

# **DELIVERY OF HIGH PURITY CHEMICALS FOR THE MANUFACTURE OF SEMICONDUCTOR MICROCIRCUITS WITH SUB-0.5 $\mu\text{m}$ GEOMETRIES**

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## **1. ABSTRACT**

Technological advances have allowed chemical management systems to meet the increasingly strict purity specifications for semiconductor process chemicals. Careful selection of system wetted materials has reduced metal extraction to analysis detection capabilities. Research on flow hydraulics has led to a better understanding of the behavior of particles in chemical delivery systems. A chemical management system installed at Motorola APRDL/MOS 13, assembled with high purity components, uses several advanced flow control techniques to minimize particulate contamination. This systems, which combines Advanced Stabilized Distribution™, fab-wide distribution and startup stabilization, delivers chemicals with very low particle concentrations ( $\leq 1$  particle/ml  $\geq 0.2 \mu\text{m}$ ) and has negligible metallic extractables.

## **2. INTRODUCTION**

The processes used to produce microcircuits with critical dimensions below  $0.5 \mu\text{m}$  are extremely sensitive to contamination. Both elemental contaminants, especially metallic species, and particulate contaminants are very detrimental to device yield and reliability. One source of these contaminants is the chemicals used in the cleaning, etching and stripping processes used to produce the devices.

Advances in chemical management technology have kept pace with the increasingly strict purity specifications for process chemicals. Careful selection of system wetted materials has reduced metal ion contamination [1]. Improved measurement tools and research on the effects of flow hydraulics on filter performance have led to a better understanding of the behavior of particles in chemical delivery systems [2]. Chemical delivery systems with Advanced Stabilized Distribution and startup stabilization have been designed to minimize particulate contamination through control of chemical flow.

Chemical delivery systems with Advanced Stabilized Distribution maintain a constant flow rate through system filters at all times. Both internal stabilization and fab-wide distribution can be maintained. In fab-wide distribution, chemical flows continuously through the system filters, past the fab points of use and back to a supply tank. When internal filter stabilization is used, chemical flowthrough the system filters and is returned to the supply tank. Chemical is supplied to the fab points of use through a line that branches from this loop downstream of the system filters. There is no flow through the branch except during a chemical demand.

Startup stabilization is used to control particulate contamination when a chemical delivery system is shut down for maintenance or for another reason. The system filters are subjected to a hydraulic shock upon startup, releasing a very large number of particles into the chemical [3]. Startup stabilization prevents these particles from reaching the points of use. The chemical is polished, that is, particles are removed by recirculating it through the system filters, prior to release to the fab.

Delivery systems incorporating both Advanced Stabilized Distribution and startup stabilization were designed to deliver the high purity chemicals needed to manufacture PowerPC<sup>®</sup> chips at Motorola APRDL/MOS 13. The chemicals delivered by these systems were 49% hydrofluoric acid, 37% hydrochloric acid, 29% ammonium hydroxide, 30% hydrogen peroxide, 96% sulfuric acid and isopropyl alcohol. Specifications for contaminant levels in incoming chemicals ranged from < 1 ppb to < 10 ppb. The systems were required to add < 1 ppb of total metallic contaminants to the delivered chemical. Particle specifications at the points of use ranged from < 2 to < 5 particles/ml ( $\geq 0.20 \mu\text{m}$ ).

### 3. SYSTEM METALLIC EXTRACTABLES

Each system was tested using the Dynamic Extraction<sup>™</sup> technique over a one-week period during which no chemical entered or exited the system. Concentrations of 34 elements were measured during this time using a combination of inductively coupled plasma-mass spectroscopy (ICP-MS) and graphite furnace atomic absorption (GFAA). Total elemental concentrations in the chemicals were essentially invariant over time. All the systems were able to achieve the specification of < 1 ppb of total metals added within three days of initial chemical contact and were predicted to add < 0.1 ppb of total metals within one month [4]. The systems typically met specification within one day, as shown in Table 1. The major element extracted was iron.

*Table 1.* Time required for chemical delivery systems to achieve selected extraction rates

Chemical	Time to < 1 ppb total metals added (days)	Time to < 0.1 ppb total metals added (days)	Main elements extracted
29% Ammonium hydroxide	< 1	< 1	None
37% Hydrochloric acid	3	31	Iron
49% Hydrofluoric acid	< 1	< 1	None
30% Hydrogen peroxide	< 1	< 1	None
70% Nitric acid	< 1	< 1	None
96% Sulfuric acid	2	16	Iron

#### 4. SYSTEM PARTICLE CONCENTRATIONS

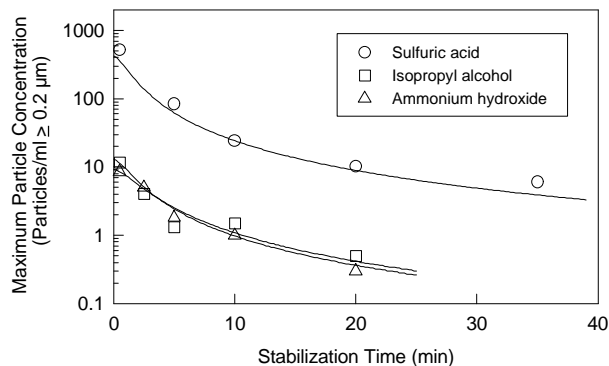
Particle concentrations were measured at the end of the distribution loop using an on-line laser optical particle counter. When the systems were operated under normal conditions, particle concentrations were well below design specifications, as shown in Table 2. Concentrations ranged from < 0.1 to 1.0 particle/ml ( $\geq 0.20 \mu\text{m}$ ).

**Table 2.** Particle concentrations in delivered chemical under typical operating conditions

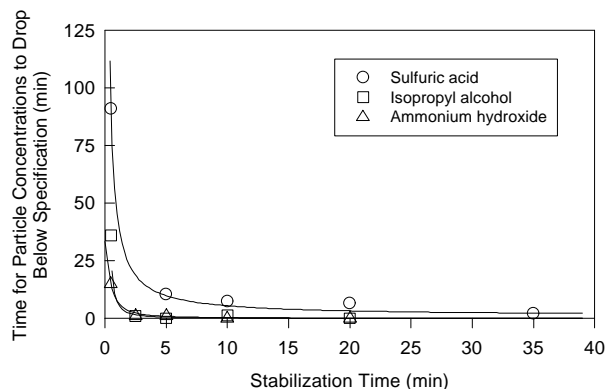
Chemical	Typical concentration (#/ml $\geq 0.2 \mu\text{m}$ )	Specification (#/ml $\geq 0.2 \mu\text{m}$ )
29% Ammonium hydroxide	0.5	< 3
37% Hydrochloric acid	< 0.1	< 2
49% Hydrofluoric acid	< 0.1	< 2
30% Hydrogen peroxide	1.0	< 2
96% Sulfuric acid	< 0.1	< 5
Isopropyl alcohol	1.0	< 2

Experiments were performed at APRDL/MOS 13 to verify the effect of startup stabilization on particle concentrations at the points of use. Three chemicals, sulfuric acid, isopropyl alcohol and ammonium hydroxide, were monitored for particle concentrations after startup. The duration of the startup stabilization time was varied from 0 to 20 minutes. Figure 1 presents the peak particle concentrations at the end of the distribution loop as a function of startup stabilization time. For all three chemicals, the peak concentration decreased as the startup stabilization time increased.

In addition, the length of time during which the particle concentrations were above specification decreased with longer startup stabilization time (Figure 2). These data indicate that chemical specifications can always be met for ammonium



**Figure 1.** Effect of stabilization time on maximum particle concentrations



**Figure 2.** Effect of stabilization time on time for particle concentrations to drop below specification

hydroxide and isopropyl alcohol with a ten-minute delay in chemical availability following system startup. The startup stabilization time required for sulfuric acid is approximately 40 minutes.

## 5. CONCLUSION

The chemical management systems at Motorola APRDL/MOS 13 incorporate advanced particle and metal control features. The particle control features maintain constant flow through the system filters at all times (Advanced Stabilized Distribution) and prevent particles released during startup from reaching the points of use (startup stabilization). Metal control is accomplished by proper selection of system materials. These systems consistently deliver chemicals with < 1 particle/ml ( $\geq 0.20 \mu\text{m}$ ) and add < 1 ppb total metal ions within three days of chemical contact.

## REFERENCES

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