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# Validation of thermodesorption method for analysis of semi-volatile organic compounds adsorbed on wafer surface



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## ABSTRACT

To prevent the degradation of the device characteristics it is important to detect the organic contaminants adsorbed on the wafers. In this respect, a reliable qualitative and quantitative analytical method for analysis of semi-volatile organic compounds which can adsorb on wafer surfaces is of paramount importance.

Here, we present a new analytical method based on Wafer Outgassing System (WOS) coupled to Automated Thermal Desorber–Gas chromatography–Mass spectrometry (ATD–GC–MS) to identify and quantify volatile and semi-volatile organic compounds from 6", 8" and 12" wafers.

WOS technique allows the desorption of organic compounds from one side of the wafers. This method was tested on three important airborne contaminants in cleanroom i.e. tris-(2-chloroethyl) phosphate (TCEP), tris-(2-chloroisopropyl) phosphate (TCPP) and diethyl phthalate (DEP).

In addition, we validated this method for the analysis and quantification of DEP, TCEP and TCPP and we estimated the backside organic contamination which may contribute to the front side of the contaminated wafers.

We are demonstrating that WOS/ATD–GC–MS is a suitable and highly efficient technique for desorption and quantitative analysis of organophosphorous compounds and phthalate ester which could be found on the wafer surface.

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## 1. Introduction

The most common source of organic contamination in silicon technology is the presence of polymer materials in the cleanroom. In fact, polymeric materials are found almost everywhere in the production lines and cleanrooms, starting from the bottles and containers for the media up to storage and transport containers for wafers and including such things as the welding foils that cover the boxes when they leave the cleanrooms [1,2].

In order to avoid the exposition of wafers to the contamination from the cleanroom environment caused by the production process, the airborne molecular contaminants (AMC) and particle contamination, the wafers are stored in wafer storage containers such as pods and Front Opening Unified Pods (FOUPs). Unfortunately, these two types of storage containers could represent another additional significant source of organic contamination. Despite being an efficient protection from particle contamination, wafers stored in those containers are frequently exposed to higher

levels of organic contaminants than the wafers in the open cleanroom atmosphere [2].

Nguyen et al. measured the total organic contamination present in the cleanroom air, in a new FOUP and in a cleaned FOUP and they found 7 ppb, 55 ppb and 37 ppb, respectively [3].

The organophosphorus triesters (OPE), which are present in polymers as flame retardants, may migrate in the plastic material and can be emitted to the surroundings [4–6]. A number of OPE have been identified and quantified as airborne substances in common indoor environments [5,7–9]. They are not chemically bound to the plastic polymer; and can migrate from the plastics to the environment [10,11].

Kang et al. applying the TD–GC–MS technique have determined the concentrations of two common organic contaminants emerging from the storage containers such as diethyl phthalate (DEP) and dibutyl phthalate (DBP). They found that the surface density of DBP can reach higher levels than the ITRS (International Technology Roadmap for Semiconductors) recommendation ( $0.3 \text{ ng cm}^{-2}$ ) and higher than the organic contamination level found by Kitajima and Shiramizu to cause a break-down of gate oxide performance ( $0.2 \text{ ng cm}^{-2}$ ) [12].

Tamaoki et al. found that phthalic species such as dioctyl phthalate (DOP) have a tendency to continually adsorb on wafers despite their low gas-phase concentrations [13].

It has been reported that undesirable electrical effects can occur when organic compounds release phosphorus heteroatoms

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upon decomposition at the wafer surface during processing [2]. The organophosphorus compounds are an important concern because the presence of phosphate contamination could lead to unintentional n-type doping into doped layers [14]. Lebens et al. observed electrical effects from unintentional doping of wafers because of an organophosphate flame retardant present at low levels in cleanroom air. This organophosphate was traced to the polyurethane sealant used extensively within certain installed HEPA filters [15].

In a recent study [16] desorption and adsorption constants of volatile organic compounds (VOCs) (acetone, ethyl acetate, xylene and propylene glycol methyl ether acetate (PGMEA)) and semi-volatile organic compounds (SVOCs) (DEP, TCEP and TCPP) were compared. Authors found that the desorption rates of VOCs are approximately 100 times higher than SVOCs desorption rates. The later implies that once the SVOCs deposit on the wafer surface, they hardly desorb and the contamination will remain on the wafer surface in contrary to the VOCs that will rapidly desorb from the surface of the wafer [17]. Authors demonstrated that even at very low gas-phase concentrations these compounds could reach very high surface concentration levels [16–18].

This study represents a continuation of the effort towards comprehensive understanding of the organic contamination issue related to the silicon wafer surface. For this reason we developed and validated a new analytical method for desorption and subsequent quantification of organic compounds from the contaminated wafers. A Wafer Outgassing System (WOS) coupled to Automated Thermal Desorber–Gas chromatography–Mass spectrometry (ATD–GC–MS) was employed for desorption and quantification of TCEP, TCPP and DEP.

## 2. Experimental

### 2.1. Standards

Tris-(2-chloroethyl) phosphate (TCEP; 98.5%) and tris-(2-chloroisopropyl) phosphate (TCPP; 99.5%) were purchased from Dr. Ehrenstorfer GmbH. Methanol (Chromasolv,  $\geq 99.9\%$ ), diethyl phthalate (DEP; 99.5%) and the deuterated internal standard tris-(2-chloroethyl) phosphate- $d_{12}$  (TCEP- $d_{12}$ ; 97%) from Sigma Aldrich.

Prior to each measurement individual stock solutions of each analyte were prepared in methanol. Solutions of DEP, TCEP, TCPP and the TCEP- $d_{12}$  were mixed in methanol. The calibration standards were prepared by serial dilutions of the mixture solution in methanol.

### 2.2. Sorbent materials and standard tubes preparation

Tenax TA tubes (TERA Environnement) are made of stainless steel and packed with 250 mg of sorbent. The sorption material is a porous polymer resin (2,6-diphenylene oxide) with a specific surface area of approximately  $35 \text{ m}^2 \text{ g}^{-1}$ , that is suited for adsorption of less volatile organic compounds with boiling point ranging from  $100 \text{ }^\circ\text{C}$  to  $400 \text{ }^\circ\text{C}$  [19]. To minimize their blank values, prior to each use the Tenax TA tubes were conditioned by Adsorbent Thermal Regenerator (ATR, TERA Environnement) at temperature of  $310 \text{ }^\circ\text{C}$  for 8 h by Nitrogen gas flow rate of  $50 \text{ ml min}^{-1}$ . Under such experimental conditions a satisfactory background level was obtained since the post-conditioning tube blank analyses showed no measurable contamination.

Identical sampling tubes and tube conditioning method were used for analyzer calibration and experimental samples. To establish calibration curves,  $1 \mu\text{l}$  of the liquid standard solutions containing the three organic compounds and internal standard mixed was directly syringe-injected onto the sorbent bed via the

sampling end of the standard tubes. The spiked tubes were then sealed with brass caps having PTFE seals and stored for more than 3 h at  $4 \text{ }^\circ\text{C}$  to allow the sorbent bed to equilibrate. We tested the stability of the three compounds in the sorbent tubes storing them up to 65 days and the same quantity was obtained as for 3 h stored compounds. The following RSD were obtained for DEP, TCEP and TCPP: 5%, 1% and 5%, respectively.

### 2.3. Instrumentation

#### 2.3.1. Wafer Outgassing System (WOS)

The Wafer Outgassing System (WOS 2000 series, A&B Analytical and Bio Science instruments Co., Ltd.) is fourth generation equipment (the prototype was launched in 1999 and the Latest i.e. fourth generation was released in 2005) used to desorb VOCs and SVOCs from 6", 8" and 12" wafers. In order to desorb the compounds under study, the wafer polished face (frontal side) was placed in contact with the quartz chamber while the back side was in contact with a quartz cover. The top of the chamber envelopes all parts and as a whole was heated at the set temperature. A Nitrogen flow was injected into the quartz chamber via several vents while other vents extract the Nitrogen charged with VOCs and SVOCs desorbed from the wafer face in contact with these vents (Fig. 1).

The contamination on the frontal side of the wafer was extracted by the vents until the Tenax TA tube which is cooled to  $10 \text{ }^\circ\text{C}$  to allow the adsorption of organic compounds on the adsorbent. The contamination on the back side of the wafer is extracted to the waste by the gas vent of the quartz cover. The design of the device would allow a single-side analysis, but we observed experimentally that one of the in-flow vents and one from the out-flow vents were not covered by 8" wafers. These non-covered vents may induce a possible overestimation of the front side contamination resulting in the trapping of a small fraction of compounds coming from the back side of the wafer. As a result, it is important to evaluate this overestimation.

#### 2.3.2. Automated thermal desorber–Gas chromatography–Mass Spectrometry (ATD–GC–MS)

Amounts of DEP, TCEP and TCPP adsorbed on Tenax TA tubes were determined with a Perkin Elmer Automated thermal desorber (ATD) TurboMatrix 650 coupled to a Clarus 500 Gas chromatography–Mass spectrometry (GC–MS) equipped with a PE-5MS (5% diphenyl, 95% dimethyl polysiloxane, length 30 m, i.d. 0.25 mm, film thickness  $1 \mu\text{m}$ ) analytical column and a quadrupole mass detector was used for the analysis of DEP, TCEP, TCPP and TCEP- $d_{12}$ . The ATD unit contains a two-stage thermal desorption process. In the first stage, the samples were heat-extracted for 30 min at  $300 \text{ }^\circ\text{C}$  from the sorbent tubes and carried by a reverse gas flow into a cold trap cooled to ( $-20 \text{ }^\circ\text{C}$ ) to re-concentrate. In the second stage, the concentrated organic compounds of interest were desorbed by rapid heating to  $360 \text{ }^\circ\text{C}$  maintained for 5 min during which they are transferred by helium gas into the capillary column with a flow rate of  $1.2 \text{ ml min}^{-1}$ . To further enhance the method detection limits (MDLs) and signal-to-noise (S/N) ratio of the MS detector, the inlet (tube to cold trap) and outlet (cold trap to GC column) split flows were adjusted in a way that the amount of organic compounds into GC column was maximized. Consequently, the inlet split flow was turned off in order to transfer all trace species into the cold trap, whereas the outlet split flow was controlled at  $20 \text{ ml min}^{-1}$  to avoid residual species in the cold trap that may lead to over-extended chromatographic peaks. Also, in order to prevent condensation the transfer lines and the valve were maintained at  $300 \text{ }^\circ\text{C}$  and  $250 \text{ }^\circ\text{C}$ , respectively.

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