tube lengths does not vary significantly for PFA, ESD PFA and stainless steel.

4. With reduced flow rates, the maximum absolute field voltage was reduced for both grounded ESD PFA and PFA tubing (**FIGURE 9**).

5. No fluid leak paths were generated throughout this testing in either the PFA or ESD PFA tube.

6. The capacitance of a four-inch long PFA tube was measured to be 56 pF. Using this capaci- tance value and 20 KV levels of voltage measured by the field meter in this test, the energy of discharge is calculated as 11.2 mJ. This energy level exceeds the MIE of fluids listed in Table 4 and would be expected to cause fumes from these fluids to ignite.

Applying this same equation to grounded ESD tubing where a maximum of 1.5 KV field was measured along with 52 pF capacitance, the discharge energy was calculated at 0.059 mJ and was below the threshold of ignition energy of the fluids listed in Table 4.

Conclusion

As semiconductor processes such as photolithography and wet etch and clean become more metal sensitive at advanced process nodes, fabs are converting to fluoropolymer fluid handling systems. The increased use of fluoropolymer systems creates new concerns with electrostatic discharge (ESD) in components such as PFA tubing. Electrostatic discharge increases the risks of leaks, flammability and potential explosions.

Solvents transported in fluoropolymer systems pose a significantly greater risk of static charge generation and discharge due to the nonconductive nature of the fluoropolymer materials and the frequent low-conductivity properties of the solvents. Understanding the factors that influence static charge generation and

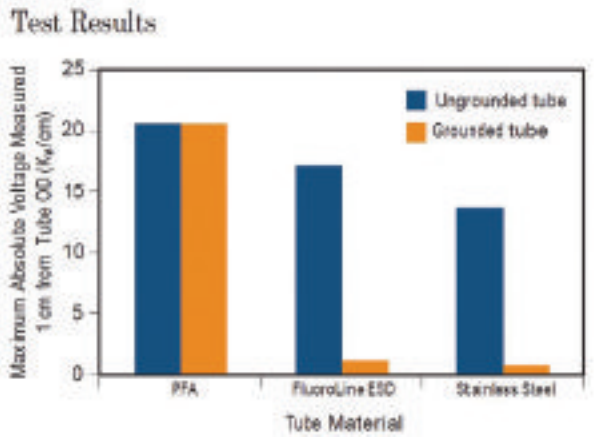

FIGURE 8. Field voltage on the outside of the tube.

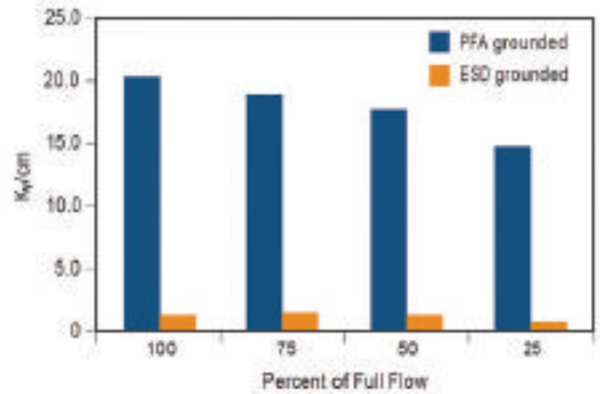

FIGURE 9. Field voltage on the outside of the tube with reduced internal flow rates.

accumulation in a fluoropolymer fluid handling system, Entegris developed an effective solution that is proven to dissipate static charge accumulation on the exterior of the tubing. Entegris' FluoroLine ESD tubing has external static dissipative PFA carbon stripes that redirect charge accumulation from the outside of the tube to external ground paths. This tubing maintains chemical purity, and when properly grounded, minimizes electrostatic discharge events, helping to increase process yields while ensuring safety.

References

1. Walmsley, H. L., "The Avoidance of Electrostatic Hazards in the Petroleum Industry," p. 19 and p. 33.
2. Walmsley, H. L. (1996). "The electrostatic fields and potentials generated by the flow of liquid through plastic pipes," Journal of Electrostatics, Volume 38, p. 249 – 266.
3. NFPA 77: 3.3:16, 6:9:1, 7.4.3.4, 779.3.3.1. National Fire Protection Association.
4. NFPA 77 (A.10.2) National Fire Protection Association. ◆