



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 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 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 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 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 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.

The GC–MS operated at a programmed oven temperature from 40 °C to 100 °C at a rate of 10 °C min⁻¹, and remained at 100 °C for 7.5 min, then ramped to 160 °C at a rate of 7.5 °C min⁻¹ and maintained at 160 °C for 5 min and finally ramped to 320 °C at a rate of 7.5 °C min⁻¹ and remained at 320 °C for 4.2 min. The ion-source temperature was maintained at 250 °C, and electro-impact mass spectra were recorded in the range from 33 to 400 m/z units.

2.3.3. Time of flight-secondary ion mass spectrometry (ToF-SIMS)

ToF-SIMS measurements were performed using ToF-SIMS⁵ (IONTOF) apparatus (Biophy research). Primary beam of Bi₃⁺ ions at 25 KeV was used. Contrary to the WOS only a part of the wafer can be analyzed (200 × 200 μm²); three measurement points were achieved for the positive ions spectrum and three other points for negative ions spectrum. All the measurements were made in a cryogenic mode to avoid desorption of the organic compounds from the wafer surface due to the vacuum in the sample room during analysis.

2.4. Optimization and validation procedures

The American Society for Testing and Materials (ASTM F1982-99) [20] and Semiconductor Equipment and Materials International (SEMI E108-0301) [21] recommends to heat the wafer at 400 °C to desorb the organic contamination adsorbed in its surface. In order to optimize the desorption temperature and duration and to verify if the 400 °C is a suitable temperature for the three test compounds used in this study, an experimental procedure was undertaken to establish the optimization method. The wafer was spiked with 1 μl of the same standard solution containing a mixture of the organic compounds and then heated at six different experimental conditions. Three replicates for each condition were carried out. Three temperature values were tested 200 °C, 300 °C and 400 °C; and each temperature was applied for 30 min or 60 min of extraction. The temperature was chosen according to the chemical properties of the organic compounds (Table 1).

The organic contaminants under study are SVOCs with boiling point ranging between 294 and 358 °C. Hence, an operating temperature less than 200 °C will not desorb rapidly a significant

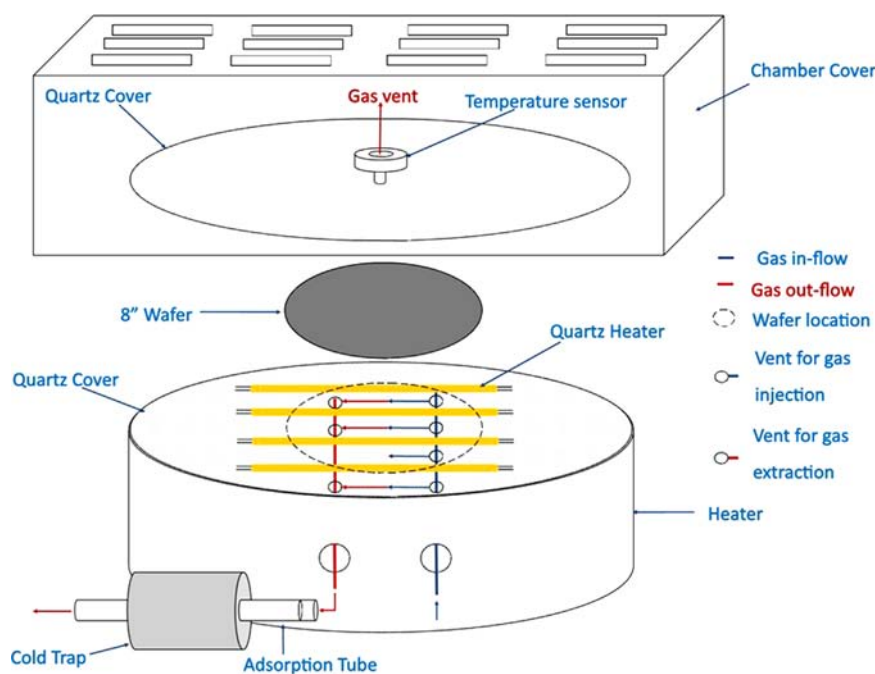
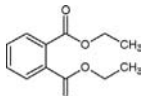
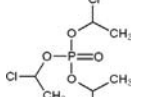
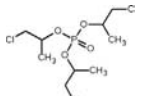


Fig. 1. Scheme of the Wafer Outgassing System.

Table 1

Physicochemical properties of the studied organic compounds.

Compound	CAS number	Chemical formula	Chemical structure	Boiling point (°C)	Vapor pressure (mmHg) at 25 °C
Diethyl phthalate (DEP)	84-66-2	C ₁₂ H ₁₄ O ₄		294 ^a	1.67 × 10 ^{-3a}
Tris(2-chloroethyl) phosphate (TCEP)	115-96-8	C ₆ H ₁₂ Cl ₃ O ₄ P		347 ^a	1.08 × 10 ^{-4a}
Tris(2-chloroisopropyl) phosphate (TCPP)	13674-84-5	C ₉ H ₁₈ Cl ₃ O ₄ P		358 ^a	5.25 × 10 ^{-5a}

^a SciFinder (2013).

amount of these contaminants while a temperature higher than 400 °C could lead to decomposition of the compounds.

To determine the repeatability, reproducibility and the recovery of the three tested compounds in the WOS, wafers were spiked with 1 µl of standard solution and immediately desorbed in the WOS system. Wafers were spiked on the front face, front and center back face; front and edge back face in order to determine the effect of the contamination on the back side of the wafer and its position on the extracted amount and to test the relative standard deviation (RSD) of the method.

3. Results and discussion

3.1. Validation of the method

3.1.1. ATD–GC–MS

The three organic compounds DEP, TCEP and TCPP and the internal standard TCEP-d12 were identified according to their retention time on the chromatogram. In order to confirm the identification of each compound, the mass spectrum was examined. The specific fragments are: (*m/z* 149) for DEP, (*m/z* 249) for TCEP, (*m/z* 99 and 125) for TCPP and (*m/z* 67) for TCEP-d12. The method detection limits (MDLs) were defined as three times the standard deviation of the standard solution at the lowest dilution level while the limits of quantification (LOQ) were defined as ten times the standard deviation for the same standard. Ten tubes were spiked with 1 µl of standard solutions and analyzed by ATD–GC–MS to determine these values. The MDLs, the LOQ and the linearity in the response of the detector are listed in Table 2.

Quantification of DEP, TCEP and TCPP was made by using internal standard (TCEP-d12) calibration to compensate possible errors in the volume of solution spiked. Calibration curves were made by plotting the ratio between analytes and internal standard peak area vs. the ratio between analytes and internal standard amount. Correlation coefficients obtained were between 0.98 and 0.99.

3.1.2. Wafer Outgassing System

3.1.2.1. Wafer Outgassing System optimization. In the WOS system the experimental conditions such as the gas flow, desorption temperature and the duration of desorption are controlled. The gas flow is a fixed parameter to avoid any perturbation of the gas dynamics in the WOS system while the desorption temperature and duration could have an important impact on the contaminant quantity desorbed from the wafer.

Fig. 2A shows the concentration ratios of the studied organic compounds (DEP, TCEP and TCPP) over the internal standard (TCEP-d12) under different temperatures and various extraction durations.

The ratio of the surface area of the compounds from the tubes spiked with standard solutions vs. the surface area of the internal standard was plotted against the ratio of the concentrations of these compounds vs. concentration of the internal standard. From the slope and the intercept of this plot we calculated the concentration ratio of the compounds desorbed from the wafer.

Table 2

Limits of detection, limits of quantification and linearity domain of DEP, TCEP and TCPP from Tenax TA tubes.

Compound	LOD (µg)	LOQ (µg)	Linearity domain (µg)	Correlation coefficient
DEP	0.056	0.187	0.187–8.32	0.9960
TCEP	0.032	0.107	0.107–4.24	0.9898
TCPP	0.015	0.052	0.052–3.65	0.9863

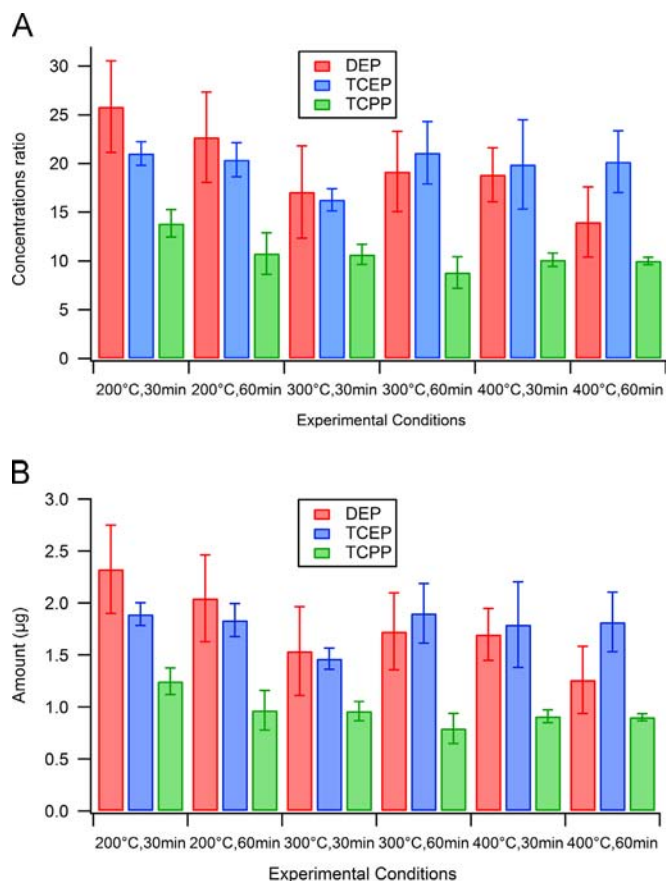


Fig. 2. (A) Extracted amount of DEP, TCEP and TCPP for different extraction conditions in the WOS expressed in the terms of concentrations ratio. (B) Extracted amount of DEP, TCEP and TCPP for different extraction conditions in the WOS.

As can be seen in Fig. 2A, there is no significant impact of the temperature and duration of extraction on the concentration ratios.

The internal standard (TCEP-d12) was chosen as such to have similar physico-chemical properties as the three compounds under study. As a result, the internal standard and the three SVOCs could have the same behavior regarding desorption which can mask the difference between the amount of desorbed compounds under the various experimental extraction conditions. For this reason, in Fig. 2B we plotted the extracted amount of each compound (µg) under the different experimental conditions. The amount of each compound can be estimated as follows:

$$Xc (\mu\text{g } \mu\text{l}^{-1}) \times V (\mu\text{l}) \quad (1)$$

where *X* is the concentrations ratio obtained from calibration curves made by analysis of Tenax TA tubes spiked with the standard solutions, *c* is the concentration of the internal standard added on the wafer surface and *V* is the spiked volume on the wafer surface.

By comparison of Fig. 2A and B it can be noticed that there is no difference if we take into consideration the amount of the internal standard and the spiked volume. This later implies that the error made on the volume is negligible and the absolute value of the compounds can be used expressed in term of quantity (µg) instead of concentration (µg/µl).

According to the analytical margin of error, neither the temperature nor the duration of extraction have a significant impact on the extracted amount. Hence, it can be concluded that the proposed temperature by the ASTM and SEMI (400 °C) is suitable in our case study. By comparing the obtained results for 30 min of

extraction or 60 min of extraction the duration of 30 min allows a sufficient extracted amount. Therefore, the conditions chosen were 400 °C and 30 min and they were used for the rest of the experiments. According to these conditions, recovery tests were carried out both to determine the extraction yield of the organic contaminants and to calculate the analytical error associated.

3.1.2.2. Repeatability, reproducibility and recovery tests. The recoveries are calculated according to the following equation:

$$\text{measured amount } (\mu\text{g}) \times 100 / \text{spiked amount } (\mu\text{g}) \quad (2)$$

where the “measured amount” is the quantity obtained by WOS/ATD–GC–MS analysis of the spiked wafer and the “spiked amount” is the theoretical quantity added on the spiked wafer. The desorptions were performed in triplicates. The amount obtained for a non-spiked reference wafer is negligible compared to the amount measured for the spiked wafer. As a result, this amount is not included in the calculations of the recoveries. The extraction efficiency of the three compounds ranged between 69% and 92% with relative standard deviation (RSD) ranging between 12% and 14% (Table 3).

The best recovery is obtained for DEP which has the highest vapor pressure among the three tested compounds. Presumably the spiked amount is not completely desorbed or there are losses in the WOS that are the cause of recoveries less than 100%. In order to verify these hypotheses, a spiked wafer was desorbed two successive times in the WOS and the two Tenax TA tubes derived from these desorptions were analyzed by ATD–GC–MS. The amounts of the three compounds adsorbed on the second desorption tube which correspond to the second desorption of the wafer were less than the quantification limit of the used method.

Therefore, a second desorption of the wafer in the WOS and analysis by ATD–GC–MS could not be used to find the real cause of the losses in the desorption. As a result, a more sensitive method is needed to analyze the wafer surface after the first desorption in the WOS. The ToF–SIMS was chosen for this purpose. This technique allows a local measurement of the contamination which means that the portion of the wafer used for analysis should be representative of the overall contamination on the wafer surface. In order to respect this condition and to obtain representative results of the total contamination of the wafer, the ToF–SIMS method was applied to wafers contaminated in a homogeneous way. The contamination method, the ToF–SIMS analysis and the results are described in details in Section 3.2.

The precision of the WOS/ATD–GC–MS method was tested based on relative standard deviation (RSD) corresponding to desorption of one side spiked wafer. Six desorptions were made on several days, the RSD values ranged from 8% to 10%. These results represented by “reproducibility” in Table 3 show that there is a good reproducibility of the method.

3.1.2.3. Effect of the contamination position on the back side of the wafer. The WOS device is designed to measure the contamination on the frontal side of the wafers. Nevertheless, the presence of contamination on the back side of the wafer may induce an

Table 3

Extraction recovery for the WOS/ATD–GC–MS from spiked wafers ($n=4$ repetitions) and reproducibility of the method expressed in terms of RSD ($n=6$ repetitions).

Organic compound	WOS/ATD–GC–MS	
	Extraction recovery \pm RSD (%)	Reproducibility (%)
DEP	92 \pm 14	10
TCEP	73 \pm 13	10
TCPP	69 \pm 12	8

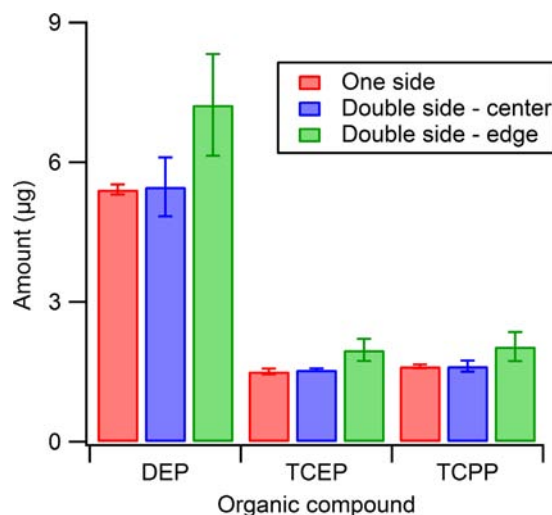


Fig. 3. Extracted amount obtained for one side spiked, double side-center (the back contamination deposited on the wafer center) and double side-edge (the back contamination deposited on the edge of the wafer).

overestimation of the frontal side contamination. In order to test this possibility, wafers were spiked on both i.e. the frontal side and the back side and directly analyzed by WOS/ATD–GC–MS. The analytical results were compared with those obtained for wafers spiked on the frontal side only. Further, to study the effect of the position of the contamination on the back side, wafers were spiked on the frontal side as usual in the center and on the back side at the center and at the edge of the wafer. Three repetitive experiments were carried out for each position. As can be seen in Fig. 3 when the back side contamination is deposited on the center of the wafer there is no significant difference between the single side and the double side – center contamination. This result is explained by the fact that the contamination on the center of the back side is positioned under the gas vent of the upper quartz cover (Fig. 1) which implies that it is mainly extracted by this vent into the waste.

When the back side contamination is deposited on the edge of the wafer, a significant difference in the collected amount of the organic compounds can be appreciated (Fig. 3). 14% of the back side contamination for DEP, 13% for TCEP and 8% for TCPP were collected on the Tenax TA tube with less than 22% of RSD. These overestimations are probably induced by the proximity between the position of the back side contamination and the uncovered vents of the lower quartz cover. The deposition of the organic contamination on the edge of the wafer is an extreme case therefore the obtained values under such conditions represent the upper limit of the overestimation. In real case, the contamination is spread all over the wafer surface hence, the percentages and the RSD presented above will be a non-reached maximum for real samples.

3.2. Application of the method

3.2.1. Deposition of an homogeneous contamination on wafer surface

The contamination procedure using a local deposition of organic contaminants in a liquid solution induces an unrealistic contamination. In reality, one could think that the contamination is more or less homogeneous or at least several spots of contamination could be found in various positions on the wafer surface due to the contact with the equipment that could be contaminated. This unrealistic contamination could possibly have an impact on the experimental recoveries presented above. To test

this possible artifact and to simulate a more realistic case scenario the contamination was spread all over the surface using a different contamination procedures.

Two wafers were contaminated by this approach in the same way and at the same time. Before to apply this contamination procedure the wafers were cleaned from possible traces of organics by heating in the WOS at 500 °C for 60 min and then placed in a pod where a flux of nitrogen, containing the known and controlled gaseous concentrations of the three compounds, flows continuously. By gas–solid equilibrium, it is possible to obtain a homogeneous contamination on the two sides of the wafer. The contamination levels on the solid phase are controlled by both temperature and the gas-phase concentration of the organic compounds [16,22,23]. For details about the gas-generation system the readers are referred to our previous article by Nieto-Gligorovski et al. [17].

3.2.2. Analysis of homogeneously contaminated wafers by the validated method and semi-quantitative inter-comparison with ToF-SIMS and HS-PTR-quad-MS analysis

In order to validate the extraction yields obtained by WOS, a comparative analysis has been undertaken with two other analytical techniques i.e. ToF-SIMS and High Sensitivity-Proton Transfer Reaction-quadrupole-Mass Spectrometry (HS-PTR-quad-MS).

3.2.2.1. ToF-SIMS analysis. As discussed previously in Sections 2.3.3 and 3.1.2.2, ToF-SIMS technique allows only local measurements of contamination on a small surface (0.04 mm²) of the wafers. However, because the contamination is spread all over the wafer, a local analysis on a part of the wafer is representative of the contamination on the entire wafer. The ionization mode used in the ToF-SIMS (ion beam of Bi³⁺) induces a strong fragmentation of the organic molecules. However, the DEP, TCEP and TCPP can be analyzed by their characteristic fragments (phthalate ions (C₈H₅O₃⁺) and phosphate (PO₄⁻)). The high ionization energy represents a disadvantage because of the confusion between the two organophosphorous compounds but it allows an accurate analysis of physisorbed and even strongly bound chemisorbed organic compounds on the wafer surface. In addition, ToF-SIMS has a lower detection limit than the WOS/ATD-GC-MS. One of the homogeneously contaminated wafers was immediately analyzed by ToF-SIMS while the other one was desorbed in the WOS for the ATD-GC-MS analysis before being analyzed by ToF-SIMS. The desorption yields were calculated as the ratio of the difference between the relative intensities of the contaminated and the desorbed wafer over the relative intensity of the contaminated wafer. The obtained yields were 93% for both the organophosphorous compounds and phthalate.

These results confirm that the desorption in the WOS is not complete as 7% of the compounds remains on the wafer surface after WOS desorption. Unfortunately, because ToF-SIMS is a semi-quantitative method the calculated desorption yields are only indicative values.

3.2.2.2. HS-PTR-quad-MS analysis. One of the wafers homogeneously contaminated was analyzed by WOS/ATD-GC-MS. The raw results corresponding to the amount (μg) of each compound measured using one thermal extraction in the WOS following by ATD-GC-MS are given in Table 4.

In order to calculate the total amount of each compound adsorbed on the wafer surface the raw results are divided with the recoveries obtained by the wafers spiked with local contamination. The obtained results can be appreciated in Table 4 as “measured amount/recoveries”.

Table 4

Comparison between the measured amounts and the theoretical amounts and the corresponding recoveries.

Compound	Measured amount ^a (μg) ± RSD (%)	Measured amount/recoveries ^b (μg) ± RSD (%)	Theoretical amount ^c (μg) ± RSD (%)	Recoveries ^d (%) ± RSD (%)
DEP	0.98 ± 10	1.07 ± 10	0.81 ± 35	121 ± 36
TCEP	1.37 ± 10	1.88 ± 10	2.06 ± 52	67 ± 53
TCPP	2.47 ± 8	3.58 ± 8	3.05 ± 39	81 ± 40

^a Measured using one thermal extraction in the WOS followed by ATD-GC-MS.

^b Measured amount divided by recoveries obtained from local contamination.

^c Calculated from the SVOCs concentrations in the gas phase measured by HS-PTR-quad-MS.

^d Recoveries are expressed by 100 times the ratio between the measured amount of each compound and the theoretical amount of the same compound.

The theoretical adsorbed amount of organic contaminants on a wafer surface was calculated on the basis of the equilibrium between the solid and the gas phase. The concentrations of the gas-phase compounds were measured by a HS-PTR-quad-MS [16,17]. The “theoretical amount” of the three compounds adsorbed on the wafer surface is also reported in Table 4.

Comparing the “measured amount” with the “theoretical amount”, it is possible to calculate the recoveries of the homogeneously contaminated wafers (“recoveries” in Table 4). According to the margin of error on the gas-wafer surface equilibrium which vary between 35% and 52% [16] and the WOS/ATD-GC-MS analytical method (between 8% and 10%), the error bars of the “recoveries” are 36%, 53% and 40% for DEP, TCEP and TCPP, respectively. Taking into account these errors it can be noticed that the “recoveries” are of the same order as those obtained for local contamination (Cf. Table 3). The phenomenon of non-complete desorption observed in the case of local contamination and in the case of homogeneous contamination of whole wafer surface are similar which in turn implies that the two contamination methods are consistent.

As a result of the findings presented above, a correction factor should be applied to the measured amount obtained by WOS/ATD-GC-MS analysis in order to obtain the entire adsorbed amount of the wafer's surface. Since, as mentioned before the ToF-SIMS technique provides semi-quantitative results and it determines only local contamination one cannot use the recoveries calculated from this technique. Therefore, the obtained recoveries from the WOS/ATD-GC-MS measurements for local contamination have to be employed as a correction factor. The raw results should be divided by 0.92, 0.73 and 0.69 for DEP, TCEP and TCPP, respectively.

4. Conclusions

When assessing strategies for monitoring and control of organic contaminants, it is of crucial importance to understand the synergy of the organic contaminants that deposit on wafer surfaces and those found in the cleanroom air [14].

We demonstrated that WOS/ATD-GC-MS is a suitable technique for desorption and quantitative analysis of organophosphorous compounds and phthalate ester which are present on the wafer surface.

The presence of back side contamination and the position of this contamination were also tested in such way that the wafers were contaminated on single side and on the back side at the center and at the edge. When the back side contamination is deposited on the center of the wafer there is no significant overestimation of the front side contamination of the wafer. The

deposition of the organic contamination on the edge of the wafer can induce an overestimation ranging between 8% and 14% depending on the compounds under study but this case is not a realistic scenario and these values have to be considered as an upper limit.

Finally, in order to test the developed analytical method on a wafer contaminated homogeneously, two wafers were intentionally contaminated simultaneously by a gas stream mixture of DEP, TCEP and TCPD and then analyzed by WOS/ATD–GC–MS and ToF-SIMS technique. This experiment showed that a fraction of the contamination remain on wafers after WOS desorption and the recovery yields were calculated ranging between 69% and 92%. These values can be used as a correction factor to the measured amounts by WOS/ATD–GC–MS to calculate the total contamination.

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