Thermal Desorption Technical Support

Note 62: Materials emissions testing in the semiconductor and associated industries

Keywords:

airborne molecular contamination, outgassing, witness wafers, sensitivity, automation, heterogeneous, PVC foam sheet, paint

Introduction

Airborne Molecular Contamination (AMC) is a serious issue in the semiconductor industry as the presence of volatile and semi-volatile organic vapours adversely affects the growth and performance of silicon wafers which in turn affects the performance of microprocessors, data storage devices and other key electronic components. AMC is classified as follows:

- **A**cids (HCl, HF, HNO_3, H_2SO_4)
- **B**ases (NH_3, amines, NMP)
- **C**ondensables (organic compounds with boiling point (bp) >150°C)
- **D**opants (P, B, As compounds)

Although some compounds are not covered by this classification, and some compounds belong to more than one class, the largest group of contaminants are the condensables. There are two major sources:

i) materials outgassing (emissions) from materials used in the construction of cleanroom/fabrication facilities and

ii) materials outgassed from components used to manufacture electronic consumer goods *e.g.* PCs and hard disk drives.

Compounds known to be problematic include:

- siloxanes
- plasticizers *e.g.* phthalates
- flame retardants *e.g.* oganophosphorus compounds
- antioxidants *e.g.* butylated hydroxytoluene
- PAHs *e.g.* napthalene

The sources of these types of compounds are numerous and include:

- sealants
- paints
- plastics
- lubricants
- adhesives
- floor, wall, ceiling tiles
- consumables such as gloves, protective clothing, *etc*.
- chemicals
- HEPA/ULPA filtration systems
- electronic assemblies
- people!

The trend within the semi-conductor industry is for smaller and smaller silicon wafers (from 130 nm in 2001 to 65 nm projected in 2007) which leads to increased sensitivity to contamination from organic condensables. Acceptable levels of contamination are expected to reduce from 2.6 x 10^{14} carbon atoms/cm^2 in 2001 to 1.0 x 10^{13} carbon atoms/cm^2 in 2007 making materials outgassing measurements even more critical.

Analytical methods for measuring materials outgassing

The semiconductor industry uses two principle methods for outgassing measurements:

- Direct outgassing - looking directly at the components being outgassed by particular materials or components (motors, hard drives, disk drives *etc*.) under fixed conditions of temperature, time, gas flow *etc*.

- Indirect outgassing measurement using "Witness Wafers" - blank silicon wafers (test wafers) are placed inside the environment under study (*e.g.* cleanroom). Any outgassed volatiles which may cause problems with real production components are deposited on these wafers. These are then analysed to identify the compounds.

Thermal desorption (TD) is used in both methods because of its inherent advantages compared to conventional solvent-based sample preparation methods (liquid extraction, solvent exchange, steam distillation, *etc*.).

Key benefits of TD include:

- 10^3 - 10^4 fold sensitivity improvement (there is no extraction solvent to dilute compounds of interest). Optimum sensitivity is essential when looking at the ultra-trace levels required.

- Automation – Vapours or test materials are collected/weighed into sample tubes which are introduced directly to the automated thermal desorber (Figures 1, 4 and 5). No additional sample preparation is required, which saves labour and cost

- Selective focusing/concentration of compounds of interest with elimination of matrix interferences such as water

- Eliminates chromatographic interference from the solvent

- Reduced manual preparation reduces errors

- Reusable sorbent tubes (where applicable)

- Compatibility with process/on-plant measurement as well as laboratory work

- Eliminates environmental health and safety issues associated with solvent use.

Direct outgassing measurements can be made in one of two ways:

- direct desorption of materials weighed into empty sample tubes using TD-GC(MS)

- offline purging and trapping of vapours onto sorbent tubes followed by TD-GC(MS) analysis

Analysis of witness wafers is almost invariably done by off-line purge and trap onto sorbent tubes with TD-GC(MS).

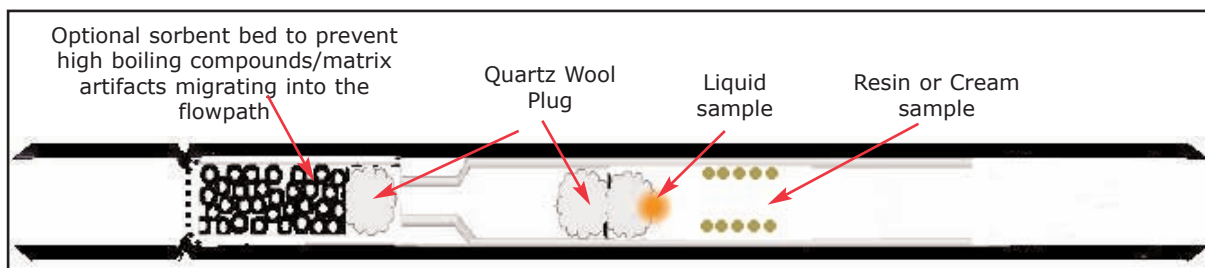## Direct Desorption of Materials

This is often used to investigate the VOCs that could be emitted by a material, suspected to be the source of a contamination problem within a cleanroom environment. A small representative piece of the material to be tested is placed into a thermal desorption tube (or PTFE liner) and desorbed directly.

Direct thermal desorption is compatible with a wide range of different material types such as suspensions, resins, lubricants and plain solids. The only "rules" for success are as follows:

- Solid materials should have a high surface area *e.g.* powders, granules (particle size <1 mm^3), fibres or films. Bulk solids such as plastics used for fume hoods *etc*., should be ground with a coolant such as solid carbon dioxide, before the material is weighed into the empty sample tubes.

- The gas flow path must not be blocked with sample. Thermal desorption is a dynamic process and gas must be allowed to pass through the sample tube unrestricted. This can be an issue with resinous samples such as adhesives. In this case the best technique is to use a PTFE liner and 'smear' the resin around the inner walls of the liner, ensuring that gas may still flow unimpeded. The PTFE liner is then inserted into an empty stainless steel or inert coated sample tube (Figure 1).

- Ensure sample is placed inside the sample tube such that it is well within the heated zone of the thermal desorber used.

(See TDTS 9 for more information on direct desorption of materials)

Direct thermal desorption is only appropriate if the desired extraction takes place at a temperature below the decomposition point of other materials in the sample matrix. In addition, the relatively small sample size that can be measured into a thermal desorption tube may not be representative of a heterogeneous material. In this case purge and trap of the bulk sample, followed by TD-

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Figure 1: Liquid or resinous materials measured into a PTFE liner, and placed inside an empty tube, for direct desorption
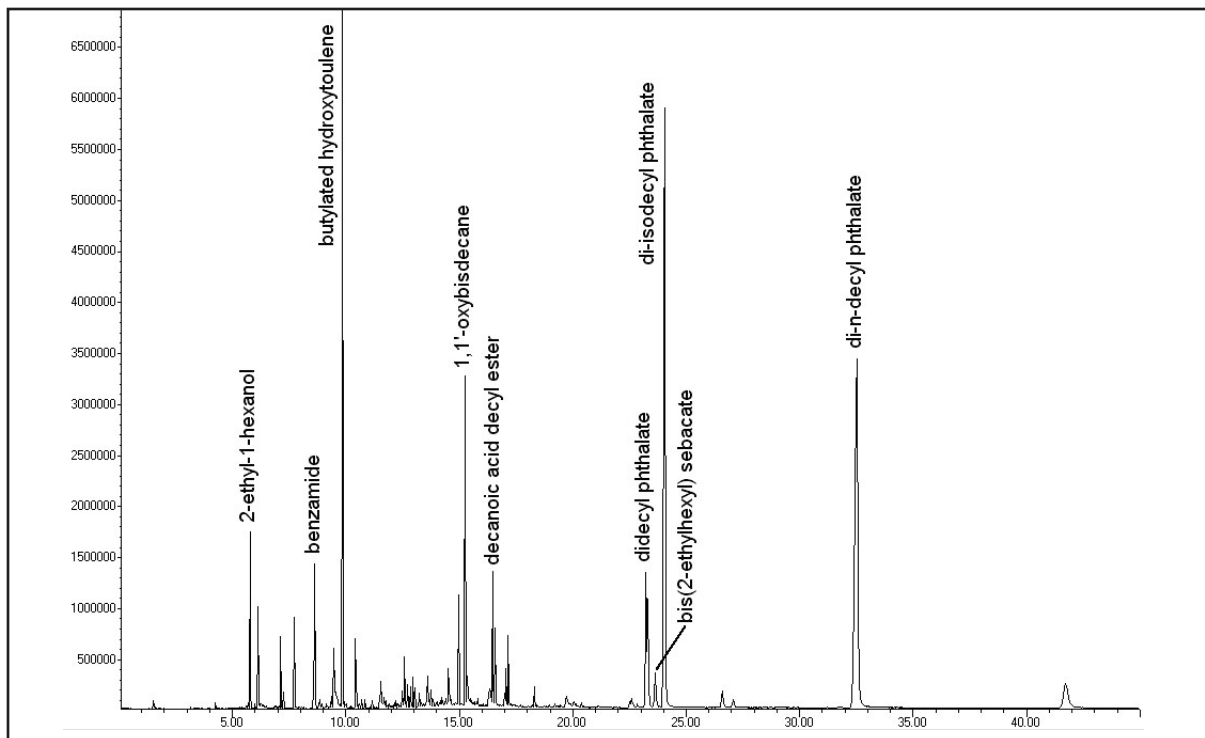
Figure 2: Direct desorption of a 30 mg sample of PVC foam sheet

GC(MS) analysis, is the better option.

However, within these limitations, direct thermal desorption provides automatic on-line extraction/preparation system for all materials that may be found in the cleanroom environment.

Application Examples

PVC Foam Sheet

A 30 mg PVC foam sheet sample was directly desorbed under the following conditions:

Primary Desorption: 60 mins @ 120°C; general purpose hydrophobic cold trap at -10°C

Secondary Desorption: 300°C (20 min hold)

A number of compounds were seen which could cause problems within a cleanroom environment, including butylated hydroxytoluene and a range of phthalates (Figure 2).

Dried Paint Flakes

Even 'old' dried paint still emits a wide range of volatiles. 2 mg of dried paint was desorbed under the following conditions:

Primary Desorption: 10 mins @ 200°C; general purpose hydrophobic cold trap at -10°C

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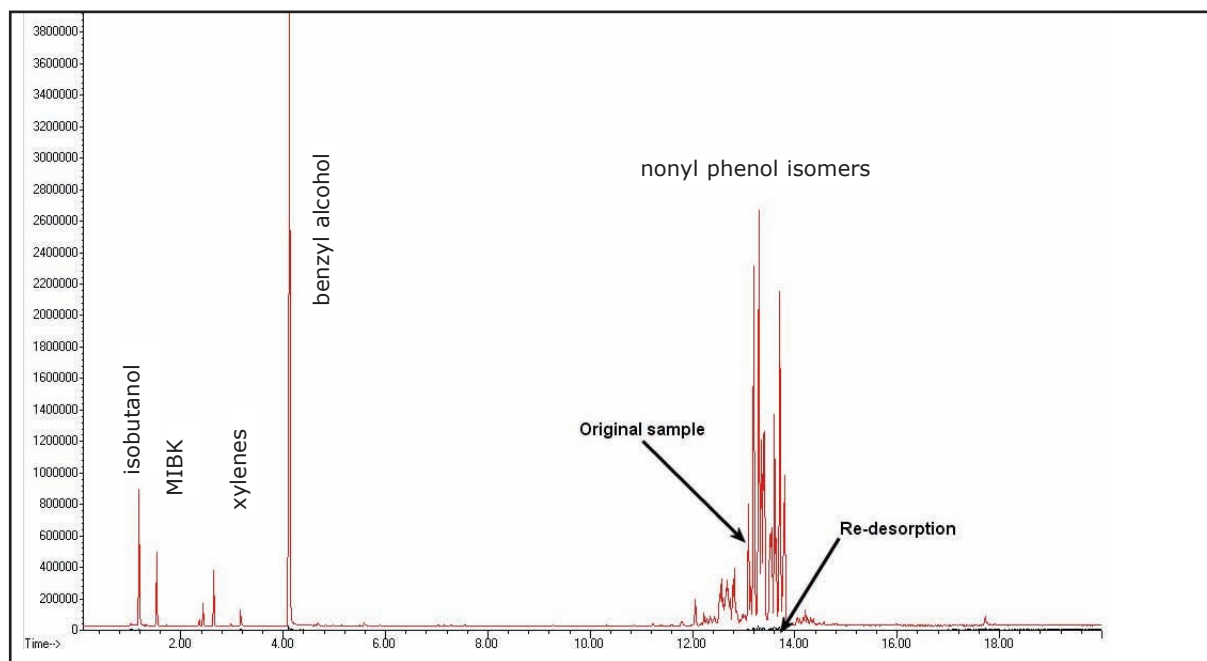
Figure 3: Direct desorption of a 2 mg sample of dried paint

Secondary Desorption: 300°C (3 min hold)

The sample was redesorbed and showed effectively no carryover, confirming complete extraction of the volatiles in one run (figure 3).

Purge and Trap Sampling

Though simple and convenient, direct desorption is not always suitable and off-line purge and trap sampling of volatiles is required. This is the case, for example, when the sample is heterogeneous or when the entire part requires analysis (*e.g.* hard drive, witness wafer) and is too large to be placed into a standard TD tube. Example apparatus is shown in Figures 4 and 5. Samples can either be purged into ambient temperature sorbent tubes for subsequent off-line analysis (Figure 4) or purged/pumped directly into the focusing trap of an on-line desorber for semi real-time measurement (Figure 5).

The combination of purge and trap with thermal desorption not only improves sensitivity, but also facilitates selectivity. Tube and focusing trap sorbents may be used which selectively retain specific analytes while allowing bulk ingredients – water and/or solvent for example - to break through.

Application Examples

Hard Drive motor

The motor was placed into a sample chamber which was incubated at 85°C. High purity nitrogen was purged through the chamber at 50 ml/min for 3 hours and the effluent (containing any outgassed VOCs), was passed onto a sorbent tube packed with 2 graphitised carbon black sorbents suitable for trapping VOCs ranging in volatility from C_5 to C_{20}. The sorbent tube was subsequently desorbed under the following conditions:

Primary desorption: 320°C for 10 mins

Secondary desorption: 320°C for 3 mins

Conclusions

As is seen in the examples, thermal desorption is an ideal technique for measuring the range of components outgassed by both cleanroom/ fabrication facilities and by electronic components themselves. Both types of sample can be easily analysed on the same analytical system, with the technique providing the sensitivity required.

Applications were performed using the stated analytical conditions. Operation under different conditions, or with incompatible sample matrices, may impact the performance shown.

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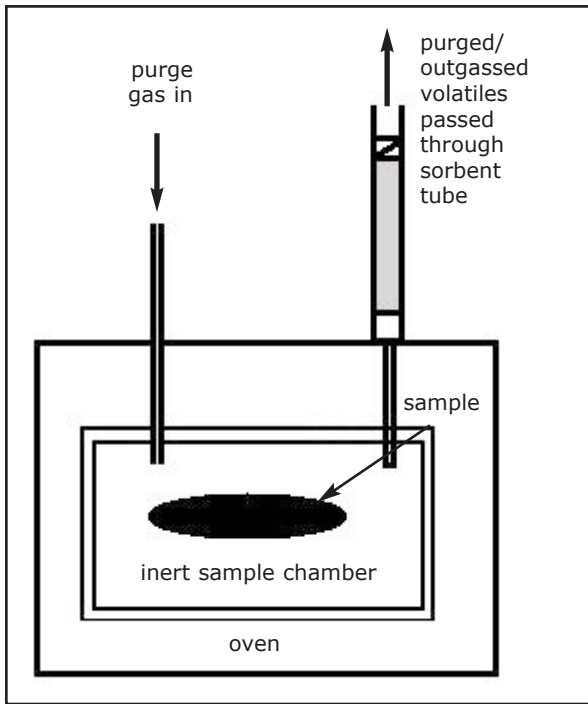
Figure 4: Schematic diagram showing off-line purge and trap onto a sorbent tube
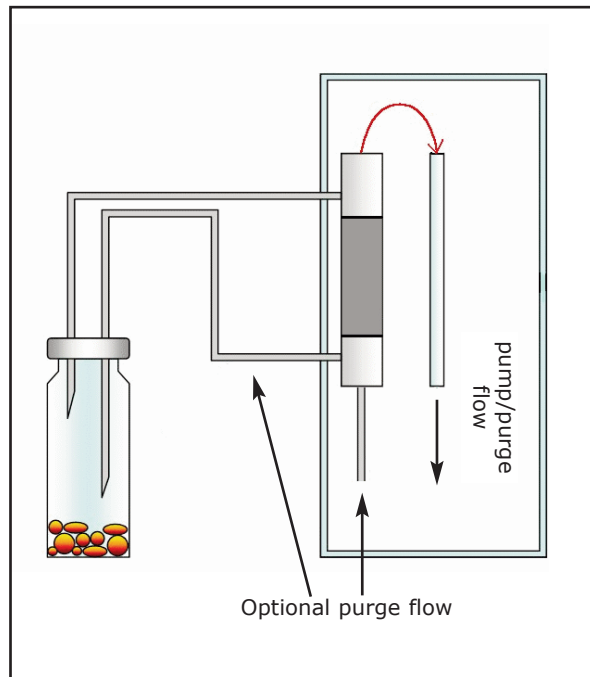
Figure 5: Schematic diagram showing off-line purge and trap directly into a focusing trap, with optional purge flow
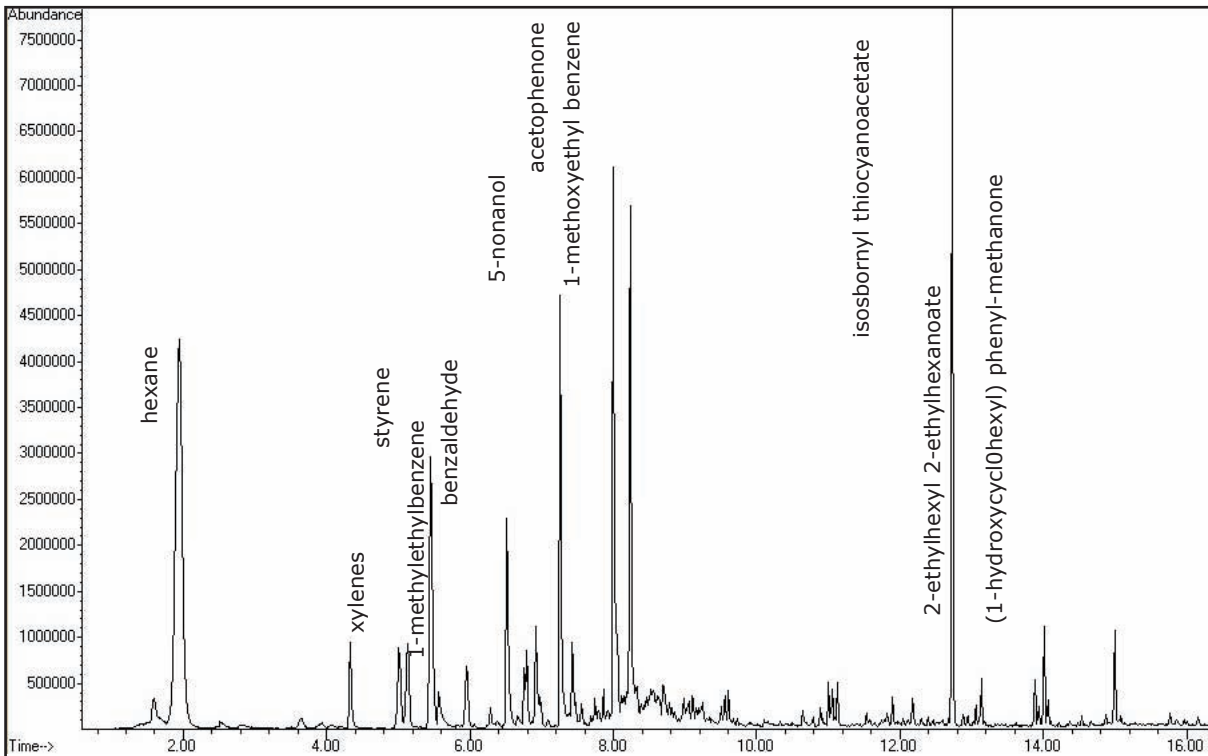
Figure 6: VOC emissions from PC motor incubated at 85°C and the outgassed VOCs collected onto a two-bed sorbent tube

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