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Direct quantitative analysis of phthalate esters as micro-contaminants in cleanroom air and wafer surfaces by auto-thermal desorption–gas chromatography–mass spectrometry

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Abstract

This study established an analytical method for the trace analyses of two phthalate esters, including diethyl phthalate (DEP) and di-*n*-butyl phthalate (DBP), known as the major constituents of cleanroom micro-contamination detrimental to the reliability of semiconductor devices. Using thermal desorption coupled with a GC–MS system, standard tubes were prepared by delivering liquid standards pre-vaporized by a quasi-vaporizer into Tenax GR tubes for calibration. This method was capable of achieving detection limits of 0.05 $\mu g\,m^{-3}$ for 0.1 m^3 air samples and 0.03 $ng\,cm^{-2}$ for 150-mm wafer surface density. Actual samples collected from a semiconductor cleanroom showed that the concentration of DBP in a polypropylene wafer box (0.45 $\mu g\,m^{-3}$) was nearly four times higher than that in the cleanroom environment (0.12 $\mu g\,m^{-3}$). The surface contamination of DBP was 0.67 $ng\,cm^{-2}$ for a wafer stored in the wafer box for 24 h. Furthermore, among the three types of heat-resistant O-ring materials tested, Kalrez® was found to be particularly suitable for high-temperature processes in semiconductor cleanrooms due to their low emissions of organic vapors. This analytical procedure should serve as an effective monitoring method for the organic micro-contamination in cleanroom environments.
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Keywords: Airborne molecular contaminants; Phthalate esters; GC–MS; Cleanroom; Wafer contamination; Surface desorption

1. Introduction

The increasing complexity and miniaturization of modern integrated circuits (ICs) demand a higher device yield, and lower defect density in the active region of the silicon devices. This, in turn, necessitates the reduction of airborne molecular micro-contamination in the device production environments. When the thickness of gate-oxide layer of the field-effect transistor is scaled down to below 10 nm, organic contaminants adsorbed on the wafer surface can cause substantial degradation of gate-oxide integrity. Numerous studies have shown that the quality of thin gate-oxide was closely related to the degree of trace organic contamination on the silicon wafer surfaces from the cleanroom environment [1–5]. In addition, the trace condensable organic contaminants adsorbed onto wafer surfaces can also induce changes in contact resistance and voltage shift [6]. Therefore, trace organic compounds outgassing from the construction materials in cleanroom, process equipment, and wafer carrier boxes, are gradually drawing attention as possible sources of micro-contamination.

The tendency and behavior of organic contaminants adsorbing on the wafer surfaces strongly depend on their vapor pressure, molecular weight or chemical nature. For example, organic compounds with high boiling points (b.p.s) tend to remain on the wafer surfaces and gradually replace species with lower b.p.s, even though their concentrations in

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the cleanroom ambience are much lower [7]. Many of these compounds belong to the organo-polymeric additives (e.g., antioxidant, plasticizer, cross-linking agent) that can easily outgas from polymeric surfaces such as wafer carrier boxes, sealants, and construction materials. In particular, families of alkyl phthalate esters and methyl siloxanes have been probed as the major constituents that are persistent in cleanroom ambience, consequently their deposition behaviors onto wafer surfaces have been studied on both long-term and short-term basis [8–11]. Therefore, developing a simple and reliable method for the quantitative analyses of these high b.p. organic compounds from cleanroom air and wafer surfaces is of great practical interest to the field of environmental control for semiconductor fabrication.

In general, monolayer adsorption of organic contaminants on wafer surfaces is difficult to quantify by surface analysis techniques. Although X-ray photoelectron spectrometry (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SI-MS) have been used for the detection of the organic contamination on silicon wafer surfaces [12–14], both methods require high vacuum conditions under which the loss of volatile components of the samples could become significant. Alternatively, gas chromatography in conjunction with mass spectrometry (GC–MS) has been known for its superior separation of complex organic compounds, greater sensitivity, and shorter measuring time, hence is better suited for the detection and identification of volatile organic compounds (C_2 to n-C_{10}) [2]. However, organic molecules with high b.p.s (e.g., phthalate esters) tend to adhere onto the surfaces of the sampling and analytical apparatus, substantially reducing the quantitative capability of GC–MS for trace concentration ranges. Consequently, information on the concentrations of phthalate esters in cleanroom air is quite limited. In one previous analysis, Hill et al. [15] used GC–MS to quantify the phthalate esters contamination of air through polyvinyl chloride tubing based on the calibration of direct injection of standard solutions. They did not, however, discuss the sample collection and recovery efficiencies of the analytical method. Otake et al. [16] demonstrated low detection limits using GC–MS for samples collected by charcoal tubes, followed by solvent (toluene) extraction and separation in sequence through ultrasonication and centrifugation. This procedure, while giving remarkably low detection limits, could be overly elaborating and time-consuming in meeting the requirement of frequent analyses for monitoring purposes.

The goal of this study is to develop a convenient and cost-effective sampling and analytical procedure tailored to the need of frequent quantitative measurements of phthalate esters in cleanroom environments and on wafer surfaces. Calibrating materials selected to represent the alkyl phthalate esters are diethyl phthalate (DEP) and di-*n*-butyl phthalate (DBP), both of which are widely used as the plasticizer ingredients and have been identified as parts of the major outgassing compounds from wafer storage boxes [17,18]. Their physicochemical properties are listed in Table 1. The procedures described in this report include an analytical technique using auto-thermal desorption GC–MS (ATD/GC–MS) at low part-per-billion (ppb) levels, as well as the application of a heat-desorption compartment for surface analyses similar to the procedure described in the ASTM test method [19]. Another objective is to present the results of quantification for samples collected from various places in an actual semiconductor cleanroom.

2. Experimental

2.1. Chemicals

Analytical-grade DEP and DBP obtained from Acros Organics (USA) were used for the preparation of liquid standards. The stock solutions were prepared by separately dissolving DEP and DBP in methanol or *n*-hexane (analytical grade, Sigma-Aldrich, USA) at 100 μg ml^{-1}. By serial dilutions of the stock solution with the same solvent, the calibration standards were prepared for the linear range of calibration between 5 ng and 100 ng for both compounds.

2.2. Sorbent material and preparation of standard tubes for calibration

Tenax GR tubes (2.5 cm o.d. × 8.9 cm long, Supelco, USA) made of stainless steel shell and packed with a 6 cm

Table 1
Basic physical and chemical properties of DEP and DBP

Compound	Molecular formula	Molecular structure	Boiling point (°C)	Melting point (°C)	Molecular weight	Vapor pressure (mmHg)
Diethyl phthalate	$C_{12}H_{14}O_4$		299	−40.5	222	2.1×10^{-3} (at 25 °C) [25]
Di-*n*-butyl phthalate	$C_{16}H_{22}O_4$		340	−35	278.3	2.01×10^{-5} (at 25 °C) [26]

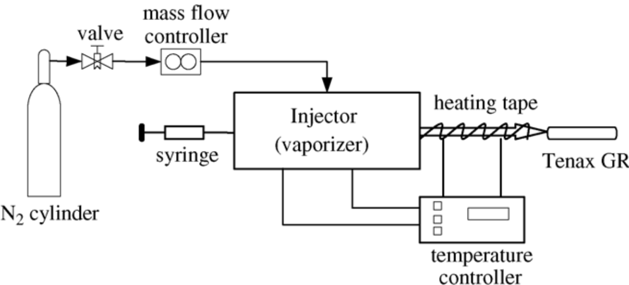

Fig. 1. Schematic diagram of experimental apparatus for preparing standard tubes using a quasi-vaporizer.

sorbent bed were employed to collect the semi-volatile phthalate esters in the air. The sorption material is a porous polymer resin (2,6-diphenylene oxide plus 30% graphite) with a specific surface area of approximate 35 $m^2 g^{-1}$, and is suited for analyses of specimens with boiling point ranging from 100 °C to 450 °C as well as n-C_7 to n-C_{30} [20]. To minimize their blank values, the Tenax GR tubes were conditioned by ATD-400 (Perkin-Elmer, USA) at temperature of 320 °C for 8 h with an inert gas flow rate of 300 ml min^{-1} before each use. These conditions were sufficient to eliminate artifact interference as the post-conditioning tube blank analyses showed no measurable peak. In addition, since the sorbent material has a hydrophobic surface and low affinity for water, the interference of water vapor during sampling of air was negligible.

For the preparation of standard tubes to be used for establishing calibration curves, two different approaches were attempted. The first method was to directly syringe-inject (1 μl) the liquid standards onto the sorbent bed via the sampling end of the tube. The loaded tubes were then sealed with PTFE caps and stored for more than one hour to allow the sorbent beds to equilibrate. The second approach involved the procedure of pre-vaporization rather than direct liquid loading. In this method, a GC injector was modified (hereinafter referred as quasi-vaporizer) to serve as an apparatus for introducing liquid external standard into sorbent tubes, as shown in Fig. 1. The quasi-vaporizer was connected to a temperature controller and set at a temperature of 345 °C, which was sufficiently high for complete vaporization of DEP and DBP. The vaporized sample was then transferred to the sorbent bed by 99.999% pure-grade nitrogen gas at a flowrate of 200 ml min^{-1}. All transferring tubing in between the quasi-vaporizer and the Tenax GR tube was PTFE-coated and maintained at a temperature of 270 °C by heating tapes to prevent vapor condensation. The Tenax GR tube was held below room temperature by a cold cloth-wrapper to enhance trapping of the vapor standard. To ensure complete sorption, a second sorption tube was serially connected and analyzed. Five-level calibrations using the pre-loaded standard tubes were carried out.

2.3. Instrumentation

An ATD/GC–MS (TurboMatrix/TurboMass Gold, Perkin-Elmer) system equipped with a Restek Rtx-5MS (5% diphenyl 95% dimethyl polysiloxane, length 30 m, i.d. 0.25 mm, film thickness 0.25 μm) analytical column and a quadrupole mass detector was used for the analysis in this study. The ATD unit contains a two-stage thermal desorption process. In the first stage, the sample specimens were heat-extracted (290 °C for 10 min) from the sorbent tubes and carried by a reverse gas flow into a cold trap (−30 °C) to re-concentrate. In the second-stage, the concentrated specimens were desorbed again by rapid heating at a rate of 40 °C min^{-1} (325 °C for 15 min) and transferred by helium gas into the capillary column as a narrow band to improve the chromatography and sensitivity. 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 such that the amount of specimens into GC column was maximized. Consequently, the inlet split flow was turned off in order to transfer all trace specimens into the cold trap, whereas the outlet split flow was controlled at minimum of 10 ml min^{-1} to avoid residual specimen in the cold trap that may lead to over-extended chromatographic peaks. Also, the ATD/GC–MS system was located in a Class 1000 cleanroom to minimize environmental contamination of particles and organic vapors, and all Teflon-based transfer lines were maintained at 220 °C to prevent condensation.

The GC–MS operated at a programmed oven temperature from 40 °C to 280 °C at a rate of 10 °C min^{-1}, and remained at 280 °C for 10 min. The ion-source temperature was maintained at 200 °C, and the MS detector was operated in full scan electron ionization (EI) mode where data over the range of m/z 50–400 were acquired. The base peak at m/z 149 was common to dialkyl phthalates, and the ions diagnostic of DEP and DBP are m/z 177, 195 and 205, 223, respectively.

2.4. Recovery tests

To determine the recovery of the concentrated phthalate esters in the sorption tube, solutions of known masses of DEP or DBP in n-hexane were prepared. The solutions were either spiked into the sorption tubes for subsequent ATD/GC–MS analyses or directly injected into the GC–MS using the identical analytical conditions.

2.5. Analysis of cleanroom air and wafer surfaces

Air samples of 0.1 m^3 were collected from the photolithographic section of a large-scale IC foundry in Hsinchu, Taiwan, by the pre-calibrated sampling pumps connected to Tenax GR sorbent tubes. The sampling flow rate was fixed at 200 ml min^{-1}, which was sufficiently high for high molecular-weight compounds to prevent loss due to reverse diffusion or breakthrough. Air samples from a plastic wafer case were also collected by passing a stream of nitrogen gas through the case into the sorption tube. The sorption tubes

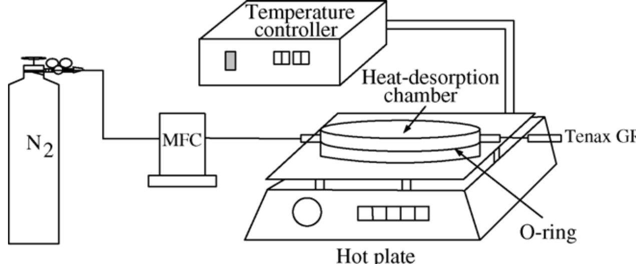

Fig. 2. Experimental apparatus for the determination of wafer surface concentration featuring a heat-desorption compartment.

were recapped, stored, and subjected to ATD/GC–MS analysis using the same analytical conditions described above.

To evaluate the density of the organic contaminants on the wafer surfaces, a standard 150-mm silicon wafer (crystal orientation in the ⟨1 0 0⟩ plane) coated with SiO_2 thin film was placed vertically in the wafer case for 24 h. The contaminated wafer was immediately transferred into a custom-made surface desorption compartment and heated at 200 °C for 100 min. The desorption compartment, which accepts 150 mm wafer as shown schematically in Fig. 2, was fabricated with stainless steel shell whose interior surface was coated with Teflon thin film. During heat desorption, a stream of ultra-high purity N_2 gas was passed through the compartment at a flow rate of 200 ml min^{-1} into a Tenax GR tube to collect the desorbed vapors. Special attention was given to the selection of O-ring material for securing airtight condition of the desorption compartment, because O-rings inevitably outgas organic vapors that could interfere with the analytical results. Therefore, three types of heat-resistant O-rings, including Kalrez (model 4079, DuPont Dow Elastomers, USA), Viton (DuPont Dow Elastomers), and silicone (Dow Corning, USA), all commonly used in semiconductor manufacturing processes, were examined in this study. The tested O-rings had the same dimension of 190 mm (i.d.) × 3.53 mm (cross section) to fit the wafer desorption compartment shown in Fig. 2.

3. Results and discussion

3.1. Standard tube preparation and calibration curves

As described in Section 2, liquid standards were introduced into the Tenax GR tubes for the preparation of “standard tubes” by either direct liquid injection or via a quasi-vaporizer, and the loaded tubes were all subjected to the identical ATD/GC–MS analytical conditions. The use of standard tubes for calibration removes the step involving solvent extraction from sampling tubes usually performed before GC–MS analysis, and thus is expedient for frequent monitoring of cleanroom environments. For the procedure using the quasi-vaporizer, the GC analyses for the second sorption tube showed no measurable peaks, verifying the complete retention of vaporized standard by the primary Tenax GR tube. Table 2 summarizes the results of calibration using various preparation procedures for the standard tubes. All calibration curves were highly linear since the corresponding correlation coefficients (r^2) were mostly better than 0.995. The precision of the analysis was represented as relative standard deviation (RSD), which was defined as the ratio between standard deviation (SD) and mean calibration factor. The results indicated that analyses using direct liquid injection method were imprecise for both phthalate esters, as the RSD for DEP and DBP were both in the proximity of 50%. The precision of the analyses using the quasi-vaporizer was much superior, although the results were less precise for DEP analysis. The larger value of RSD for DEP analysis were likely attributed to thermal cracking of DEP molecules in the quasi-vaporizer operating at 345 °C, causing the added bias for DEP analyses. The occurrence of thermal cracking will be further discussed in the later section of this report.

It was noted that the peak areas corresponding to the direct injection method were always smaller than those corresponding to the quasi-vaporizer method for both DEP and DBP, as indicated by the values of detector peak areas (DPAs) in Table 2. This result suggested that quantitative loss might have occurred due to incomplete vaporization of liquid standards at the room temperature for the method

Table 2
Calibration curve and precision ($n = 6$) of analysis of DEP and DBP

Compound	Preparation of standards	Dilution solvent	Linear range (ng)	Correlation coefficient (r^2)	RSD[a] (%)	DPA[b]	
						10 ng	100 ng
DEP	Direct injection	*n*-Hexane	5.0–110	0.9964	53.6	61	2230
	Quasi-vaporizer	*n*-Hexane		0.9984	14.0	354	2845
		Methanol		0.9956	25.9	357	2844
DBP	Direct injection	*n*-Hexane	5.0–100	0.9926	47.1	202	4674
	Quasi-vaporizer	*n*-Hexane		0.9972	6.3	418	4937
		Methanol		0.9978	7.2	484	4787

[a] The precision is indicated as RSD, defined as the ratio of SD to the mean calibration factor ($\overline{CF}$) expressed in the following equations, where CF_i is the ratio of signal peak area to the standard mass for a particular analysis. RSD (%) $= \frac{SD}{\overline{CF}} \times 100\%$ and SD $= \sqrt{\frac{\sum_i^n (CF_i - \overline{CF})^2}{n-1}}$, $\overline{CF} = \frac{\sum_i^n CF_i}{n}$.

[b] The detector peak area (DPA) is calculated based on the corresponding linear regression curve.

of direct injection into sorption tubes. In particular, the differences in the DPA values for DEP calibrations between the two standard-tube preparation methods were noticeably larger than those for DBP, an outcome that could be associated with the difference in the vapor pressure (Table 1) between DEP and DBP. As liquid solution was directly syringed into the tube, a small portion of the liquid inevitably lingered on the gauze that supported the sorbent bed. Compounds with higher vapor pressures (i.e., DEP), however, would tend to be stripped from the gauze faster than those with lower vapor pressures (i.e., DBP) by the carrier gas during air purging preceding thermal desorption of the tube, hence losing greater amount of sample. In contrast, the use of the quasi-vaporizer introduced the analyte into the sorption tube in the form of vapor phase, much parallel to the air sampling procedure with a sorption medium, and thus the loss of analyte due to unwanted sorption can be minimized. For this reason, standard tube preparation with the quasi-vaporizer was employed throughout the subsequently analysis of DEP and DBP.

To determine whether the selection of dilution solvents for DEP and DBP affects the results of calibration, a polar solvent in methanol and a non-polar solvent in *n*-hexane were examined for the preparation of standard tubes via the quasi-vaporizer. As shown in Table 2, the calibration curves of DEP and DBP showed no significant difference between the uses of the two solvents, as the values of DPA were nearly identical.

3.2. Optimization of quasi-vaporizer

During the initial tests of the quasi-vaporizer, the blank values of the ATD/GC–MS analysis using the vaporizer gradually but noticeably increased after several trials. Reasoning that condensation of liquid droplets might have occurred in the transferring line between the syringe and the sorption tube, a small quantity of glass wool was fitted onto the injection end of the vaporizer to prolong the time needed for complete vaporization, and heating tapes were wrapped around the transfer line to minimize condensation. Fig. 3 shows the comparison of the GC–MS response between the DEP and DBP analyses using the original quasi-vaporizer apparatus, that with the addition of glass wool, and that with the addition of both glass wool and heating tape. The peak intensities of the analysis using the method of direct injection of liquid standards were also included in the figure as the basis of comparison. Evidently, the addition of either glass wool or heating tape enhanced the responses of both DEP and DBP. However, only in the conditions where the quasi-vaporizer was amended with both glass wool and heating tape did the analytical response improve from that using the method of direct liquid injection.

The temperature setting of the quasi-vaporizer could potentially interfere with the analytical accuracy due to thermal decomposition of the target analyte. Fig. 4 illustrates a set of typical gas chromatograms of DEP using quasi-vaporizer at the two different temperatures: 320 °C and 400 °C. It was observed that naphthalene ($C_{10}H_8$) had been produced at the temperature setting of 400 °C, and the amount of naphthalene increased with the concentration of DEP. This result confirmed that the formation of naphthalene was a consequence of thermal cracking of the DEP structure, similar to the formation of phthalic anhydride and octanol from the thermal degradation of di-*n*-octyl phthalate (DOP) as previously reported [8]. In contrast, no naphthalene was formed for the temperature setting of 320 °C, and the peak intensity of DEP was noticeably greater than that at 400 °C. Hence, the temperature was set at 345 °C for the quasi-vaporizer to satisfy vaporization of both DEP and DBP while avoiding thermal cracking.

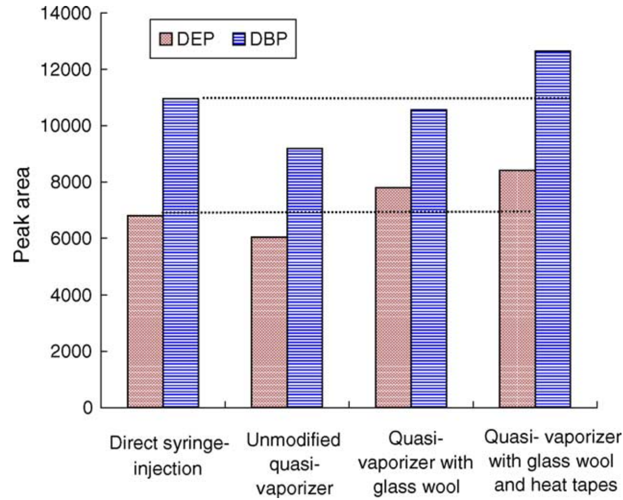

Fig. 3. Comparison of GC–MS responses between DEP/DBP standard tubes prepared by (1) direct syringe-injection and (2) quasi-vaporizer, as well as (3) quasi-vaporizer with the addition of glass wool, and (4) heat-taped tubing (injected mass: DEP 332 ng, DBP 310 ng, carrier gas flow rate: 200 ml min^{-1}, duration: 5 min).

The flow rates of the carrier gas passing through the quasi-vaporizer may also affect the analytical results by GC–MS. Smaller flow rates presumably allow for longer liquid retention time for more complete vaporization, but also require longer specimen collection time. Therefore, to assess the optimum condition, carrier gas flow rates were varied between 20 ml min^{-1} and 200 ml min^{-1}. Fig. 5 illustrates the analytical results of DEP and DBP with respect to the peak intensity under various flow rates. In these experiments, the sorption tubes were collected and analyzed for a collection duration segment of 5 min, up to 15 min of total collection duration. It can be observed that, for DEP analysis, duration of 5 min would be sufficient for flow rates greater than 100 ml min^{-1}, with the corresponding collection efficiencies exceeding 97.4%. Longer duration (10 min) was necessary for smaller flow rates (20 ml min^{-1}) to approach collection efficiency of 97% (Fig. 5a). In comparison, the collection efficiencies for DBP were significantly lower than those for DEP at the duration of 5 min, since an acceptable collection efficiency (98.2%) could only be achieved at the flow rate of 200 ml min^{-1} (Fig. 5b). As a result, the flow rate of 200 ml min^{-1} and the collection duration of 5 min were

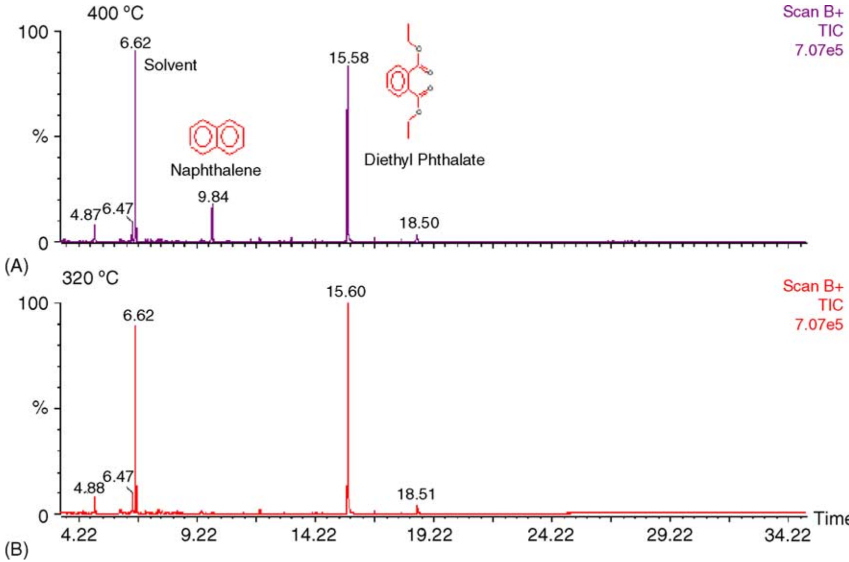

Fig. 4. Gas chromatograms of DEP with standard tubes prepared by the quasi-vaporizer operating at (A) 400 °C and (B) 320 °C.

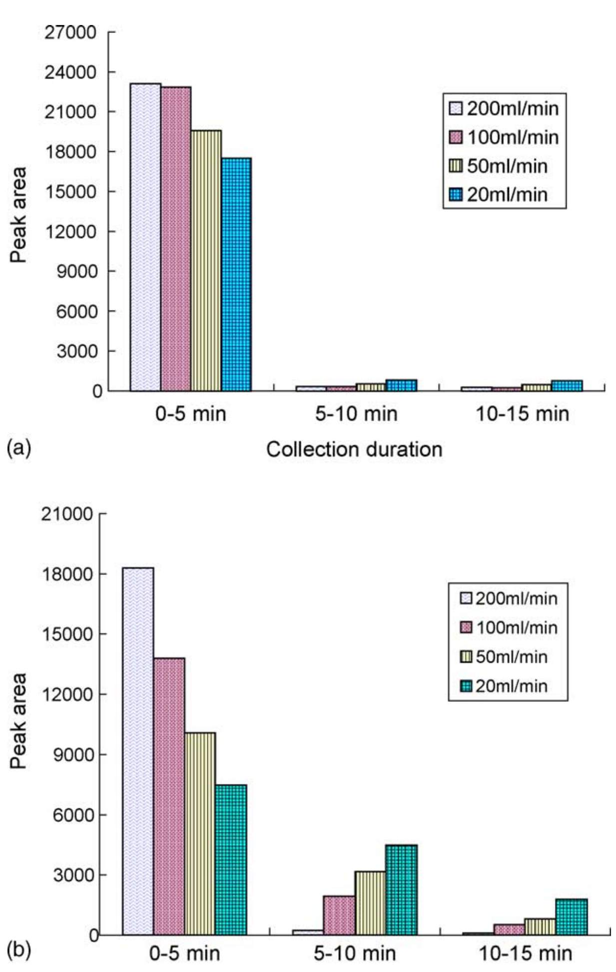

Fig. 5. GC–MS analysis of (a) DEP and (b) DBP for standard tubes prepared by the quasi-vaporizer at various carrier gas flow rates with three intervals of collection duration.

deemed appropriate to completely sweep both DEP and DBP vapors into the sorption tubes.

3.3. Method detection limits and recovery rates

The mean procedural blanks, SD, MDLs and the recovery rates of DEP and DBP were listed in Table 3. The procedural blanks included contribution from the injector, tube, and cold trap of the corresponding analysis. The procedural blanks of DBP were always higher than those of DEP, a result attributed to the lower saturation pressure of DBP that caused greater amount of residues in the sorbent tube or the ATD.

In this study, MDLs were defined as three times the SD at the lowest concentration of the standards, giving MDLs of 3 ng and 4 ng for DEP and DBP, respectively. These MDLs corresponded to concentration detection limits of approximately 0.05 $\mu g\,m^{-3}$ for air samples at 0.1 m^3, and of 0.03 $ng\,cm^{-2}$ for 150-mm wafer surface contamination. Furthermore, the recovery rates from the sorption tubes spiked with 33.2 ng of DEP and 31.0 ng of DBP were 96% and 94%, respectively. The results of the recovery rates indicated that the methods involving Tenax GR tubes preced-

Table 3
Procedural blanks, method detection limits, and recovery rates of DEP and DBP from the Tenax GR tubes

Compound	Blank (ng)	SD (ng)	MDLs[a] (ng)	Recovery rate[b] (%)
DEP	0.05	0.96	2.9	96[c]
DBP	0.14	1.4	4.1	94[d]

[a] Method detection limits (MDLs) are defined as three times the standard deviation of the standard at the lowest dilution level ($n = 7$).

[b] Recovery rate is defined by the ratio of signal peak areas between analysis via standard tube and that via direct injection of a known mass of sample ($n = 3$).

[c] Tube spiked with 33.2 ng DEP.

[d] Tube spiked at 31.0 ng DBP.

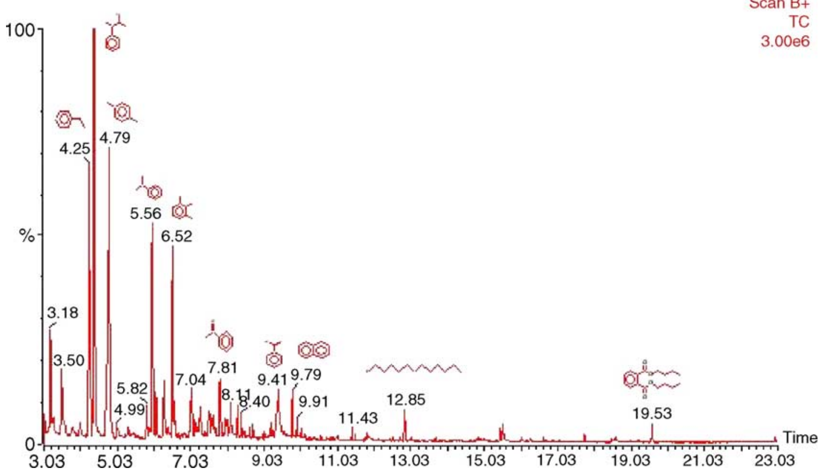

Fig. 6. Gas chromatogram of organic contaminants existing in the photolithography cleanroom of an IC foundry.

ing ATD/GC–MS were applicable for the quantitative analysis of the phthalate esters.

3.4. Analyses of DEP and DBP in cleanroom air, wafer box, and wafer surface

Air samples collected from the photolithographic processing area of an IC foundry, along with those from a polypropylene-based wafer storage box, were analyzed. Fig. 6 shows a typical gas chromatogram exhibiting the organic contaminants detected. The concentration of DBP (elution time at 19.5 min) was 0.12 $\mu g\,m^{-3}$, but DEP was below the detection limit. The concentration of DBP was in agreement with those reported by Veillerot et al. [21], who had determined a wide variation of DBP concentration in the range of 0.06–0.37 $\mu g\,m^{-3}$ in the same cleanroom. Toda et al. [22], however, found no detectable DBP (MDL of 0.1 $\mu g\,m^{-3}$) in their GC–MS analyses of cleanroom air. In addition, the presence DEP was always much lesser than DBP. Other identified organic contaminants shown in Fig. 6 included low b.p. compounds such as xylene (C_8H_{10}) and 3-phenyl-2-butanol ($C_{10}H_{14}O$). These compounds were likely originated from the solvent emissions of photo-resists, resist developers and strippers frequently used in the photolithography area.

For the air sample obtained from the wafer box, DBP concentration was 0.45 $\mu g\,m^{-3}$, but DEP was again not detectable. This DBP concentration was nearly four times as much as that in the cleanroom air, and was higher than any of the DBP analyzed previously reported. This result indicated that the gas-phase phthalate contamination of wafer surfaces could pose a more serious threat to the requirement of wafer cleanliness, even though storage in wafer boxes prevented particulate contamination. Therefore, ventilation with purified air would be necessary to minimize vapor-induced contamination while wafers are stored in the boxes.

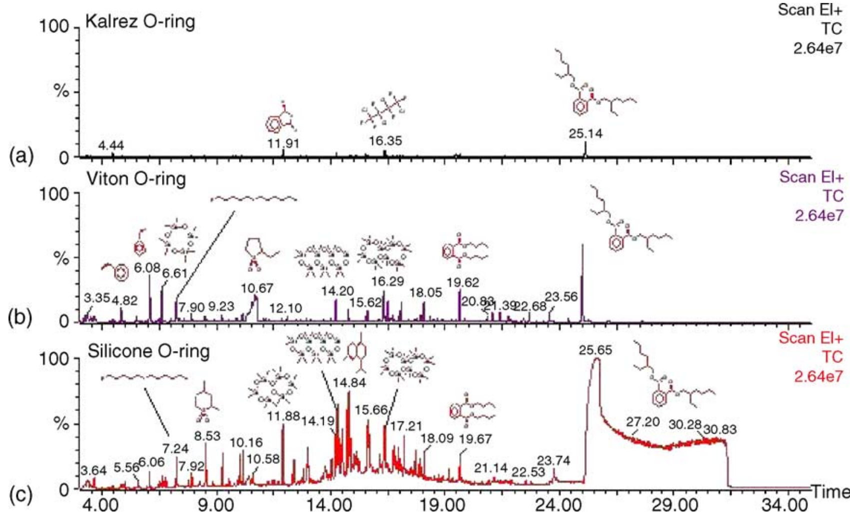

Fig. 7. Gas chromatograms of organic contaminants outgassed from (a) Kalrez O-ring, (b) Viton O-ring, and (c) silicone O-ring.

Table 4
The major organic substances outgassed from various O-rings

Kalrez	Viton	Silicone
Dioctyl phthalate, *p*-xylene, phthalic anhydride, 1,2,3,4-tetrachloro-1,1,2,3,4,4-hexafluorobutane, *n*-heptadecane	Di-*n*-butyl phthalate, di-*n*-octyl phthalate, 1-[2-(isobutyryloxy)-1-methylethyl]-2,2-dimethylpropyl, 2-methylpropanoate, D3: hexamethylcyclotrisiloxane, D4: octamethylcyclotetrasiloxane, D5: decamethylcyclopentasiloxane, D6: dodecamethylcyclohexasiloxane, D7: tetradecamethylcycloheptasiloxane, D8: hexadecamethylcyclooctasiloxane, hexadecamethylheptasiloxane, 2-ethylthiolane, *S*,*S*-dioxide, benzaldehyde, dodecyl fluoride, *cis*-stilbene, stilbene, styrene	Di-*n*-butyl phthalate, di-*n*-octyl phthalate, 1-[2-(isobutyryloxy)-1-methylethyl]-2,2-dimethylpropyl 2-methylpropanoate, D3: hexamethylcyclotrisiloxane, D4: octamethylcyclotetrasiloxane, D5: decamethylcyclopentasiloxane, D6: dodecamethylcyclohexasiloxane, D7: tetradecamethylcycloheptasiloxane, D8: hexadecamethylcyclooctasiloxane, hexadecamethylheptasiloxane, 1,2-diethoxycyclohexane, 8-isopropenyl-1,5-dimethyl-1,5-cyclodecadiene, tetradecamethylhexasiloxane, cyclotrisiloxane, mono-(2-ethylhexyl) phthalate, *trans*-2,4-dimethylthiane, *S*,*S*-dioxide naphthalene

To study the extent of wafer surface contamination, samples were also collected from the surface of a 150-mm oxide-filmed wafer by using the custom-made heat desorption compartment. The tested wafer had been placed in the sealed wafer box for more than 24 h before samples were collected and analyzed. The results showed that the surface density of DBP was 0.67 ng cm^{-2}. According to requirement of the surface critical level of organic contaminants recommended by the International Technology Roadmap for Semiconductors (ITRS) [23], the residual interface carbon contamination for the 90-nm technology mode should be less than 0.3 ng cm^{-2}. In addition, Kitajima and Shiramizu [24] reported that breakdown of gate-oxide performance occurred when organic contamination reached approximately 0.2 ng cm^{-2}. Therefore, this result clearly demonstrated that the surface cleanliness of wafers stored in a plastic box for 24 h was unacceptable without addition means of air purification.

3.5. O-Rings outgassing experiments

The organic outgassing from the three types of O-ring fitted on the wafer desorption compartment were tested under the same sampling (sampling volume of 20 l in N_2, desorption compartment heated at 200 °C) and analytical conditions. The resulting chromatograms are shown in Fig. 7 and the major organic substances detected are summarized in Table 4. It can be observed from the chromatograms that DOP (elution time of 25.6 min) was outgassed from all three types of O-ring. In particular, the tested silicone O-ring exhibited an intense and broad peak toward the end of the chromatogram, indicating the abundance of DOP and its structural homologues such as diisooctyl phthalate (DiOP) and diisodecyl phthalate (DiDP). DBP was also detected from silicone and Viton, but not from Kalrez. Furthermore, the number of organic species outgassed from Kalrez was clearly less than those from silicone and Viton O-rings, both of which emitted a wide range of siloxanes (i.e., D3–D8, represented by the peaks between 11 min and 18 min retention times) as indicated in Table 4. Therefore, it could be speculated that the silicone or Viton materials represent a major contributing source of phthalates and siloxanes micro-contamination, rendering these materials unsuitable for uses in a cleanroom environment. Based on the results of the outgassing test, Kalrez was determined to be the most appropriate O-ring material for the wafer heat desorption system as well as for the general use in any thermo-processes in semiconductor fabrication.

4. Conclusions

A method involving the preparation of standard tubes was developed for the calibration and analysis of two phthalate esters, namely DEP and DBP, using an ATD/GC–MS system. The use of a quasi-vaporizer to introduce liquid standards into Tenax GR tubes was found to enhance the analytical sensitivity by loading the target analyte into the sorbent beds in vapor phase. Addition of glass wool in the vaporizer and application of heating tapes to the transfer lines were necessary to improve the analytical performance of the method. The optimum operation conditions of the quasi-vaporizer were 200 ml min^{-1} for carrier gas flow rate with 5 min collection duration, and the operating temperature should be maintained well below 400 °C to prevent thermal cracking of the analytes. This analytical method yielded detection limits of approximately 5 ng m^{-3} for 0.1 m^3 of air samples for DEP and DBP, as well as recovery rates of at least 94%.

The analyses of air samples collected from a semiconductor cleanroom showed that the cleanroom was contaminated by DBP at a concentration of 0.12 μg m^{-3}, whereas DEP was below the detection limit. In comparison, air sample from the inside of a polypropylene-based storage box was found to be contaminated by DBP at a significantly higher concentration (0.45 μg m^{-3}) than those from the cleanroom air. Furthermore, the surface contamination study using a heat desorption compartment for a wafer contained in the storage box for 24 h showed a DBP density of 0.67 ng cm^{-2}, a level of organic contamination well above the threshold level of 0.3 ng cm^{-2} recommended by the ITRS for the 90-nm technology node.

The material outgassing tests performed on the three types of O-ring revealed significant emissions of DOP, which has been identified as a major organic contaminant on wafer surfaces. In particular, the silicone material was a highly potent emitter of DOP and its homologues, and thus should be avoided for any use in cleanroom operations. In comparison, Kalrez was relatively free from outgassing of organic vapors, and thus was regarded as the most appropriate O-ring material for high-temperature processes.

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