Amine Contamination Monitoring and Control
At the Advanced Mask Technology Center

Kamran Avary, Axel Feicke and Rusty Cantrell
Advanced Mask Technology Center, Rähnitzer Allee, 9, 01109, Dresden, GERMANY

Abstract
Amine contamination of chemically amplified resists (CARs) impacts resist performance and is a yield limiting issue. Reducing amine contamination in clean rooms is a complex process involving monitoring, detecting and eliminating sources, filtration, and access. Amine contamination sources can be detected by ion mobility spectroscopy, a powerful analytical technique, which can measure amine contaminants at low concentrations using, recommended sampling times. Reduction of ambient amine concentration levels in clean rooms requires removal of amine sources as well as protection by chemical air filtration. Furthermore, restricting the use of CARs to special routes in low amine concentration areas is also a necessary part of an overall amine contamination reduction program. At the AMTC, this overall program was successful in reducing ambient amine levels in the clean room to ~2 ppbv, and in critical CAR handling/lithography areas to < 1 ppbv.

Keywords
Amines, chemically amplified resist (CAR), chemical filtration, ion mobility spectroscopy

Introduction
The need for smaller and smaller features has pushed lithography to use Deep Ultraviolet wavelengths (DUV) in combination with high sensitive, chemically amplified resists (CARs). In a positive CAR, DUV light generates a photo acid that later diffuses and deprotects the resist using thermal energy supplied by a post exposure bake (PEB) step[1]. Before and during PEB, any airborne molecular base impurities such as amines can neutralize the photo-generated acid leading to a degradation of image formation and lithographic performance[2]. A common indicator of molecular base CAR damage is the presence of T-shaped resist profiles (T topping), which can occur even at low amine concentrations[2]. Amine levels as low as 1 ppbv have been proven to adversely affect the performance of CARs[3]. With this in mind, the AMTC set out to reduce amine concentration levels in the clean room ~2.0 ppbv with < 1 ppbv in critical CAR handling areas.

Amines are organic compounds containing nitrogen with the general formula of $R_{3-x}NH_x$ where R is a hydrocarbon group and $0 \leq x \leq 3$[4]. The nitrogen atom in an amine molecule has a pair of electrons giving it a basic character and the ability to react with acids to form quaternary ammonium salts[5]. Ammonia (NH_3) is the simplest amine, the most abundant alkaline component in the atmosphere, and is an excellent tracer of amine contamination[4]. NH_3 is a gas at room temperature (boiling point = –33 °C), lighter than air, and undetectable by humans at low concentrations[4]. Humans, machines, cooling systems, gloves, and plastics in clean rooms can all generate ammonia[6]. In addition to resist T-topping, amines can also deposit as a thin film on pattern generator lenses, giving them a haze-like appearance[5].

Monitoring of Amines in cleanroom

CARs can rapidly degrade in low amine concentration. For example, resist sensitivities for 248 nm can vary from 0.037 nm/min/ppb to 0.368 nm/min/ppb[7]. An ideal amine monitoring system should have fast response times coupled with low detection limits. Continuous real time monitoring, ease of calibration, and automatic sampling are also desired[8].

Current available amine monitoring systems are based on ion chromatography , Ion Mobility Spectrometry (IMS), and chemiluminescence's (CL). The analytical system for amine monitoring at AMTC is an IMS system manufactured by Molecular Analytics (MA). The principle of operation is based on ionization of sampled air with a radioactive source (Ni^{63}), followed by a simplified time of flight analysis at atmospheric pressure with ion current detection[9]. This MA system has a reliable method for monitoring amines such as dimethylamine, methylamine, methanolamine, ethanolamine, diethanolamine, and butylamine and has a low detection limit of 0.1 ppbv[8]. The MA system is capable of switching automatically between different sample points using a preset time interval. AMTC's MA system samples 45 different locations in the clean room, air plenum, and level below the clean room called the Subfab. Figure 1 displays one of the first amine concentration profiles of the AMTC cleanroom.

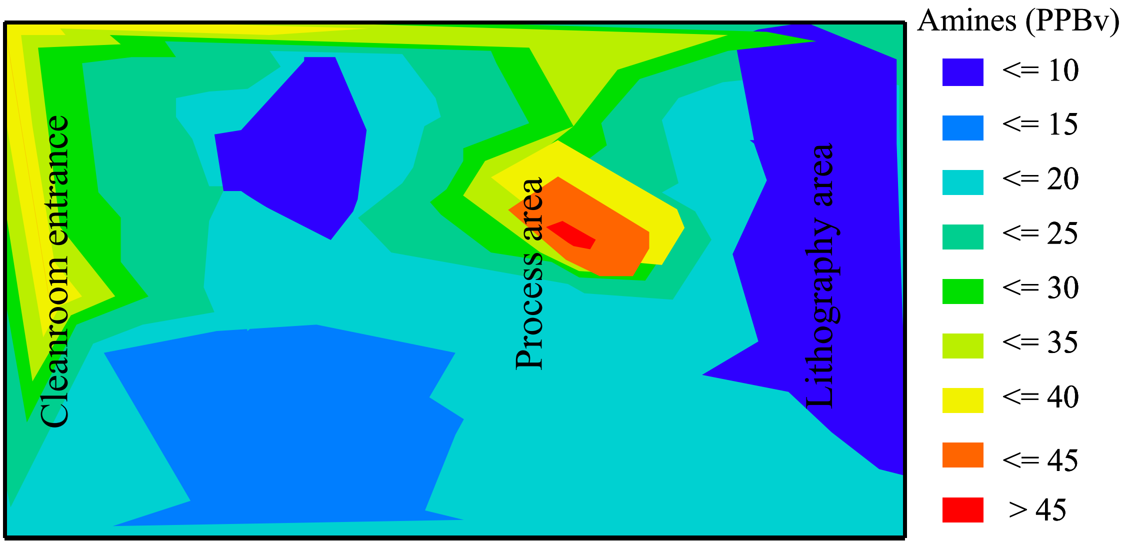

Figure 1: Amine concentration in different clean room areas.

The data for amine concentration presented in Figure 1 was collected over several days. Notice the high amine concentration in and around the process area and clean room entrance (~40 ppbv), as well as 10 ppbv in the lithography area. Both of these concentrations represent levels far in excess of AMTC desired amine concentrations. Although not displayed, amine concentrations detected in the Subfab level below the clean room showed similar values.

Figure 2 shows the amine concentration in the process area as a function of time where numerous spikes of 200 ppbv are clearly visible. These spikes were later correlated to resist stripper operation, which uses ammonia.

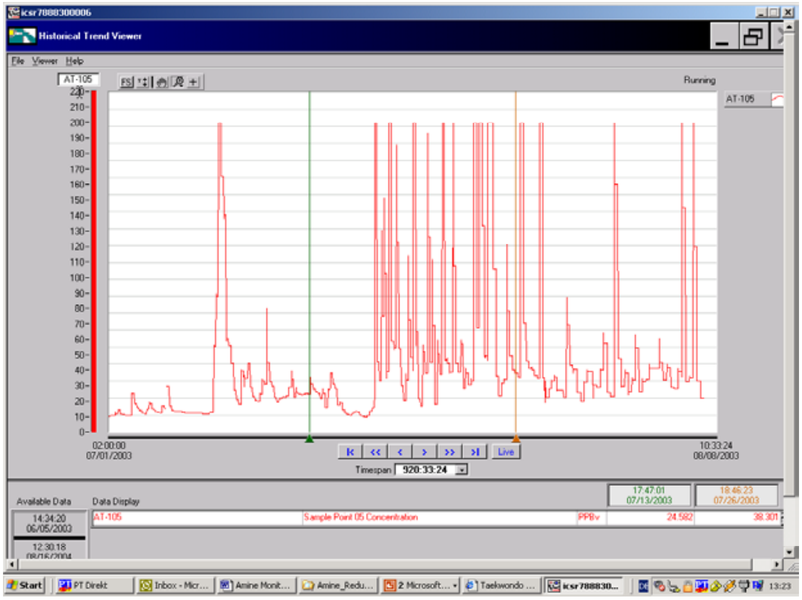

Figure 2: Amine concentrations in the process area attributed to resist stripper operation.

Reduction amine contamination

The first step to reduce amine levels was to identify sources and try to eliminate them. The resist stripper at AMTC uses ammonia and was identified to be the source of high amine levels detected in the process area. This stripper tool was designed to operate at a pressure higher than the clean room and small air leaks from the tool resulted in routine discharges of ammonia-laden air into the clean room. An aggressive effort to seal all air leaks from the stripper tool was initiated but 100% containment was not possible. Modifications in the floor tile perforations surrounding the stripper tool were also performed in order to direct more air around the tool to flow downwards, out of the clean room and into the Subfab level below. Similar efforts were employed with all tools at AMTC that use ammonia. Tool isolation coupled with airflow modifications reduced amine concentrations in the process area to an average of 20 ppbv.

Amine monitoring in Subfab level below the clean room also showed spikes of 220 ppbv. Investigations showed valves in the Subfab that regulate and supply liquid ammonia to tools in the clean room were the source of these high amine concentrations. Leaking ammonia valves were replaced and all ammonia valves were enclosed in clear plastic boxes with exhaust, resulting in an average of 10 ppbv amines in the Subfab.

Reduction efforts next focused on the clean room entrance. The source of high amine concentrations in this area was traced to the gowning room where personnel assemble for donning and removing clean room apparel. Despite the clean room entrance having a higher atmospheric pressure than the gowning room, amines were still penetrating the clean room when doors were opened to allow personnel access.

Gowning area

Personnel are one of the main amine sources and 50 ppbv was routinely detected in the gowning area. One such example is amines from personnel perspiration, evident by examining the amine concentration inside a clean room boot minutes after being removed from a foot (see Figure 3 below).

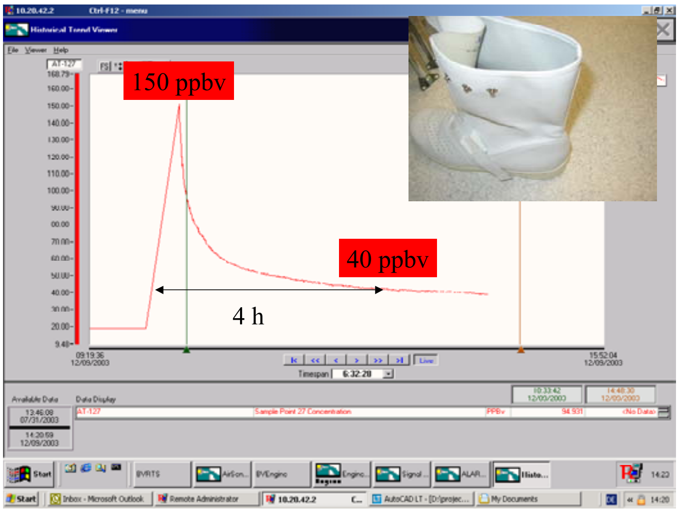

Figure 3: Amine concentration in a clean room boot as a function of time after it is removed from the foot.

Just after removal, amine concentration was observed to reach 150 ppbv, which slowly decreased to roughly 40 ppbv after 4 hours. Consider over 300 pairs of clean room boots are used and stored in the AMTC gowning room and it is immediately apparent how 50 ppbv amines was routinely detected. Special adsorbent layers were inserted into all clean room boots in order to adsorb foot perspiration and reduce emitted amines.

New, clean, nitrile gloves stored in the gowning room were also identified as a source of amines. Approximately 8 ppbv amines were detected inside a new, nitrile glove over a period of 24 hours. . Special clear plastic boxes were created to store these gloves and limit their contribution of amines to the gowning room atmosphere.

Finally, the gowning room air handling system was isolated from that of the clean room, in addition to making floor tile modifications to increase air velocity downwards and out of the gowning room. All of these efforts reduced gowning room amine levels to an average of 10 ppbv.

Amine filtration

After identifying and removing these sources, amine concentrations in the AMTC clean room showed very stable levels around 10 ppbv. To reduce amine concentrations further, the AMTC used chemical filters in the clean room air handling system, specifically designed to adsorb amines. These filters were installed in the air plenum units prior to the fan filters to adsorb amines before they reache the clean room. The AMTC selected AFP-type, V-shaped amine filters from McLeod Russell (Figure 4a) due to being compatible with existing fan filter units and also for ease of installation.

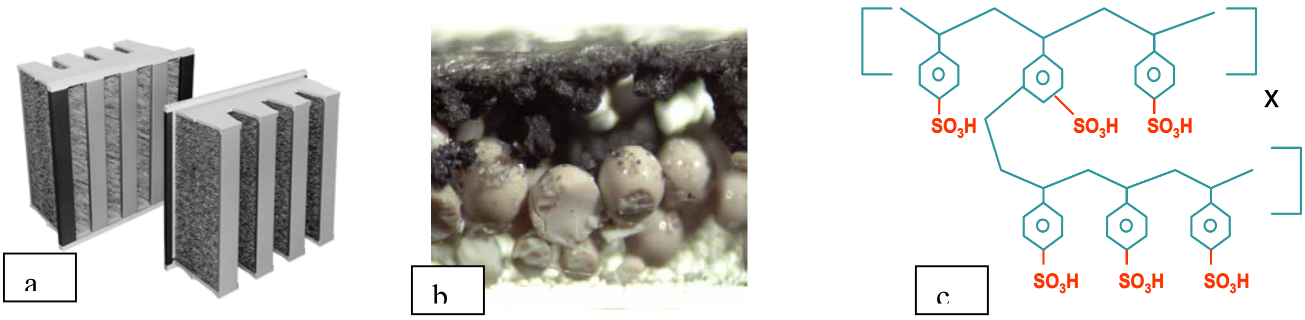

Figure 4: a) AFP-type, V-shaped amine filters by McLeod Russell; b) Media of filter; c) Structure

These filters use a micro granular adsorbent with a diameter between 0.4 mm to 0.8 mm. Figure 4b represent the media of these filters which contain a good relation of outer surface to adsorbent mass, resulting in a high amine adsorption capacity/mass. Micro granular adsorbent particles are interconnected by fibers, which limits vibration and abrasion leading to no particle shedding. Figure 4c shows the chemical structure of the amine adsorbent compound that includes sulfuric acid groups on a styrene-DVB copolymer. These filters were installed only in critical CAR handling/lithography areas and after a few hours; amine concentrations in the lithography areas were under 1.0 ppbv, with the remainder of the clean room averaging around 2.0 ppbv. Figure 5a represents amine levels in clean room after filter installation while Figure 5b displays the amine concentration trend during amine reduction efforts at AMTC.

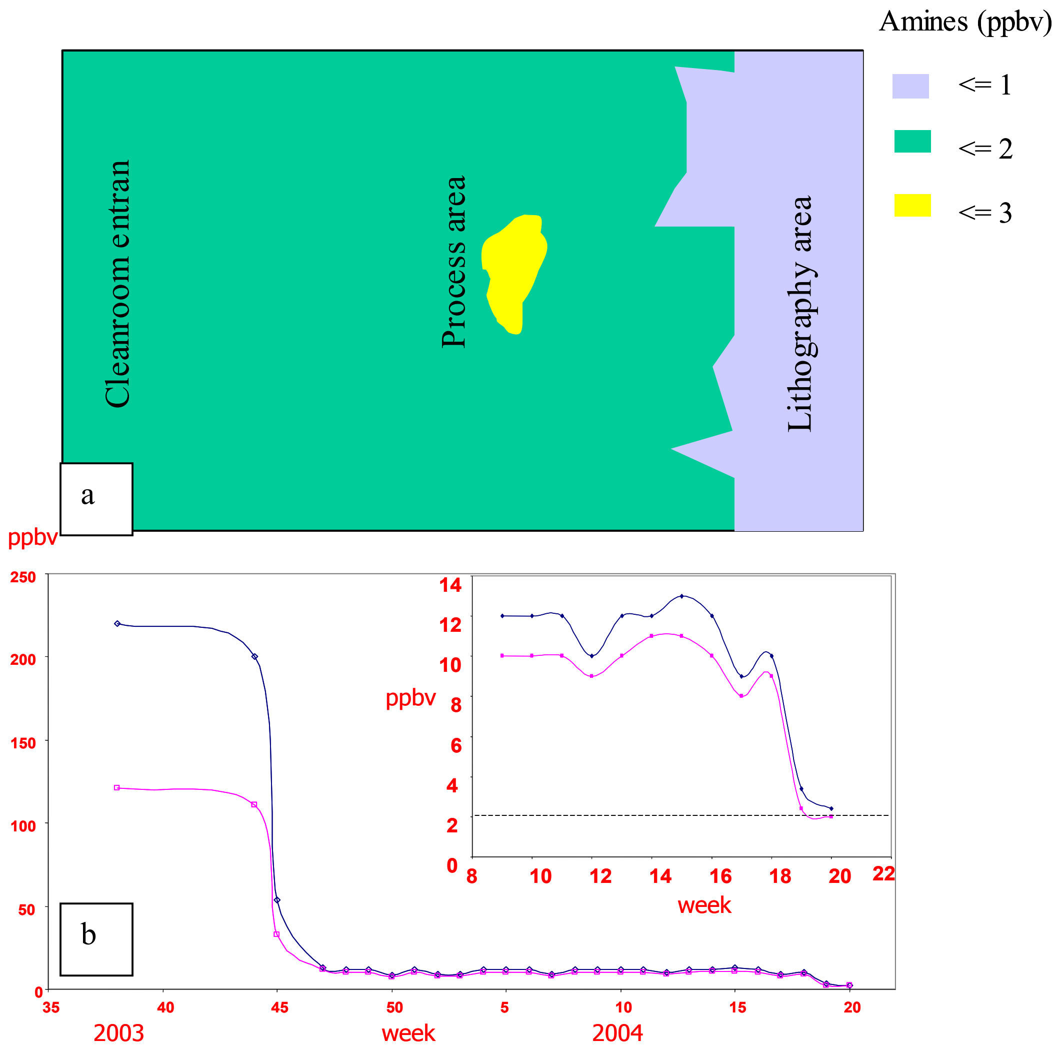

Figure 5: a) Amine concentrations after filter installation; b) amine trend during reduction efforts at AMTC. Blue line indicates the maximum values of amine level and pink line the average of amine level in the cleanroom.

Amine routes

Special routes for CAR reticle transport and handling were defined in the AMTC clean room to reduce the risk of exposure to high amine concentrations. These routes are monitored for amines with the MA tool and have alarms set at 1.0 ppbv. In the event of an upset condition causing amine concentrations to exceed 1.0 ppbv within these special routes, no CAR coated reticle transport or handling is performed until the upset condition is corrected and amine levels have returned to < 1.0 ppbv. This means a CAR coated reticle cannot be unloaded from a pattern generator and transported to a PEB tool for processing when amines concentrations exceed 1.0 ppbv. If a CAR reticle has already unloaded from a pattern generator and is residing on the unload port, it must not be moved or handled during the high amine upset. The reticle should remain on the unload port until amine concentrations have returned to < 1.0 ppbv.

Conclusions

Amine contamination sources at the AMTC are detected and monitored using an ion mobility spectroscopy tool. An amine reduction program at the AMTC was successful in reducing ambient amine levels in the clean room to ~2 ppbv, and in CAR handling/lithography areas to < 1.0 ppbv. Special routes for CAR coated reticle transport and handling were also established as part of this amine reduction program to restrict these materials for use only in low amine concentration areas.

Acknowledgements

The authors would like to thank Dr. Kames from McLeod Russell and Ernst Kindermann from Molecular Analytics for their valuable contribution in this paper.

References

1 F. Thompson et al. " The Lithographic Process: The Physics", Introduction to Microlithography, American Chemical Society, Advanced in Chemistry Series, Vol. 219, 1983

2 S.A. MacDonald et al., " Airborne Chemical contamination of a Chemically Amplified Resist", SPIE, Advances in Resist Technology and Processing VIII, vol. 1446, (1991), 2-12

3 K.Dean and R. Carpio. " Real-Time Detection of Airborne Contaminants in DUV Lithographic Processing Environment", Proceedings of Institute of Environmental Sciences, 1995

4 Wolfgang Walter, Wittko Francke," Lehrbuch der Organischen Chemie",23-Auflage, s. Hirzel Verlag Stuttgart. Leipzig 1998

5 Eric V. Johnstone, Christian Chovoino, Julio Reys, Laurent Dieu, " Haze control: Reticle/environment interaction at 193", Solid State Technology May, 2004

6 Chemical Safety handbook for Semiconductor/Electronics Industry. Secound Edition. OEM Press. Beverly, MA. 1998

7 David Ruede, Monique Ercken, Tom Borgers,"Molecular Base Sensitivity Studies of Various DUV Resists used in Semicounductor fabrication ",SPIE, Optical Microlithography XIV, vol. 4346, (2001), pp. 1020-1028

8 O. Kishkovich et al." Real-Time Methodologies for Monitoring Airborne Molecular Contamination in Modern DUV Photolithography Facilities",SPIE Proceedings, Microlithography 99,3677, (1999), pp. 857-865

9T. Bacon & Kurt Webber," Contamination Monitoring for Ammonia, Amines and Acid Gases Utilizing Ion Mobility Spectroscopy (IMS)", Available from Molecular Analytics web Page at www.ionrpo.com