Measurement and control of ammonia is critical in a variety of industrial applications including power generation, petrochemical processing, and semiconductor manufacturing. In many cases, ammonia measurement at ppb levels is required to achieve optimal process control or safeguard valuable work-in-process material.

Ammonia is difficult to measure at ppb levels because of its "stickiness" – its tendency to adsorb to surfaces – such that varying temperature and ambient moisture levels can produce erroneous measurements. Few instruments exist that can simultaneously meet the sensitivity and speed requirements of the most demanding process control applications. The Picarro G1103-*t* trace ammonia analyzer simultaneously provides both the sensitivity and the speed needed for the most demanding ammonia measurement applications. The Picarro G1103-*t* is able to achieve ppb sensitivity in a few minutes and does so directly on the gas stream.

Figure 1. Picarro G1103-*t* Ammonia Analyzer

Applications

Ammonia is generally considered the second most important compound produced in the U.S. chemical industry[1], with an estimated global annual production capacity of over 100 million tons[2]. Ammonia and its derivatives (e.g. ammonia salts) are often used as nitrogen sources in industries ranging from fertilizer to semiconductor to biopharmaceuticals. Because of its prevalence, it is often important to monitor ammonia to generate the desired chemical reaction or to prevent an undesired one.

[1] ethylene is considered the most important.
[2] "Energy Use and Energy Intensity of the U.S. Chemical Industry", Worrell, et. al., Lawrence Berkeley National Laboratories, April 2000.

In the semiconductor industry, ppb-level ammonia control is crucial to insure the integrity of the lithography process. Ammonia is emitted into wafer fab air by various semiconductor processes including CVD, wafer cleaning, coater tracks, and CMP, as well as from humans. At the lithography step, ambient ammonia can alter the photochemical properties of photoresist causing uncontrolled variation in printed wafer features. Chemical filters are in place in these areas to remove airborne contamination, but their lifetime and coverage do not offer complete protection. Constant monitoring of airborne ammonia at ppb-levels is critical to protect wafers from ammonia exposure.

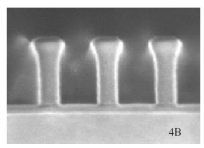


Figure 2. Photoresist "T-*tops*", which limit control of wafer feature size, can be caused by ammonia in cleanroom air.

In the auto emissions and power plant industries, a technique known as Selective Catalytic Reduction (SCR) is often used to reduce emissions of greenhouse gases. In an SCR system, urea is used as a reductant that converts to ammonia and "catalyzes" the conversion of NOx to nitrogen and water over the catalyst material. Precise ammonia measurement is required to develop and characterize optimal catalyst strategies in order to prevent excess ammonia emissions or unreacted NOx emissions.

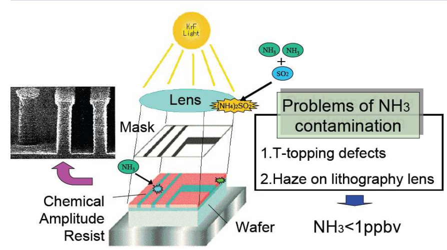
Other applications include monitoring of "controlled atmosphere" storage rooms for perishables such as post-harvest produce and biopharmaceutical cell banks. Temperature control in these storage rooms is commonly achieved using ammonia-based refrigeration systems. Small refrigerant leaks can quickly destroy materials worth >$500,000, warranting an ultra-sensitive ammonia measurement system.

Field Results I

The Picarro G1103-*t* has been compared side-by-side to other ammonia measurement techniques currently used in the semiconductor industry. One customer concluded that the Picarro G1103-*t* provided "shorter (measurement) time and more accurate measurement than Ion Chromatography."

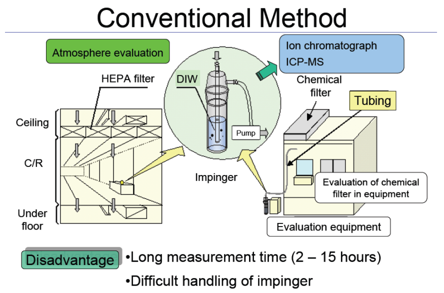
It is well known that even ppb levels of ammonia exposure during the photolithography process can lead to yield loss and unscheduled equipment downtime. Airborne ammonia can alter chemically amplified resists and lead to "T-*t*opping". Ammonia is also photoreactive and can deposit on optical surfaces of lithography systems causing expensive and unpredictable downtime.

Problems in Lithography Area



To avoid these catastrophes, semiconductor and equipment manufacturers thoroughly characterize the photolithography area under process conditions to minimize the risk from ammonia exposure. Some equipment manufacturers even require periodic audits of amine levels in the lithography area to maintain warranty status. Ammonia measurements are typically performed using ion mobility spectroscopy, chemiluminescence, or ion chromatography.

The diagram below shows the typical method for measuring ammonia levels using ion chromatography. Air, either cleanroom or equipment environment, is pumped through an impinger to capture airborne ammonia in the impinger fluid (de-ionized water, for example). The impinger fluid is then sent to a laboratory for analysis by ion chromatography. The key disadvantages to this method include a long impinging time and difficult sample handling, which can generate inaccurate results.



The data below compares ammonia measurements made by the Picarro G1103-*t* to ion chromatography over a broad concentration range. The two IC measurement sets were made at different sites and with different personnel. These results reflect the difficulty of sample handling for ion chromatography: at high concentrations, inefficiencies in trapping ammonia in the impinger lead to inaccurate measurements. Further, the Picarro G1103-*t* makes its measurements "on-line" providing further insight into the dynamics of ammonia exposure

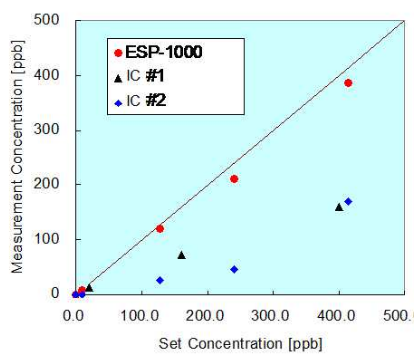


Figure 3. Ammonia measurements made by the Picarro G1103-*t* and by IC

Field Results II

The Picarro G1103-*t* was used to evaluate the ammonia filter performance. The purpose of the evaluation was to conduct an accelerated lifetest of an ammonia filter to compare with the filter manufacturer's specifications. The results below highlight the value of the Picarro G1103-*t* in a semiconductor application.

Ammonia filter manufacturers specify filter lifetimes on the order of years, depending on the ammonia challenge presented to the filter. The ammonia challenge assumed for lifetime calculations is 10 – 20 ppb, a level that is considered "normal" in semiconductor cleanrooms.

The critical ammonia measurement requirements for this application include:

- <1 ppb detection limit
- 5-minute measurement time
- stable long-term performance
- no false alarms from other, non-critical, airborne compounds

The schematic in Figure 4 shows the evaluation setup used for over 40 days of continuous testing. An ammonia source was connected at the fan intake and a flow controller was used to manually modulate the challenge to the filter. Both the ammonia challenge to the filter and the ammonia output by the filter were monitored continuously with the Picarro G1103-*t*. Other parameters, such as humidity and temperature, were allowed to vary over ranges typical of a cleanroom environment.

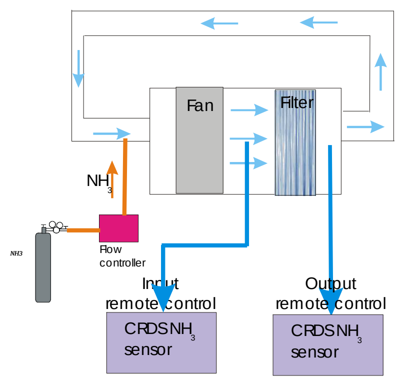


Figure 4. Ammonia test setup

Figure 5 summarizes the results of the test. The key points from this chart are:

- the Picarro G1103-*t* is able to easily monitor sub-ppb ammonia levels.
- initially, the filter is very efficient at adsorbing ammonia and the filter output is independent of ammonia challenge.
- the filter begins to fatigue after adsorbing about 65g of ammonia. This corresponds to ~2.25 years of service, assuming a constant 10 ppb challenge.
- at ~92g of ammonia adsorbed, the filter loses efficiency in adsorbing ammonia and the filter output becomes a function of filter input. This corresponds to ~3.75 years of service, assuming a constant 10 ppb challenge.
- after losing efficiency, the ammonia output by the filter increases gradually even though there is a constant (~1 ppbv) ammonia.

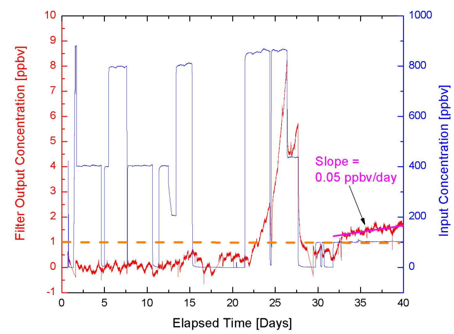


Figure 5. Ammonia lifetime test results

Technical Innovations

Instruments that measure ammonia at ppb-levels can have long-term drift in the baseline measurement or require frequent re-calibration, often because ammonia is a "sticky" gas and easily adsorbs to a variety of materials.

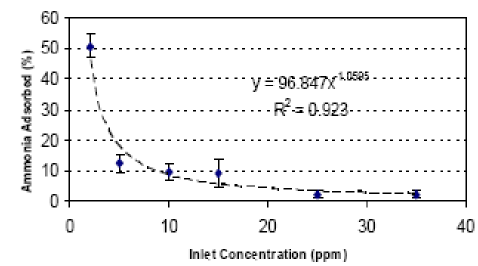


Figure 6. Ammonia adsorption onto Teflon

The measured concentration is dependent on the subsequent desorption, which can occur somewhat arbitrarily since it is dependent on humidity and temperature.[3]

To account for these effects, the following innovations have been included in the Picarro G1103-*t*:

- materials selected on all gas handling and cavity surfaces to minimize adsorption.
- precise internal temperature stability to milli-Kelvin levels.
- scanning and analysis of multiple ammonia peaks to compensate for spectral baseline drift.
- simultaneous measurement of and compensation for moisture content.

[3] "Assessment of Ammonia Adsorption onto Teflon and LDPE tubing used in pollutant stream conveyance," Mukhtar, et. al., Agricultural Engineering International, Vol. V, Dec. 2003