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Applications of Hadamard transform-gas chromatography/mass spectrometry for the detection of hexamethyldisiloxane in a wafer cleanroom

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ABSTRACT

The Hadamard transform-gas chromatography/mass spectrometry (HT-GC/MS) technique was successfully employed for the detection of hexamethyldisiloxane (HMDSO, $C_6H_{18}OSi_2$) at the sub-nL/L level in a semiconductor wafer cleanroom. Indoor air samples were collected from the room, according to EPA Method TO-17 using a Tedlar bag where the air samples were allowed to pass through an absorption tube for 24 h. The condensed components were then heated and simultaneously injected into a GC column through a Hadamard-injector, which was operated in accordance with the Hadamard codes. Compared to the single injection used in most GC/MS systems, the signal-to-noise (S/N) ratios were substantially improved after the inverse Hadamard transformation of the encoded chromatogram. Under optimized conditions, when cyclic *S*-matrix orders of 255, 1023 and 2047 were used, the S/N ratios of the HMDSO signals were substantially improved by 7.4-, 15.1- and 20.1-fold, respectively. These improvements are in good agreement with theoretically calculated values (8.0-, 16.0- and 22.6-fold, respectively). We found that when the HT-GC/MS technique was applied, HMDSO could be detected at the 0.1 nL/L level.
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1. Introduction

Organosilicon derivatives, which are not natural products, are synthesized for special industrial uses. One such derivative, HMDS (1,1,1,3,3,3-hexamethyldisilazane, $(CH_3)_3SiNHSi(CH_3)_3$) is frequently used in semiconductor wafer production to remove water from silicon oxide (or other substrate surfaces), to reduce the surface tension and to permit good photo-resist adhesion [1]. It is used either neat (undiluted) or diluted with a solvent such as PGMEA (1-methoxy-2-propyl acetate, $C_6H_{12}O_3$) or xylene and applied to the substrate surface by spin, dip or vapor methods, depending on the photo-resist used. HMDS is also used as adhesive for precision electronics during the photo process that is employed for regulating photoresistor systems [2–6].

HMDS is one of the major reasons for defects caused by airborne molecular contaminants (AMC) in cleanrooms, especially for semiconductor products [7–11]. As line widths of microelectronic devices shrink "AMC defects" have become a major concern and will need to be taken into consideration in the design of cleanrooms in the future. This is because, when the production scale is down to nano-scale, even nL/L levels of HMDS could have a negative effect on a thin photo-resist process. Hence, a method for the detection of trace amounts of organosilicon pollutants becomes very important when the process is operating on a nano-scale. HMDS is unstable in the presence of moisture and initially degrades to TMS (trimethylsilanol, $(CH_3)_3SiOH$) and then further rapidly degrades to HMDSO (1,1,1,3,3,3-hexamethyldisiloxane, $(CH_3)_3SiOSi(CH_3)_3$). As a result, the concentration of HDMSO can be used as an indicator for monitoring HMDS. In fact, many production processes are currently using high pollution-related chemical solvents to manufacture their products. As a result, SEMI (Semiconductor Equipment and Materials International) has proposed some standard procedures for cleanroom control, including SEMI F21-95 and SEMI F21-1102 methods [12–14]. The quality of cleanroom air should be monitored and strictly controlled, not only for the health of workers but also to reduce the rate of production of defects. Based on these standard methods, airborne molecular contamination (AMC) can be classed into 4 types, including acids (class MA), bases (class MB), condensables (Class MC) and dopants (class MD). The use of extraction/desorption combined with GC/MS (gas chromatography/mass spectrometry) is the generally accepted method for dealing with these 4 types of pollutants. Meanwhile, the problem associated with organosilicons continues to be serious because these compounds are difficult to detect at the low concentration levels that are typical for this process. Consequently, a novel and more sensitive method for detecting and quantifying this class of compounds

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would be highly desirable. The Hadamard transform (HT) technique has been applied to many fields, including time-of-flight mass spectrometry [15–18], Raman spectrometry [19–21], fluorescence imaging [22–25], ion mobility spectrometry [26,27], NMR [28,29] and capillary electrophoretic separations [30–34]. The application of a multiplexing technique such as a Hadamard transformation has also been demonstrated to be useful in GC [35–40] and liquid chromatography [41–46]. Trapp reported on the use of high-throughput multiplexing GC using the HT method [47]. We also previously reported on applications of the Hadamard transform-gas chromatography/mass spectrometry (HT-GC/MS) method [48–51]. In this study, we report on a HT-GC/MS method that permits the rapid and sensitive detection of HMDSO at the nL/L levels. The use of HT-GC/MS to detect trace levels of HMDSO in a cleanroom, the degree of enhancement in S/N ratios and details of the experimental conditions are described herein.

2. Experimental

2.1. Reagents

1,1,1,3,3,3-Hexamethyldisilazane (HMDS) was purchased from Sigma–Aldrich (St. Louis, MO, USA). Permeation tubes were obtained from Kin-TeK Industries, Inc. (United Kingdom). All other chemicals and gases were of analytical grade and were obtained from commercial sources.

2.2. Apparatus

An in-house fabricated Hadamard-injector (a micro-control valve that had been modified from a regular 24 V pulse electromagnetic valve), was used for the sample injection [49–51]. It was controlled via a personal computer through a PCI 6221 device (National Instruments, USA), based on a series of Hadamard codes. A gas chromatograph (GC 5890 Hewlett-Packard, Avondale, PA, USA) equipped with a mass spectrometer (Hewlett-Packard 5972 mass selective detector) was used, in which a capillary column (30 m × 0.25 mm I.D.) with an HP-5MS (cross-linked 5% PH ME siloxane) bonded stationary phase film, 0.25 μm in thickness (Agilent Technologies, USA) was employed. As a complementary method, another GC/MS experiment was carried out using a Thermo Finnigan Trace GC ultra/Thermo Finnigan Trace DSQ; Rtx-502.2 column (30 m × 0.25 mm I.D., 1.4 mm; Restek, USA). A standard gas generator (Model 8000 series; Molecular analysis LLC., USA) was used to control the concentration of HMDS.

2.3. Experimental method and conditions

Fig. 1 shows a schematic diagram of the on-line gas adsorption/desorption HT-GC/MS system. This system consists of a Tedlar bag, a sorbent tube (Tenax-GR; O.D., 1/4 in./length, 3.5 in.) as well as its container, a Hadamard-injector and a commercial GC/MS. The sample gas, in the Tedlar bag either collected from the standard gas generator or from the wafer cleanroom, was slowly passed through the sorbent tube, where a rotary pump was used to draw out the gas (the flow rate was controlled by a needle valve). When the sample gas was slowly and continually passing through the sorbent tube, the valves were closed. Following this, the sorbent tube/container and the Hadamard-injector were pressurized by background N_2 gas to 1.0 kg/cm^2 and heated to 150 °C. A personal computer was used to rapidly turn the Hadamard-injector on and off, based on a series of Hadamard codes, leading to the introduction of the pressurized gas sample through the capillary into the GC column. The optimized conditions were a background pressure of 1.0 kg/cm^2 and an injection time of 1 s. The inlet temperature was maintained at 150 °C and the column oven was also held at 120 °C (carrier gas: helium, flowrate 1.2 mL/min operating in either the splitless or split mode). The mass spectrometry conditions were as follows: ionization energy, 70 eV; and ion source temperature, 230 °C. The selected ion monitor (SIM) mode was used for HMDSO by selecting ion peaks at m/z = 147 and 162, respectively. The dwell value was set at 33 and 32 ms; 10 data points/second could be recorded. Data were collected using Hewlett-Packard Chem-Station software with transfer to an ASCII text file. The average was calculated for each 10 data points that were treated as one bin to fit the HT calculation. The HT-GC-chromatograms were calculated using the LabVIEW program, as described previously [50]. As a complementary method, another GC/MS experiment was carried out. Herein, the GC oven temperature was initially set at 35 °C, and held for 8 min, then ramped at 5 °C/min to 120 °C, and held for 6 min; 8 °C/min to 200 °C, and finally held for 10 min at 200 °C.

2.4. Preparation of HMDSO gas

A permeation tube (load releasing rate, 22 ng/min) was placed in the oven of the standard gas generator at 80 °C for 3 h to prepare HMDSO. Meanwhile, zero air (carrier gas) was passed into the standard gases generator from the inlet, drained from the outlet and passed through a humidifier (MH^{TM} Series; Perma Pure LLC., USA), leading to the conversion of HMDSO. The concentration of HMDS was determined by the flow rate of the zero air. When the flow rate was set at 160 mL/min, the generated HMDSO concentration was determined to be 21 nL/L, assuming the complete conversion of HMDS to HMDSO, and was directly used as the standard gas. Gas sampling bags (Tedlar®; Jensen Inert Products, USA) were used for the collection of both standard gas and clean-room air. In the case of clean-room air (obtained at a local wafer factory in Hsinchu, Taiwan), the gas sample was collected, according to EPA Method TO-17, using a Tedlar bag. The air samples were allowed to pass through the Tenax-GR tube at flow rate of 100 mL/min for 24 h at 25.5 °C.

2.5. Operation of the automated thermal desorber (ATD)

An automated thermal desorber (Perkin Elmer Turbo Matrix 150 ATD) was used for sample adsorption and desorption. The temperature program of the ATD was initially set at 250 °C for 10 min, to desorb the adsorbed compounds, which were then concentrated in a cold trap, a quartz tube containing a small quantity of sorbent (Tenax TA; Perkin Elmer, USA) at −20 °C. The sorbent tube was then quickly thermally desorbed again (250 °C for 5 min) and introduced into the gas chromatograph/mass spectrometer through a heated transfer line (200 °C).

3. Results and discussion

Various concentrations (500 and 20 nL/L) of HMDSO standard gas were prepared. Fig. 2 shows typical GC/MS chromatograms for the HMDSO standard gas (20 nL/L) using the SIM (selective ion monitoring) mode (ion peaks of m/z = 147 and 162). Fig. 2A, inset, shows the mass spectrum of HMDSO. In this case, the temperature program was set at 120 °C (head pressure, 8 psi; split purge, 30 mL/min). Under these conditions, HMDSO is rapidly detected at a retention time 1.5 min; the injection time was 0.25 s and sample injection volume was 4 μL. When a singly injection was employed, the S/N ratio appeared to be poor (S/N ∼2.8), as shown in Fig. 2A. However, under the same experimental conditions, when the Hadamard injection was performed (as shown in Fig. 2B; cyclic *S*-matrix order, n = 2047), the S/N ratio was dramatically improved by 21.2-fold (total injection volume 45 mL, during a period of 70 min). This value is quite consistent with the theoretical values. The inset

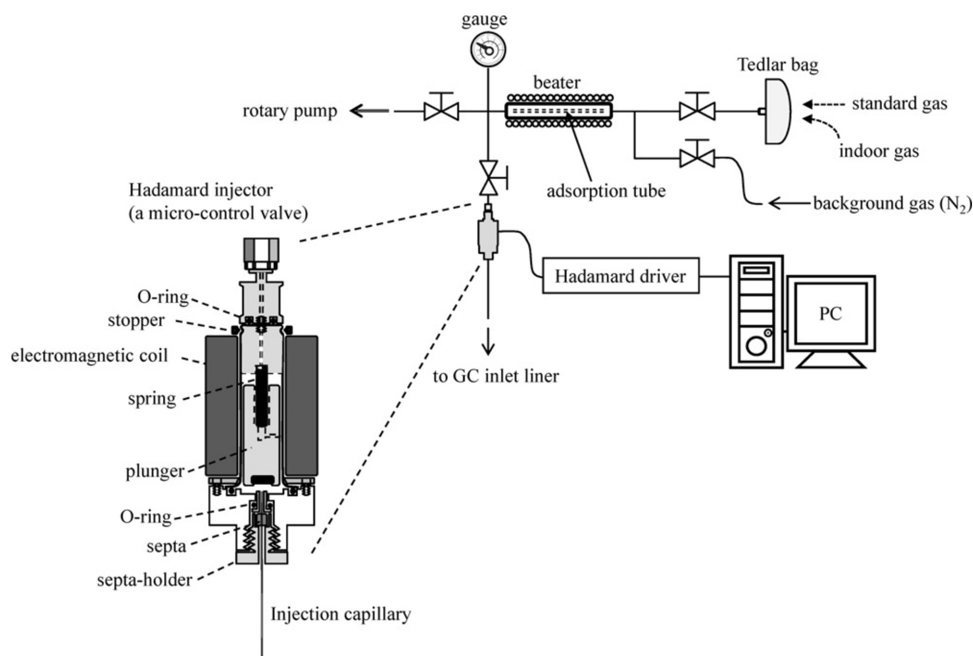

Fig. 1. Schematic diagram of the on-line gas adsorption/desorption HT-GC/MS system.

in Fig. 2B shows the raw data before the Hadamard transform was performed. The ion intensities of HMDSO slowly decreased with longer injection times (∼70 min). In the other words, HMDSO continued to be released from the sorbent tube even 1 h later, so that a further high order Hadamard transform could be used, provided a fast GC/MS technique could be applied. Although some noise is evident in the inset of Fig. 2B, taking this into account it would be possible to further improve the SNR and sensitivity of the method. Table 1 summarizes the results (cyclic *S*-matrix orders, $n = 255$, 1023 and 2047, respectively). It can be clearly seen that the S/N ratio is significantly enhanced, as predicted from the theory.

In order to evaluate the applicability of the present method for the practical detection of HMDSO in air from a wafer cleanroom, a complementary experiment was performed. Fig. 3 shows typical HT-GC/MS chromatograms obtained for the adsorption/desorption components (SIM mode: $m/z = 147$ and 162). The GC and MS conditions are the same as described above. As can be seen, when a single injection is used (Fig. 3A) it is difficult to identify the peak at the 0.1 nL/L level. Several cleanroom samples were examined and similar results were obtained.

For comparison, the inset shows a TIC (total ion current) chromatogram obtained when an automated thermal desorber (ATD) assisted GC/MS process was used, although an inter-day sample was used; the experimental conditions were as described above. It was found that, during the period of retention times (RT) from 5 to 45 min, at least 56 types of volatile organic compounds (VOCs) could be identified by comparison with standards, including DCM (dichloromethane; RT 11.93 min/0.37 nL/L), hexane (RT 13.19 min/1.21 nL/L), PGME (propylene glycol monomethyl ether; RT 19.79 min/0.13 nL/L), toluene (RT 25.13 min/0.9 nL/L), cyclopentanone (RT 27.97 min/0.32 nL/L), PGMEA (1-methoxypropan-2-yl acetate; RT 30.86 min/0.06 nL/L), *m*-, *p*-xylene (RT 31.23 min/0.12 nL/L) and *o*-xylene (RT 32.95 min/0.1 nL/L), respectively. After expanding the scale (data not shown), HMDSO was identified at 17.01 min/0.01 nL/L. It should be noted that such a low concentration of HMDSO

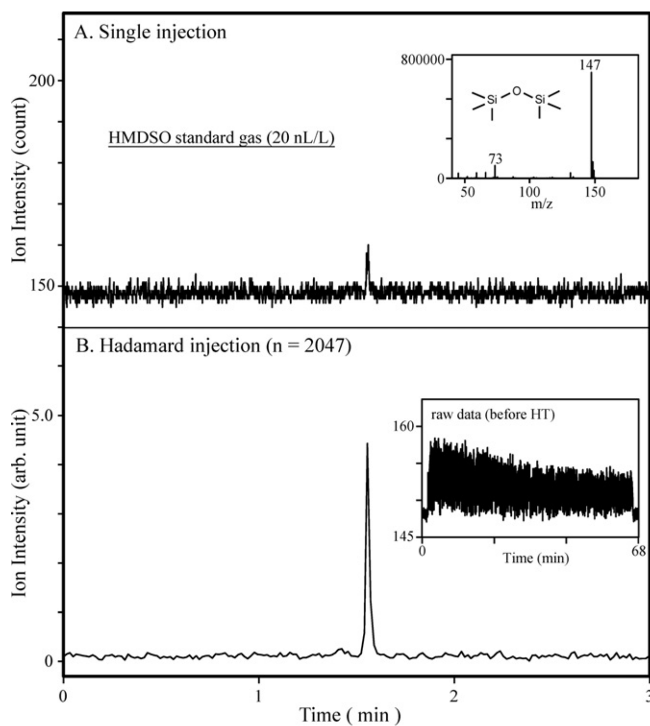

Fig. 2. (A) A typical GC/MS chromatogram of HMDSO standards (20 nL/L) obtained by single injection based on the SIM mode (ion peaks at $m/z = 73$ and 147 were selected for monitoring); the inset shows the mass spectrum of HMDSO. (B) HT-GC/MS (order of matrix, 2047) chromatogram of HMDSO; inset shows the raw data before Hadamard transformation.

Table 1
Relationship between the cyclic *S*-matrix orders, enhancement of the S/N ratio for HMDSO by a SIM mode: $m/z = 147$ and 162.

Matrix order	Theoretical S/N improvement	Observed S/N improvement
255	8.02	8.0
1023	16.01	15.1
2047	22.63	21.3

The enhancement in S/N ratio was calculated as the ratio of S/N values obtained in the chromatograms, as measured by HT-GC/MS and a single injection method.

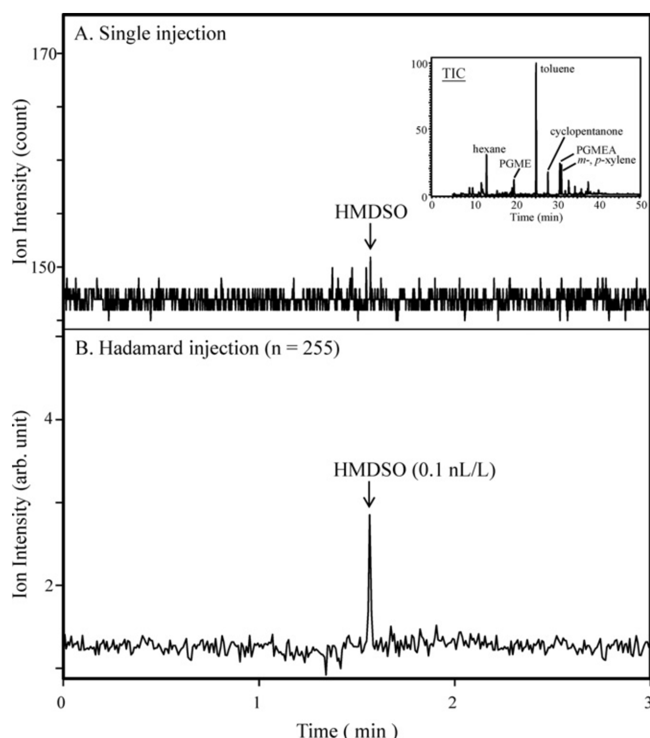

Fig. 3. (A) A typical GC/MS chromatogram of HMDSO extract (0.1 nL/L), from a wafer cleanroom, obtained by single injection based on the SIM mode; the inset shows a TIC (total ion current) chromatogram obtained by the assistant of an automated thermal desorber (ATD). (B) HT-GC/MS (order of matrix, 255) chromatogram of HMDSO.

would be very difficult to identify if the automated thermal desorber (ATD) method was not used. In contrast to this, the S/N ratio is substantially improved when the Hadamard injection method is used (Fig. 3B; matrix order, $n = 255$), when the absorption/desorption system and a 255 order of Hadamard matrix were applied (head pressure, 8 psi; injector pressure: 1.0 kg/cm^2; split purge, 30 mL/min; oven temperature: 120 °C). If a higher matrix order were to be used (e.g., $n = 2047$), further improvement would be expected. The detected absolute amount of HMDSO was determined to be 97 ng, corresponding to a level of 0.1 nL/L in the cleanroom. The observed improvement of S/N of the detected peak conforms to the improvement in S/N that would be mathematically expected after application of an n-order Hadamard transform, suggesting that the HT-GC/MS injection device functions very well, even for HMDSO at the nL/L level in a wafer cleanroom. The RSD (related standard deviation) values of intra-day and inter-day were determined to be 0.5% and 1.93%, respectively, indicating the stability and reproducibility of the procedure. Several experiments showed similar results indicating that the present adsorption/desorption method and the use of a Hadamard-injector, with a simple design, permits precise multiple injections for cleanroom sample determinations.

4. Conclusion

In this study, we successfully demonstrated that the HT-GC/MS method using a Hadamard-injector is applicable to sensitive detection by GC, where HMDSO is present at very low levels. The enhancement factors for the S/N ratios were in good agreement with theoretical values, even at a high matrix order ($n = 2047$). We also found that the present technique could be employed for monitoring HMDSO and related compounds in a variety of conditions. In the other words, if a higher matrix order ($n > 2047$) could be used, the adsorption/desorption system may not needed. This is particularly important for satisfying industry needs where traditional methods may not be viable. The present method has a variety of applications and could potentially be used in practical trace analysis.

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