

# In-situ Measurement of outgassing from Chemically Amplified Resist during exposure to 248nm light

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The outgas components from photoresists exposed to light sometimes form on the lenses and mirrors of aligners and are detrimental to their optical properties. This has recently become a major problem, and thus it is important to know the extent of outgassing from such resists when considering the effects of the outgas. We attached a QCM mass spectrometer to a 248 nm reaction analysis exposure tool equipped with a mercury-xenon (Hg-Xe) lamp light source and traced the change in the photoresist mass to investigate the amount of outgassing from a 248 nm chemically amplified photoresist during exposure. We collected the outgas generated from the resist during exposure in a TENAX absorber and identified the outgas components using a GC-MS. We also conducted an in-situ observation of the reaction in the photoresist using a PAGA-100 deprotection reaction analysis system and investigated the relationship between the outgas emission and the deprotection reaction. The results of these experiments are reported in this paper.

**Keywords:** chemically amplified resist, deprotection reaction, outgas during exposure, QCM, GC-MS, FT-IR

## 1. Introduction

The problem of molecular scale chemical contamination is becoming conspicuous in the production environments of semiconductors and liquid crystal displays (LCD). In particular, the outgassing from photoresists exposed to light has recently become a major problem as the outgas components that form on the lenses and mirrors of aligners are detrimental to their optical properties.

<sup>[1-2]</sup> Use of chemically amplified resists with acid catalysts started with the research of Ito et al. in 1987,<sup>[3]</sup> and it is now an indispensable tool for the production of semiconductor devices in the sub-half-micron scale or less. A chemically amplified positive resist generates an acid from the photo acid generator (PAG) through photochemical reaction, and this acid is a catalyst in deprotecting the protecting group during the heating process after the exposure, known as the post exposure bake (PEB). In the next process, the deprotected resin is dissolved into the developer forming the resist pattern,<sup>[4-6]</sup> and the outgassing occurs during the exposure due to the photodecomposition of the PAG. Recently, protecting groups with low activation energies have also been used to reduce

the effects of the post exposure delay (PED).<sup>[7]</sup> With a resist containing protecting groups with low activation energies, deprotection reactions occur easily during exposure and generate outgas.<sup>[8]</sup> It is thus important to know the extent of outgassing from the resist under exposure when considering the effects of the outgas. In recent years, there have been many reports concerning outgas analysis using QCMs.<sup>[2, 9, 10, 11]</sup> We applied the method invented by Shirai et al.<sup>[11]</sup> to the 248 nm exposure; we attached a QCM monitor to a UVES-2000 reaction analysis exposure tool equipped with a Hg-Xe lamp light source for the 248 nm exposure and conducted in-situ measurements to clarify the relationship between the amount of outgas generated and the exposure energy by observing the change in the mass of the acetal-based chemically amplified resist under 248 nm exposure. We also placed an outgas collection unit in the exposure chamber,<sup>[12]</sup> collected the outgas in a TENAX absorber,<sup>[13]</sup> and attempted to analyze the components using a GC-MS. We also conducted an in-situ observation of the deprotection reaction during exposure using the PAGA-100, an FT-IR based deprotection reaction analysis system,<sup>[14-17]</sup> and investigated the

relationship between the outgas generation and the deprotection reaction. The results are reported herein.

## 2. QCM observation of the change in the resist mass during exposure

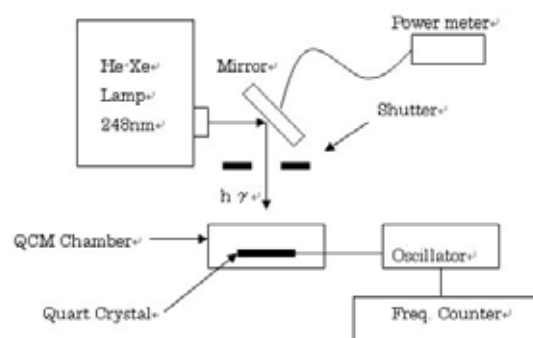
The change in the mass of the resist film during exposure is observed using a QCM unit. The light source is a HOYA-SCHOTT Hg-Xe lamp with a 248 nm band pass filter (FWHM=5nm) attached. The 248 nm light is extracted from the source and emitted on the substrate, and the exposure area is a 10 mm square with the uniformity of  $\pm 10\%$ . The exposure is controlled by adjusting the shutter time in such a way that the in-situ monitor of the power meter measured through the beam splitter is maintained at the intended energy value. The illuminance is  $1.0 \text{ mW/cm}^2$  at 248 nm on the wafer. Figure 1 shows a schematic diagram and a photograph of the view of the QCM mass spectrometer unit in the UVES-2000. The unit consists of a chamber for QCM measurement, a PC for data collection, a frequency counter, and a voltmeter. The frequency counter and the voltmeter for impedance measurement are connected to the PC through GPIB interfaces. The QCM substrate coated with the resist is placed in the QCM measurement chamber and the air in the chamber is replaced with nitrogen gas. The chamber is then transferred into the optical path, the shutter is opened for the exposure, and the relationship between the exposure energy and the resonant frequency is measured during the exposure. A QCM substrate for a resonant frequency of 9 MHz is used in this apparatus to measure extremely small mass variations.

QCM stands for "Quartz Crystal Microbalance." When substances form on the surface of the quartz oscillator electrode, the resonant frequency changes in accordance with the adsorbed mass. Thus, if outgas is generated and the membrane mass reduces when the resist on the substrate is exposed to light, the resonant frequency increases. The following Sauerbrey equation expresses the relationship between the change in the resonant frequency and the change in the mass:<sup>[18]</sup>

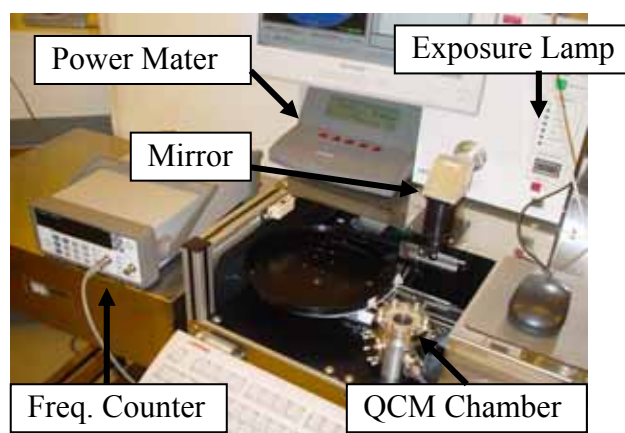
$$\Delta F = - \frac{2 \cdot F_0^2}{A \sqrt{\mu \cdot p}} \cdot \Delta m \quad (1)$$

Here,  $\Delta F$  is the change in the frequency,  $F_0$  is the sensor frequency,  $A$  is the area of the electrode,  $\mu$  is the shearing stress of quartz ( $2.947 \times 10^{10} \text{ kg ms}$ ),  $p$

is the specific gravity of quartz, and  $\Delta m$  is the change in the mass.



(a)



(b)

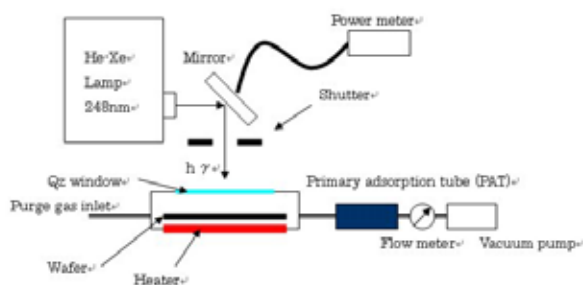
**Fig. 1. QCM mass spectrometer unit: (a) schematic diagram and (b) photograph of the system.**

## 3. The GC-MS analysis of the outgas from the resist during exposure

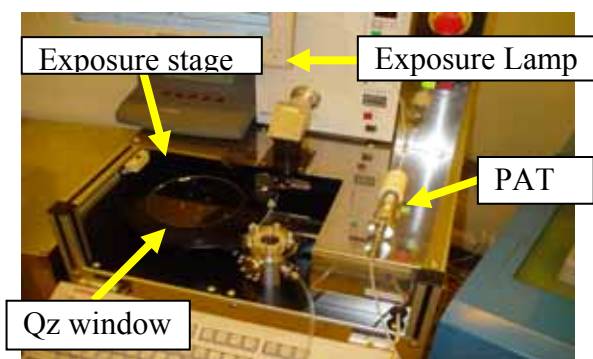
### 3.1 Collection of the outgas during exposure

Figure 2(a) shows the schematic diagram of the outgas generation chamber. The outgas generation unit is a closed chamber containing ultrapure  $\text{N}_2$  gas as the carrier gas. A quartz window is placed in the upper part of the chamber, through which the sample is exposed. The outgas generated during exposure is carried with the carrier gas to the primary absorption tube (PAT) containing TENAX/TA,<sup>[13]</sup> which adsorbs the outgas. Baking plates are placed in the chamber to prevent contamination in the chamber, and after collecting the outgas these plates are used to bake the chamber at  $200^\circ\text{C}$  to remove the substances adsorbed on the inner walls of the chamber. The tube connecting the chamber and the PAT can also be heated with the ribbon heaters wrapped around it and this prevents

the adsorption of the gas components by the inner wall of the tube.



(a)



(b)

**Fig. 2. Outgas collection unit: (a) schematic diagram and (b) photograph of the device in system.**

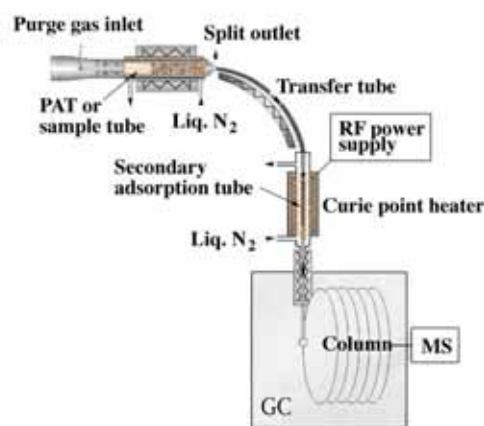
**Table 1. shows the types of absorbers and their characteristics.**

Absorbent type	Boiling point range	Pore size (nm)	Applications	Pyrohoil
Glass wool	400°C or above		High-boiling point compounds	423°C or below
TENAX/GC	400°C below	720	General	358°C or below
TENAX/TA	400°C below	2000	General	358°C
TENAX/GR	400°C below		Moisture-containing samples	358°C or below
Carbon fiber	100°C below		Residual solvent	358°C or below
Silica gel	200°C below		Multiple purposes	358°C or below

TENAX-GC and TENAX-TA are composed of poly-2,6-diphenylphenylene, and if these are used for a sample rich in water, the absorber swells, thereby prohibiting the purge gas to pass. These items cannot be used for samples rich in organic solvents, such as chloroform, as they swell and dissolve in organic solvents. TENAX-GR is poly-2,6-diphenylphenylene with 30 % graphite added, and it can pass the purge gas without swelling even when the sample contains a large amount of water. TENAX-TA is typically used for collecting the outgas from resists.<sup>[13]</sup>

### 3.2 Analysis of the outgas

The outgas collected in the PAT is thermally desorbed using a Curie point head space sampler (hereafter referred to as a purge and trap: P&T Japan Analytical Industry ) and analyzed with a GC-MS.<sup>[12]</sup> Figure 3 is a schematic diagram of the P&T apparatus.



**Fig. 3. Schematic diagram of the Curie point purge and trap system**

The P&T system heats the sample (the PAT) with a sample heater, purges the volatile components generated from the sample using the purge gas, and traps the gas in the secondary the PAT through an 8-port valve. The secondary collection tube is cooled using liquid nitrogen. Next, the adsorbed components are thermally desorbed with Curie-point heating and directly carried into the GC for analysis. The advantage of this system is that Curie-point heating allows an instantaneous evaporation of volatile components, thus enabling pulsed input of the evaporated gas into the GC.<sup>[12]</sup>

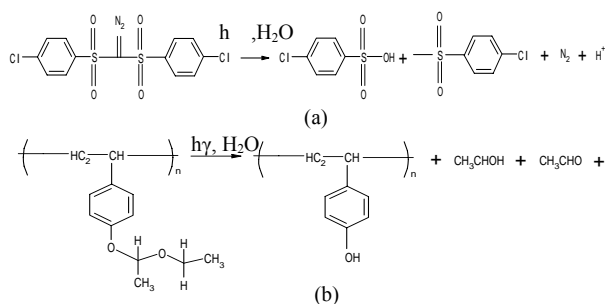
### 4. In-situ FT-IR observation of the deprotection reaction during exposure

We reported the details of the deprotection reaction analysis system in "Journal of Photopolymer Science and Technologies" last year.<sup>[17]</sup> We attached a Hg-Xe lamp to the FT-IR equipment. The system has a mechanism in the measurement optical path for focusing the light through the 248 nm filter (FWHM=5nm) with a lens and emitting it onto the wafer vertically. The resulting illuminance on the wafer surface is 1.0 mW/cm<sup>2</sup>.

## 5. Experiments and results

### 5.1 QCM observation of the outgas during exposure

With this system, we attempted an observation of the change in the mass of the 248 nm chemically amplified resist during exposure. The resist examined was a 248 nm chemically amplified resist with a PHS base polymer and acetal protecting group. The protection ratio was 25%. For the PAG, di(4-chlorophenylsulfonyl)diazomethane(DCPSD) was used. 700nm of this resist was coated onto the QCM substrate with a diameter of 14 mm. The pre-baking condition was 90°C for 90 seconds. Figure 4(a) shows the reaction scheme of the PAG during the exposure and Figure 4(b) shows the reaction scheme for the deprotection reaction of the protecting group during exposure.



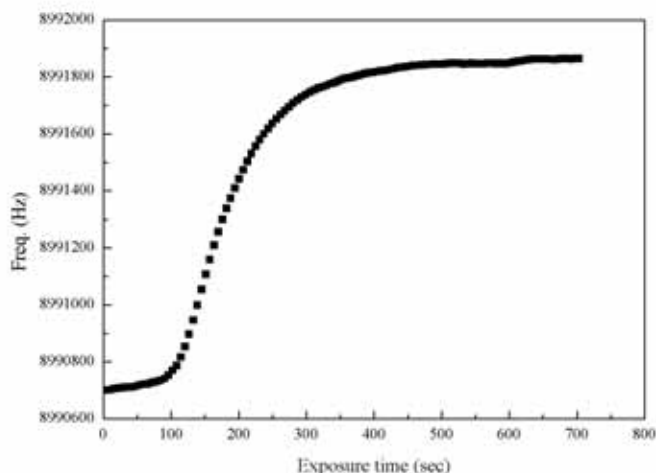
**Fig. 4.** The reaction scheme: (a) the reaction of the PAG during the exposure and (b) the deprotection reaction of the protecting group during exposure.

**Table 2. Experimental conditions**

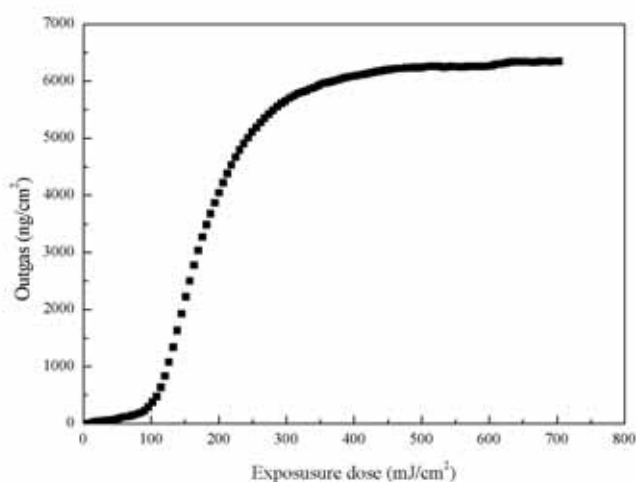
Resist	KrF CA (EA)resist
Base polymer	PHS
Protection Group	1-Ethoxyethyl (Ethylacetal)
PAG	di(4-chlorophenylsulfonyl)diazomethane(DCPSD)
Pre-bake	90 ,90s
Thickness	700nm

Exposure	1.0mW/cm <sup>2</sup> at 248nm
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The resist is exposed in the UVES-2000 and the change in the mass of the resist film is calculated using the Sauerbrey equation from the change in the resonant frequency of the QCM substrate. Figure 5 shows the relationship between the exposure time and the resonant frequency, and the relationship between the exposure time and change in mass. Figure 6 shows the relationship between the amount of the outgas generated per unit area and the exposure.



**Fig. 5.** The relationship between the measurement time and the resonant frequency.



**Fig. 6.** The relationship between the amount of outgas and exposure.

The results of the experiment show that the mass of this resist film starts to decrease (the outgas starts to be generated) at an exposure energy of

approximately 100 mJ/cm<sup>2</sup> and that the generation of outgas ends at approximately 300 mJ/cm<sup>2</sup>.

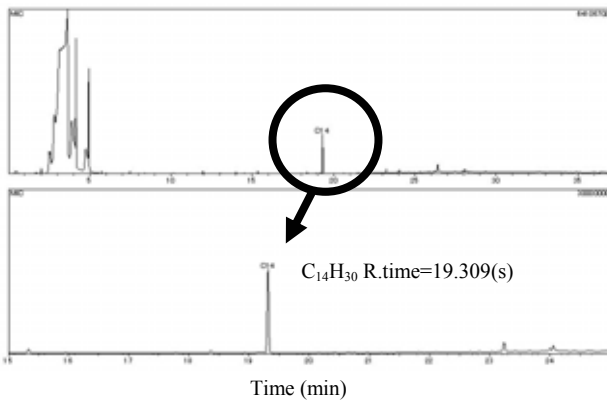
**5.2 GC-MS analysis of the outgas components**

The collection conditions are as follows. A 6 inch Si substrate is coated with 700 nm of this resist and placed in the UVES-2000 chamber for collecting the outgas. A exposure area is 10 mm x 10 mm, and 9 exposure shots are applied to the sample; one exposure shot is set at 600 mJ/cm<sup>2</sup> in order to ensure enough deprotection reaction. The carrier gas used is ultrapure N<sub>2</sub> gas, and is carried into the collection chamber at the rate of 1 l/min, and collected in the PAT at the same rate. The analysis conditions are as follows: The equipment used for the outgas desorption is a P&T system (JTD-505: Japan Analytical Industry Co., Ltd.). The PAT is placed in the P&T apparatus preheated to 230°C, it is treated with purge and trap for 10 minutes, and the desorbed volatile components are absorbed and concentrated with a secondary trap tube filled with quartz wool cooled at -60°C. Next, the sample goes through high-frequency induction heating (Curie-point heating) using pyrofoil at 255°C for thermally desorbing the trapped volatile organic components (VOC), which are carried into the GC-MS for separation analysis.

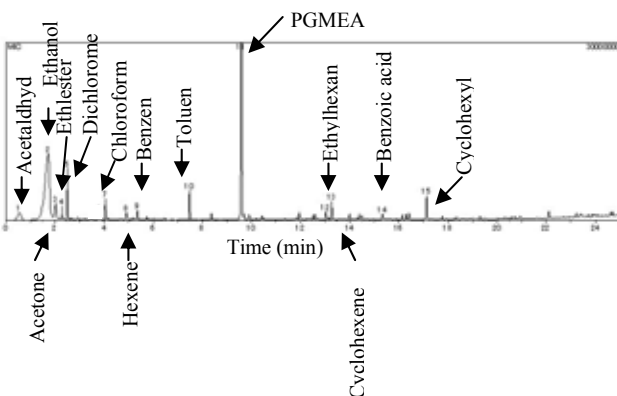
The GC-MS setup is as follows:

GC-MS:GC-17A/QP-5000 (Shimadzu Corporation)

Column: DB-WAX (0.25mm x 60mm)



**Fig. 7. The chromatogram of the standard.**



**Fig. 8. The chromatogram of the outgas collected from the KrF resist during exposure.**

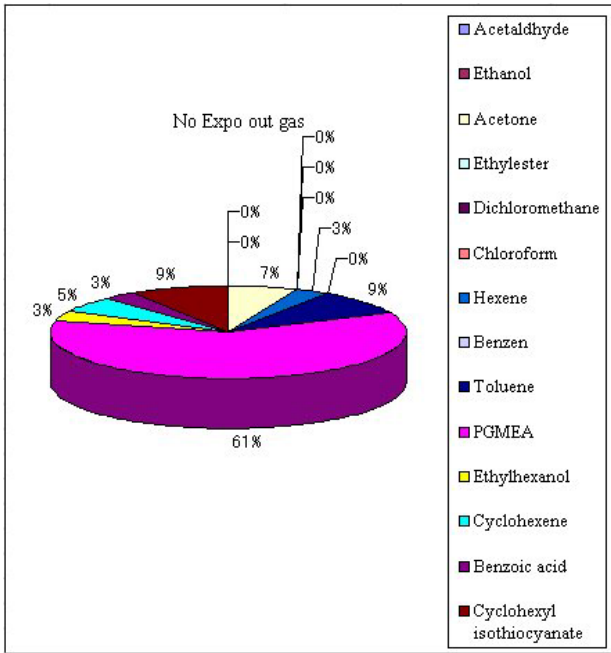
The column flow rate is set to 1.0 l/min, and the split ratio is 1:50. 6mg C<sub>14</sub> (C<sub>14</sub>H<sub>30</sub>: Tetradecan) are added as the standard. The outgas from the Si substrate without resist coating is collected and analyzed as the blank, and the measured value here is subtracted from the measurement of the exposure samples obtained to correct the results. Figure 7 shows the chromatogram in the mass range of 98 for the standard and the enlarged chromatogram for a retention time of 15–24 min. The figure shows clear chromatogram peaks for C<sub>14</sub>. Figure 8 shows the chromatogram of the outgas collected from the KrF chemically amplified resist under exposure. Table 3 shows the analysis results of the outgas components. The main components of the outgas include PGMEA, ethanol, acetaldehyde and dichloromethane.

**Table 3. The results of the outgas analysis for unexposure and during exposure.**

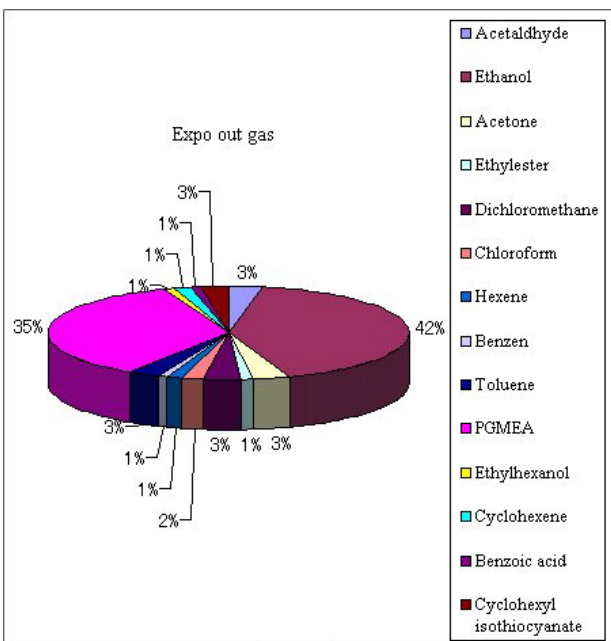
	NO Expo				Expo				Expo-NO Expo
	Area	%	ng	ng/cm <sup>2</sup>	Area	%	ng	ng/cm <sup>2</sup>	
Acetaldehyde	0	0.00	0	0	11912631	3.18	1621	180	180
Ethanol	0	0.00	0	0	154662139	41.31	23049	2339	2339
Acetone	4918112	4.53	940	104	12338918	3.30	1679	187	82
Ethylester	0	0.00	0	0	3935373	1.05	536	60	60
Dichloromethane	0	0.00	0	0	12866561	3.46	1765	196	196
Chloroform	0	0.00	0	0	7314641	1.95	996	111	111
Hexane	3014700	2.85	410	46	4487028	1.20	611	68	22
Benzen	0	0.00	0	0	3877372	1.04	528	59	59
Toluene	9156827	8.65	1248	138	10243887	2.74	1394	155	16
PGMEA	64728111	61.13	8809	979	150656223	34.90	17762	1976	997
Ethylhexanol	3673761	3.47	500	56	3537939	0.94	481	53	-2
Cyclohexane	5757589	5.44	784	87	5599181	1.50	762	85	-2
Benzoeic acid	3231393	3.05	440	49	3351744	0.90	456	51	2
Cyclohexyl methacrylate	9418882	8.89	1282	142	8536458	2.35	1288	144	2
Total	10581807	100.00	14411	1601	734419474	100.00	50957	5662	4061

Figure 9 shows the component ratio of the outgas generated unexposure and during the exposure, and Figure 10 compares the amounts of the outgas generated from the resist per unit area. 1976ng/cm<sup>2</sup> of PGMEA was detected from the exposed resist, and this is thought to be due to the evaporation of the resist solvent; it should be noted however that the quantity involved is extremely rauge. The detected amounts of ethanol, acetaldehyde are 2339 ng/cm<sup>2</sup>, and 180 ng/cm<sup>2</sup>, respectively. These components of the outgas are considered to be generated by the deprotection reaction, as the protecting group (ethyl acetal) used in this resist has a low activation energy resulting in a deprotection reaction even during exposure. A slight amount of

dichloromethane, which is thought to be a result of the decomposition of the PAG, was also detected. The total amount of the outgas is 5662ng/cm<sup>2</sup>, which is approximately equal to the total amount of the outgas (6347ng/cm<sup>2</sup>) obtained in the QCM measurement. This indicates that the change in the mass obtained in the QCM measurement is almost entirely emitted into the air as outgas.

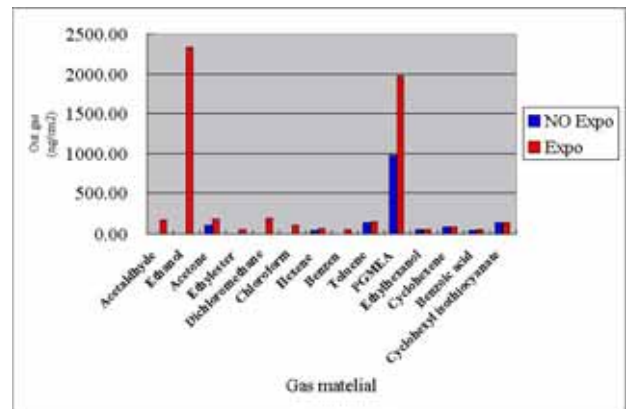


(a)



(b)

**Figure 9: The component ratios of the outgas (unexposure and exposure).**



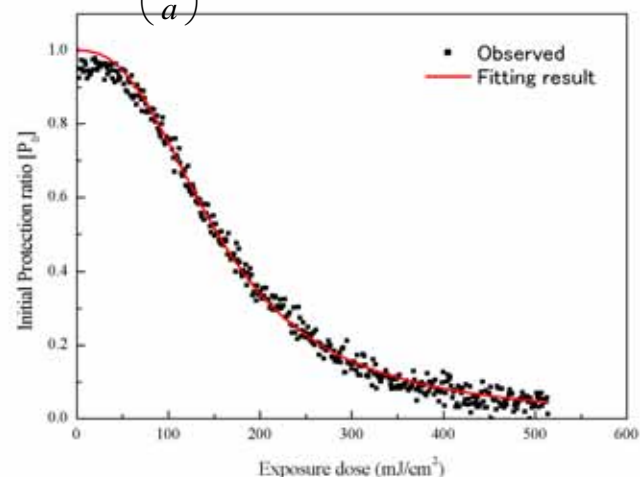
**Fig. 10. The amount of outgas release for each component.**

**5.3 In-situ FT-IR observation of the deprotection reaction of the resist during exposure**

Figure 11 shows the relationship between the exposure and the protection ratio of the protecting group. The deprotection reaction starts at the exposure of approximately 100 mJ/cm<sup>2</sup> and ends at approximately 300 mJ/cm<sup>2</sup>.

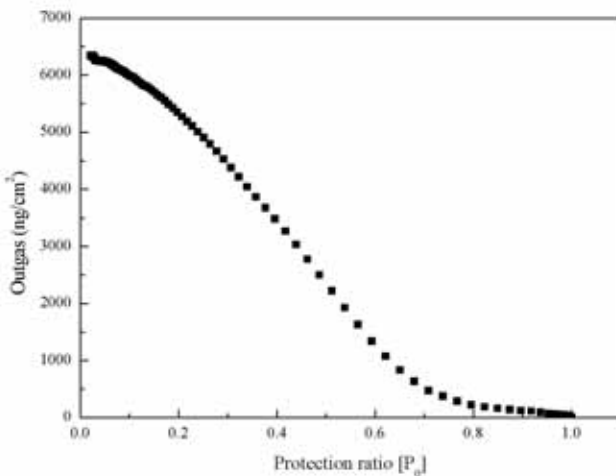
We tried fitting by using equation (2) for protection ratio and exposure dose. We have got a fitting result a=154.1631 b=2.5304.

$$[P_0] = \frac{1}{1 + \left(\frac{E}{a}\right)^b} \quad (2)$$



**Fig. 11. The relationship between the exposure and the protection ratio during exposure**

The same exposure energy is eliminated from Figures 6 and 11 to obtain the relationship between the amount of outgas generated and the protecting group (Figure 12). The result shows that the amount of outgas varies linearly with the amount of deprotection, and it is verified that outgas obtained in the QCM mass spectrum results is almost entirely due to the deprotection reaction.



**Fig. 12. The relationship between the amount of outgas and the deprotection ratio.**

## 6. Summary

A QCM mass spectrometer unit was attached to a 248 nm reaction analysis exposure tool equipped with a Hg-Xe lamp light source. The extent of outgassing generated from the 248 nm chemically amplified resist was investigated by tracing the change in the mass of the photoresist during exposure. The outgas generated from the resist during the exposure was also collected with a TENAX absorber to identify the components using a GC-MS. The reactions in the resist during exposure were observed using a PAGA-100 deprotection reaction analysis system, and the relationship between the outgassing and deprotection reaction was studied. The QCM results show that the generation of the gas starts at the exposure of approximately 100 mJ/cm<sup>2</sup> and ends at approximately 300 mJ/cm<sup>2</sup>. The FT-IR observation of the deprotection reaction indicates that the change in the mass is almost entirely due to the deprotection reaction. The results of the GC-MS

analysis show that the main components are ethanol and acetaldehyde. This experiment confirms that the present analysis system can measure the outgas from resists under exposure as a change in mass. Our next investigate will focus on the 193 nm chemically amplified resists.

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