Gas Cell Selection For Analysis Of Electronic Gases

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APIMS and FTIR remain the preferred analytical tools for monitoring impurities in the electronic specialty gases used by the semiconductor industry, although other tools such as CRDS are currently finding application in selected cases. FTIR spectroscopy offers the advantage of the simultaneous measurement of all gaseous species that exhibit dipole moment changes during vibrations at concentration levels down to the ppb level. FTIR also offers the advantage of transferring all contact with the corrosive and/or toxic gases to a long or short path gas cell that contains the sample gas. Therefore, the design and the materials of which the gas cell is fabricated become the critical features determining the quality of the impurity analyses. This paper will present and review the advantages and disadvantages of several gas cell configurations on the market today, including the following features: optical design (multipass "white cell," folded path, direct pass), pathlength, materials of construction (stainless steel, aluminum, glass), mirror substrates and coatings, windows, cell finishes/coatings, cell volumes, measurement wavelength (IR & UV), sample gas composition, cell pre-treatment and decontamination, energy throughput, and sensitivity.

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The uses of electronic specialty gases in semiconductor applications are several, including:

- Ion Implantation
- Thin Film Deposition
- Sputtering Operations
- Physical Vapor Deposition
- Chemical Vapor Deposition
- Wafer Cleaning and Etching
- Synthesis of Compound Semiconductors

Many of these applications involve the use of very high purity gases that are both corrosive and toxic, such as HCl, HBr, Cl_2, WF_6, SiH_4, SiH_2Cl_2, NH_3, PH_3, etc. It is the chemical nature of these gases that creates great problems for most analytical methods. Among the problems for both the user and the analyst are:

1. Many of these gases can not be produced at the highest purity required by the semiconductor industry, a major contaminant being moisture;
2. The moisture content of the halogen-type gases makes them highly acidic;
3. The chemical reactivity of these gases and their impurities leads to degradation of optics, materials, and seals in both process tools and analytical instruments;
4. The acid gases react with and destroy the electronic elements in some mass spectrometers, gas chromatographs, and electrical conductivity devices; they also chemically degrade the mirrors and windows in gas absorption cells;
5. When sampling of a gas stream is required, the expansive cooling of the gas can yield liquid droplets, which are even more chemically destructive of electronic and optical elements because of their highly concentrated nature;
6. For the process tool operator, these gases are highly toxic if leakage occurs due to any number of equipment failures: breaks in process lines, bad welds, degraded vac-

Figure 1. Widely-Used Long Path Gas Cells

uum connectors or seals, operator error, etc.;

7. Most critical, perhaps, is the fact that variations in the quality of the process gas, due in many cases to moisture as an impurity, interferes with the kinetics of the semiconductor wafer etching or treatment process.

APIMS	FTIR/Gas Cell	CRDS
High PPT sensitivity	Low PPB sensitivity	High PPT sensitivity
Ionizer in direct contact with sample	SS gas cell/mirrors interface with sample, not FTIR	High reflectivity glass mirrors contact gases
Best for monotomics & diatomics with simple ion fragment patterns	All heteropolar species simultaneously	Single species at a time
	"Fingerprint" spectra	Limited to H_2O & O_2
Tunable for optimization	Chemometrics applicable	Matching laser wavelength required
O_2 not susceptible	Acid gases are okay	Absolute concentration determinations from first principles
Not applicable to corrosive acid gases	Remote computer operational	
Very expensive: $300K	Moderately priced: $75-100K	Moderately priced: $75K

Table 1. Comparisons of APIMS, FTIR/Gas Cell, and CRDS

The analytical tools being used today for monitoring the quality of the electronic specialty gases all have their advantages and disadvantages. Key points for each are given in Table 1.

Both APIMS and FTIR are the standard analytical methods accepted by the semiconductor industry for qualifying the purity of cleaning, etching, and treatment gases. FTIR is broadly used also for PFC emission measurements.

When FTIR is coupled with long path gas cells, it is not only applied to semiconductor gas monitoring but also to a broad spectrum of other analytical applications, including combustion and stack gas compositions, tobacco blen-ding, fire and forestry, hydrogen fuel cells, battery tests, and medical and air reduction gases. This breadth of applications has led to a multiplicity of long path gas cell designs and manufacturers. Illustrated in Figure 1, are a few of these cells, from Infrared Analysis, Gemini Scientific Instruments, Axiom Analytical, Thermo Nicolet, CIC Photonics, among others.

Several different optical designs of long path gas cells exist in the field of analytical applications, each having specific or unique features as shown in Table 2.

Over the years, the white cell has been the most popular and widely used gas cell, because it can be readily fabricated from a variety of construction materials at a broad range of prices. The Folded Path cell offers fewer mirror reflections per unit pathlength, but its vertical height is not conducive to industrial applications. The Herriott cell and the CRDS Cavity cell both achieve PPT sensitivity due to their exceptionally long pathlengths, but a distinct laser frequency is required for each molecular absorption line to be monitored.

The application of long path gas cells to electronic specialty gases has introduced a number of material and performance problems due to the chemical reactivity of many of these gases. Such problems are listed in the next four tables, Tables 3 – 6. The information in these tables is based upon the experiences of the author and many customers.

Optical Design	Features
"White" Cell	High energy-throughput & SNR PPB sensitivity, multiple gases Large volume/pathlength Stainless steel, aluminum, or glass construction & mirrors Gold or silver-coated mirrors
Folded Path	Small volume/pathlength Brass or stainless steel material Nickel mirrors available Low energy throughput, SNR
Herriott	Very long pathlengths/volume PPT sensitivity w/ laser Glass cell bodies and mirrors Gold-coated mirrors Limited species detectable
CRDS Cavity	Kilometer pathlengths High reflectivity mirrors Low PPT sensitivity w/ laser Dielectric-coated mirrors Glass or stainless steel cells Limited species detectable

Table 2. Long Path Gas Cell Optical Designs

Table 3 identifies the principal problems and their frequency of occurrence. With stainless steel cells and nickel-plated stainless steel cells, degradation of the cell body rarely occurs even after years of service. Some prospective users request that the cell body be made from a high nickel-content alloy, such as Monel or Hastelloy, but fabrication from those materials is very expensive. The author has found that nickel-plated stainless steel serves equally well at much lower cost. Contamination from gas-phase produced powders on the mirrors or windows and the failure of O-rings and C-seals are also low in occurrence.

Problem Area	Occurrence
Cell Body Degradation	Very Low (with stainless steel cells)
Powder Contamination	Low
O-ring/C-seal Failures	Low
Reduced Window Transmission	Medium
User-Caused Failures	Medium to High
Mirror Degradation	Low to High
Acid Droplet Nucleation	High

Table 3. Performance Problem Occurrences

Material of Fabrication	Chemical Integrity
Glass	High HOH Retention
Aluminum	High Acid-Gas Attack
Nickel-Coated Aluminum	Acid-Gas Causes Peeling
Nickel-Plated Brass	Acid Resistant
Electropolished Stainless Steel	Moderate HOH Retention
Nickel-Plated Stainless Steel	Acid Resistant, Low HOH Retention
Hastelloy, Monel	Acid Resistant, Low HOH Retention

Table 4. Cell Body Materials of Fabrication

Substrate Material	Nature of Problem
Glass	Easily Etched by Acid Gas Breakage Prone
Aluminum	Reacts with Acid Gas Gold Peels Away
Stainless Steel	Requires Multilayer Coatings, Expensive
Hastelloy, Monel	Expensive to Fabricate Not Widely Tested

Table 5. Mirror Substrate Problems

Overall, the infrared transmission by the input and output windows remains usable, so long as the windows are matched to the gases being analyzed. But window degradation will occur after weeks or months of usage. It is recommended that the windows be replaced when the energy throughput drops below 75% of its original value or when the analysis instrument is down for switching to a different electronic gas.

Most people may find this hard to believe, but user-caused failures are ranked medium to high in frequency of occurrence. Common among these causes are: mixing of a new gas sample with a different residual gas in the gas cell, which leads to the formation of a powder or film that in turn coats the windows and mirrors; overheating the gas cell causing degradation of the O-rings; and permitting liquefied forms of the gases to condense on the mirrors without adequate flushing between periods of usage.

No highly reflective mirror coating exists that will not succumb to slow chemical degradation by the acid gases over months of continuous usage. The rate and degree of degradation varies greatly from one acid gas to another and among the other electronic specialty gases. The best way to monitor this degradation is to monitor the energy throughput on a daily or weekly basis; when the energy throughput drops below 75% of its original value, then either degradation of the windows or mirrors must be suspected.

The potential of acid droplet nucleation upon expansion of the gas at the inlet to the gas cell is controversial in practice but obviously has a measure of theoretical probability. If droplet nucleation does occur and if those droplets settle on the mirror surfaces, the rate of chemical interaction between the liquid droplet and the mirror material will be much higher than the interaction of the gas with the mirror. Physical inspection of degraded mirrors, particularly from HBr exposure, reveals microscopic size pits, which tends to support the premise of droplet nucleation.

More can be said about the chemical integrity and utility of various cell body materials, as summarized in Table 4. Borosilicate type glass is widely used in gas cells. But glass suffers from two major problems: susceptibility to breakage in industrial settings, and very high retention of moisture molecules due to hydrogen bonding with oxygen sites on the glass surface. Both aluminum and nickel-plated aluminum suffer from acid gas attack; in the latter case, it is well established that the acid gas molecules penetrate through or under the nickel plating causing peeling of the nickel and direct exposure to the aluminum. Teflon-coated glass or aluminum is also not viable because of high moisture retention.

Nickel-plated brass and electropolished stainless steel exhibit good resistance to acid attack, but once again the retention of adsorbed moisture molecules by the oxygen sites of stainless steel diminishes its utility in applications where moisture measurements are critical. Nickel-plated stainless steel and the high nickel-content alloys are the best materials for construction, because of their high resistance to acid attack and their low retention of moisture molecules.

The mirrors are certainly the most critical component of multi-path and folded-path gas cells. The chemical composition of both the mirror substrate and the reflective coating determine the resistance to attack by electronic gases and the ultimate energy throughput of the cells. Table 5 lists some of the issues associated with the selection of the substrate material. While stainless steel is a preferred substrate because of its lower cost to fabricate into a mirror, it requires multi-layer coatings, including gold as the primary reflective surface, which is expensive. There are claims that uncoated mirrors made of Hastelloy, Monel, or pure nickel are sufficiently reflective in the infrared to use in multi-path cells, but no definitive evidence exists to substantiate those claims. One exception is Axiom Analytical, which has used pure nickel mirrors in its folded-path cells, but such cells require only a few reflections.

The longevity of the reflective coatings on mirrors is partly based upon the substrate material, but it is more dependent upon the coating composition and the gases to which the coating is subjected. For years MgF_2 has been a preferred protective coating over gold because it enhances the resistance to physical contact. That property is still valid, but more important is the fact that MgF_2 enhances the chemical resistance to the electronic gases. In addition, chromium and nickel are commonly used to bind gold to the substrate. Where moisture measurements are the issue, nickel is better than chromium because of the absence of hydrogen-bonding that is associated with Cr-O sites.

Table 6 lists three reflective coating structures and their relative longevity with various gases that are within the experience of the author. For the halogen-containing acid gases, MgF_2 protective coatings greatly enhance the life of the gold coatings, except for HBr. HBr is highly reactive with many materials, and some evidence exists that it even reacts with gold. HF becomes a real problem if it liquefies and settles on the mirror surfaces.

In order to strengthen the chemical resistance of MgF_2/Au mirrors further, this author has experimented with binder elements other than Ni and with varying deposition thickness for each layer. A formulation has been devised which offers con-

Gas	Au/Ni	MgF2/Au/Ni	MgF2/Au/X
Cl_2	Low	Medium	
HCl	Medium	High	
HBr	Low	Low	High
HF	Low	Medium	
F_2	Medium	High	
WF_6	Unknown	High	High
NH_3	High	High	
B_2H_6	High	High	
SiH_4	High	High	

X = Proprietary

Table 6. Mirror Coating Longevity vs Gases

Specialty Gas	Windows
Ammonia, Arsine, Phosphine	BaF_2, ZnSe
Diborane, Silane, Germane	BaF_2
Chlorine, Bromine, Fluorine	AgCl
Hydrogen Chloride or Bromide	AgCl, IR-Quartz
Hydrogen Fluoride	BaF_2
Tungsten Hexafluoride	BaF_2, CaF_2
Dry Gases	KBr

Table 7. Preferred Window Materials

CICP Gas Cell	Number Reflections	Energy
Pathfinder-EN (10.0 meters)	49	25-30%
Ranger (9.6 meters)	47	35-45%
4Runner (4.0 meters)	31	50-60%

Table 8. Typical Energy Throughputs for "CICP" white Cells

Absorbance = absorption coefficient (k) x concentration (c) x pathlength (p)
Signal/Noise Ratio (snr) = fn(cell/FTIR parameters)
Mirror Reflectivity (r) = fn(coatings)
Mirror Performance (q) = fn(optical quality)
Energy Throughput (T) = fn(mirror alignment)

Absolute Sensitivity = fn(k, p, snr, r, q, T)

Table 9. Gas Cell Sensitivity Factors

siderable improvement over the MgF2/Au/Ni composition that is widely used for highly reflective gold mirrors. These comments apply specifically to coatings on stainless steel.

The hydrogen-containing gases employed as treatment gases in the synthesis of compound semiconductors are much less chemically reactive with various mirror coatings, but their toxicity raises concerns about the physical integrity of the gas cells and of safety for the system operators.

The reflective coatings used with mirrors for CRDS are dielectric materials. Selection of a specific dielectric must be matched with the wavelength of the laser beam employed, which in turn is dependent upon the molecular absorption line being monitored. The dielectrics offer extremely high reflectivity—of the order of 99.999%; but one must be concerned with how the reflectivity may deteriorate in the presence of corrosive acid or basic gases.

After mirrors, window materials are the next gas cell component subject to contamination and degradation. In addition, the window material must be chosen to match the infrared transmission range required for the analysis. For the determination of moisture as an impurity in the electronic specialty gases, Table 7 identifies the window materials most commonly used. BaF_2 is widely used for a number of the gases. However, AgCl is preferred for the halogen-containing gases. KBr is the least expensive window material and has high transmission throughout the infrared. Because of its hydroscopic nature, it has to be replaced more frequently than the other windows. Anti-reflective coated ZnSe is a real workhorse as a window material because of its physical strength and its wide transmission range; it is also chemically resistant to most all of the electronic gases.

Turning attention back to the physical design of the gas cells, the gas flow patterns from point of input to output become important. A variety of white cell geometries are in use, which serve as a good illustration of gas flow patterns characteristic of other cell geometries as well. The most common geometry utilizes small diameter (1/4") inlet and outlet tubes both mounted at the top of the "White" cell, as illustrated in Figure 2b. This geometry leads to an uneven U-shaped flow pattern with some dead-volume spaces and very long gas sample exchange

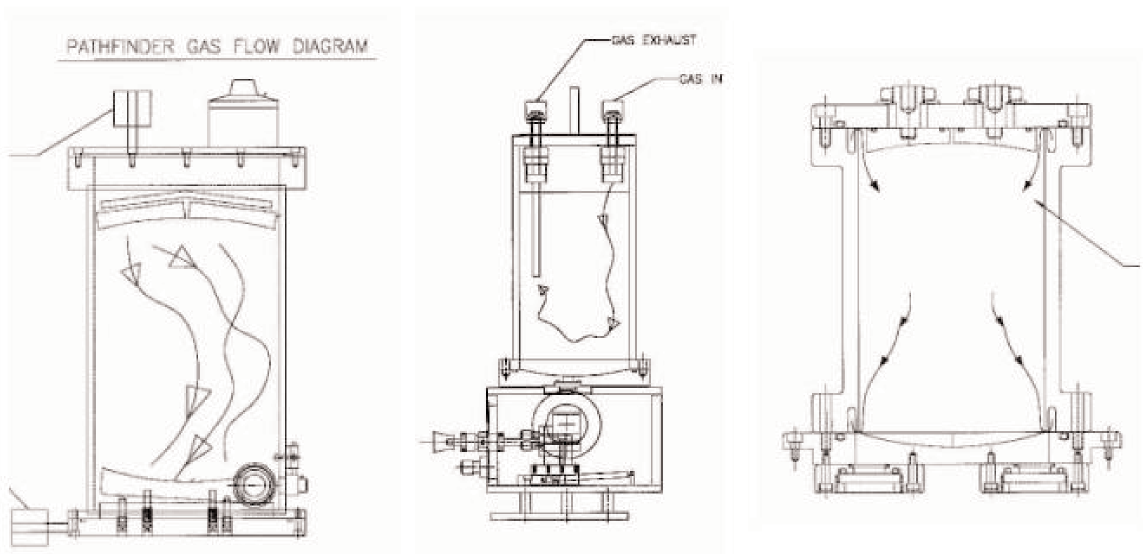

Figure 2a, 2b, 2c. Gas Flow Patterns

rates (minutes). In addition, if the inlet gas pressure is high relative to that in the cell volume, droplet nucleation may occur due to adiabatic expansion.

Figure 2a illustrates a pattern associated with the inlet and outlet ports being at the top and bottom of the gas cell. Once again the pattern is irregular and dead volume spaces are likely, both of which lead to long sample exchange times. Figure 2c shows a configuration with essentially no dead volume, laminar gas flow, and rapid sample exchanges. The specific feature producing these benefits is a circumferential gas flow trough at both the top and bottom of the cell, each being connected to a short inlet or outlet tube. The incoming gas flows around the trough and over its edge to produce a "waterfall-type" of laminar flow throughout the volume of the cell. Sample exchange times are as short as 45 seconds for a cell volume of 600 cc. Most of the electronic gases are very expensive, so the producers and users want to conserve the amount of gas required for purity analysis and verification.

With white cells and with folded-path cells, the infrared energy throughput is a strong measure of its analytical performance. The higher the net energy throughput, the higher the sensitivity for detecting small concentrations of gaseous species. However, energy throughputs vary greatly among the suppliers of the gas cells due to the surface quality of the mirror substrate, the reflectivity of the mirror coatings, the mirror surface areas, the distance between the mirrors (radius of curvature), the number of reflections required for the maximum pathlength, and the alignment of the mirror sets.

Table 8 shows typical energy throughputs for three gas cells manufactured by CIC Photonics, Inc. All three cells are alike in overall mirror quality and alignment, except for the number of reflections required. The 4Runner (4.0-meter) cell exhibits one of the highest energy throughputs, 50-60%, for a multipath cell on the market today.

For those gas cells that exhibit lower energy throughputs, the most common reason is that the mirror areas are too small relative to the size the multi-reflecting infrared beam, with much beam energy being lost over the edges of the mirrors. This situation exists because of user demands to reduce the cell volume and hence the cell diameter.

Many first users of gas cells estimate the pathlength required for their application by performing a simple Beer's Law calculation, with some assumption of the molecular absorption coefficient; alternatively, they apply a experimental value derived from a quick and easy direct path measurement. Having such an estimate, they then proceed to calculate the cell pathlength required for their new gas analysis application.

However, this approach fails to take account of the following factors that do influence significantly the total performance of a multipath gas cell: the signal to noise ratio that is influenced by the optoelectronics of the gas-cell/FTIR-spectrometer hardware system; the infrared spectral reflectivity of the mirror coating; the optical quality of the mirror surface; and the dependence of the energy throughput directly upon the alignment of the mirrors.

Therefore, it is best to characterize the absolute sensitivity of a multipath gas cell in terms of a functional relationship involving all of the above parameters. As a consequence, a 4-meter white cell with these parameters all optimized—e.g. a 4Runner, can and does perform equal to or better than a 20 to 30-meter cell when the parameters are not all optimized.

In summary, the following findings apply to the selection of the best long path gas cell for a variety of gas analysis circumstances, but apply particularly to impurity analyses of the electronic specialty gases used in the semiconductor industry:

- The FTIR/gas cell instrument is more versatile than APIMS
- Gas cells must be acid-resistant with low moisture retention
- Ni-plated stainless steel and Ni-alloys work best with the acid gases
- Mirror coatings strongly determine the cell performance
- Pathlengths less than or equal to 10-meters are adequate for ppb levels
- Window selection depends upon the gas sample

Absolute Sensitivity is a function of mirror quality factors in addition to molecular absorption coefficient and pathlength.

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