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Evaluation of Outgassing from Eslon DC Plate by Analysis of Adsorbed Substance on the Surface of Silicon Wafer

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By Analysis of Absorbed Substance on the Surface of Silicon Wafer

1. Purpose and outline of the study

In order to assess the effect of the outgassing from “Eslon DC Plate,” a model cassette was prepared using DC Plate and a silicon wafer was placed inside the cassette, intending to analyze the adsorption on the surface of the wafer. The wafer placed in the cassette was left in a stream of clean air to simulate the actual environment of the clean room.

2. Tested plates

The following Eslon DC Plates made by Sekisui Chemical Co. were studied:

Eslon DC plate PVC
Eslon DC plate Polycarbonate
Eslon DC plate PET
Eslon DC plate PMMA (Acrylic)

3. Test method

(1) Preparation of model cassettes

Model cassettes of Eslon DC Plate were prepared as shown in Fig. 1.

Slits were provided on the sides of cassette, so that the air could pass through the cassette.

(2) Silicon wafer arrangement

A test chamber shown in Fig. 2 was placed in a Class 1000 clean room. Chemical and ULPA filters were provided at the entrance of air and an exhaust fan was installed at the exit of air of the chamber, so that the clean air passes through the chamber. A silicon wafer was set in a model cassette made of Eslon DC Plate, which was then placed in the test chamber. A control wafer was set in the upper stream of air.

Speed of the fan was adjusted so as to obtain an air flow of 0.3 to 0.4 m/sec.

The chamber heater was adjusted to obtain 60 °C temperature at the position of the cassette.

The wafer was left in this environment for 24 hours before taken out for analysis of organic substances.

(3) Analysis of wafer

<Employed equipment>

Silicon Wafer Analyzer: Model-SWA256 made by GL Sciences, Ltd.

Gas Chromatography-Mass Spectrometer: Model-5973 made by HP, Ltd.

<Test conditions of SWA>

Wafer heating: The wafer was heated to 400 °C in 15 min. and kept for 10 min.

Gas absorption: Generated gas was absorbed in Tenax absorption tube

Gas desorption: Tenax tube was heated to 270 °C for desorption.

Introduction to GC: Desorbed gas was cold-trapped at 130 °C and loaded to the column by heating it to 280 °C

<Test conditions of GC>

Column: CP-SIL5GB 0.25 mm ID x 60 m, made by Chrompack.

Temperature: The column was conditioned at 40 °C for 5 min. and raised to 280 °C at the rate of 10 °C/min.

Carrier gas flow: 1.0 ml/min.

<Test conditions of MS>

Temperature of ion source: 230 °C

Ionization method: EI

Measurable range of mass: up to m/z 600

4. Test result

The detected components of each test piece are shown in Tables 1 to 4. Unit of the detected quantity is pg/c ㎡. Chromatograms of each wafer are shown in Fig. 3 to 10.

5. Discussion

A trace amount of organic substance from each wafer placed in the chamber was detected but there was nothing specifically detected, i.e. the same substance was detected in a similar manner in the blank test wafer placed in the upper stream. This fact leads us to judge that the substance is background noise that exist in the environment. Adsorbed mass of some component is greater in the blank test wafer than in the wafer in the chamber and that of another is less, which fact suggests that the data are within the dispersion of measurement or the fluctuation of background noise.

These tests were conducted in a special precaution to exclude materials and parts from the cassette that could be the source of organic contamination. Thus the test environment had the same magnitude of background noise as the highly clean environment of the actual semiconductor manufacturing process.

From the above point of view, we conclude that the mass adsorbed on the surface of wafer from the emitted gas of the cassette (DC Plate) is sufficiently small, if any, compared to that of background noise origin and, therefore, the effect of emitted gas is clearly below the level to cause problems.

Additional observation in the test:

- Cyclic siloxanes were detected in all the test pieces but DC Plate does not contain any of the corresponding compounds. Those must have been originated from the test environment or the GC column used.
- Welding rods were used to assemble the model cassettes and the rods for U-PVC and polycarbonate cassettes contained 3 to 4% of DOP, however, the data obtained from the wafers in acrylic and PET cassettes also showed equal or higher amount of DOP. This fact suggests that the DOP in the environment gives more effect than the minor amount of DOP in the welding rods. The DC Plate itself does not contain any phthalic ester such as DOP.
- It is often mentioned that antioxidants such as BHT contained in plastics give bad effects to the process of semiconductor manufacturing, but no such components were detected in this test.

<About the validity of the blank value>

In this study of the emitted gas, 1,200 to 1,600 pg/c m^2 of organic substance was detected in the blank test wafer. Below, we discuss the validity of the blank value in the analysis of trace amount of emitted gas.

The table below shows the control standards of wafer contamination described in the "Road Map of Semiconductor Technology."[1] In the table, the control standard in 2002 for organic substance is 5.3 x 10^{13} carbon atoms/c m^2.

Table Control Standards of Wafer Surface Contamination

Year Technical node	1999 189 nm	2002 130 nm	2005 100 nm	2008 70 nm	2011 50 nm	2014 35 nm
Wafer diameter (mm)	200 mm	300 mm →				450 mm
Particle diameter (nm)	90	65	50	35	25	17.5
Number of particles (per ・) **	0,064 (0.13)	0,068 (0.14)	0,052 (0.10)	0,052 (0.10)	0,052 (0.10)	0,052 (0.10)
Heavy metals (atoms/ ・) **	9×10^9 (1.8×10^{10})	4.4×10^9 (8.8×10^9)	2.5×10^9 (4.9×10^9)	2.1×10^9 (4.2×10^9)	1.8×10^9 (3.6×10^9)	1.7×10^9 (3.4×10^9)
Organic matters & polymers (carbon atoms/ ・)	7.3×10^{13}	5.3×10^{13}	4.1×10^{13}	2.8×10^{13}	2.0×10^{13}	1.4×10^{13}

** Figures in the lower line in the parentheses are values for wafers to be fed to the production line. All other values are for wafers in the transistor forming process.

Organic compound consists of carbon atoms and other kind of atoms such as hydrogen and oxygen bonded to carbon, and the molecular weight per carbon atom varies by the chemical structure. For example, the molecular weights per carbon of benzene, DOP and polyethylene glycol are:

Benzene: C_6H_6	DOP: $C_{24}H_{36}O_4$	Ethylene glycol unit: $-CH_2CH_2O-$
$\frac{Molecular \cdot weight}{Carbon \cdot number} = \frac{78.1}{6} = 13.0$	$\frac{Molecular \cdot weight}{Carbon \cdot number} = \frac{390.6}{24} = 16.3$	$\frac{Molecular \cdot weight}{Carbon \cdot number} = \frac{44.0}{2} = 22.0$

In the benzene molecule, carbon atoms occupy major part of the weight, making the weight per carbon atom small, while in the polyethylene glycol molecule, there is an oxygen every two carbons, making the weight per carbon large. In most of organic compound, the molecular weight per carbon falls in between these values.

6×10^{23} molecules together would give the weight in gram equal to the molecular weight, thus the weight of benzene equivalent to 5.3×10^{13} carbon atoms will be:

$$\frac{5.3 \times 10^{13} \times 13.0}{6 \times 10^{23}} = 1.1 \times 10^{-9} g = 1{,}100 pg$$

Similarly the weight of polyethylene glycol equivalent to 5.3×10^{13} carbon atoms will be:

$$\frac{5.3 \times 10^{13} \times 22.0}{6 \times 10^{23}} = 1.9 \times 10^{-9} g = 1.900 pg$$

As shown above, the control standards expressed in carbon number in the reference literature can be converted to mass which are usually in the range of 1,100 to 1,900 pg/c m^2. This level is same as the blank value of this test. It means that the test was conducted in the atmosphere of the control standard and quite adequate as an assessing environment.

Reference

1) International Technology Roadmap for Semiconductors, Semiconductor Industry Association, San Jose (1999)

Table 1. Analysis of Wafer Surface in the Cassette made of PVC DC Plate

peak No.	Adsorbed Chemical Substance	upper stream blank	wafer in the box	increase (%)
1	C8H16, octene	39	37	-5.1
2	cyclic siloxane (trimer)	26	30	15.4
3	2,4-dimethyl-1-heptene	0	32	
4	styrene	62	14	-77.4
5	2-ethlyhexanol	78	79	1.3
6	isopropenylacetophenone	0	0	---
7	N-Methylphthalamide	36	49	36.1
8	diacetylbenzene	0	0	---
9	1-t-butyl-2-methylpropanediol diisobutylate	4	3	-25.0
10	not identified (aromatic compound including nitrogen)	35	35	0.0
11	cyclic siloxane (octamer)	17	35	105.9
12	cyclic siloxane (nonamer)	88	121	37.5
13	dibutylphthalate, DBP	143	166	16.1
14	cyclic siloxane (decamer)	219	256	16.9
15	cyclic siloxane (undecamer)	255	221	-13.3
16	decomposition residue of polyglycol	42	45	7.1
17	cyclic siloxane (dodecamer)	87	73	-16.1
18	dioctylphthalate, DOP	354	355	0.3
	Total	1485	1551	4.4

(pg/cm2)

Table 2. Analysis of Wafer Surface in the Cassette made of Polycarbonate DC Plate

peak No.	Adsorbed Chemical Substance	upper stream blank	wafer in the box	increase (%)
1	toluene	24	30	25.0
2	C8H16, octene	30	31	3.3
3	cyclic siloxane (trimer)	23	26	13.0
4	2,4-dimethyl-1-heptene	27	4	-85.2
5	2-ethlyhexanol	73	61	-16.4
6	cyclic siloxane (pentamer)	25	11	-56.0
7	N-methlyphthalamide	26	24	-7.7
8	not identified (aromatic compound including nitrogen)	27	38	40.7
9	cyclic siloxane (nonamer)	105	117	11.4
10	dibutylphthalate, DBP	171	158	-7.6
11	cyclic siloxane (decamer)	217	227	4.6
12	cyclic siloxane (undecamer)	177	184	4.0
13	decomposition residue of polyglycol	38	30	-21.1
14	cyclic siloxane (dodecamer)	51	56	9.8
15	dioctylphthalate, DOP	202	227	12.4
	Total	1216	1224	0.7

(pg/cm2)

Table 3. Analysis of Wafer Surface in the Cassette made of PET DC Plate

peak No.	Adsorbed Chemical Substance	upper stream blank	wafer in the box	increase (%)
1	C8H16, octene	39	35	−10.3
2	cyclic siloxane (trimer)	24	29	20.8
3	2−ethlyhexanol	72	58	−19.4
4	1−t−butyl−2−methyl−3−hydroxypropylisobutylate	21	24	14.3
5	2−methyl−3−t−butyl−3−hydroxypropylsobutylate	52	58	11.5
6	N−methlyphthalamide	30	27	−10.0
7	not identified (aromatic compound including nitrogen)	39	45	15.4
8	cyclic siloxane (nonamer)	90	121	34.4
9	dibutylphthalate, DBP	153	172	12.4
10	cyclic siloxane (decamer)	230	261	13.5
11	cyclic siloxane (undecamer)	271	226	−16.6
12	not identified (aromatic compound)	29	9	−69.0
13	decomposition residue of polyglycol	53	38	−28.3
14	cyclic siloxane (dodecamer)	83	64	−22.9
15	dioctylphthalate, DOP	375	262	−30.1
	Total	1561	1429	−8.5

(pg/cm2)

Table 4. Analysis of Wafer Surface in the Cassette made of Acrylic DC Plate

peak No.	Adsorbed Chemical Substance	upper stream blank	wafer in the box	increase (%)
1	benzene	35	44	25.7
2	C8H16, octene	53	47	−11.3
3	C8H16, octene(isomer)	38	39	2.6
4	phenol	59	72	22.0
5	2−ethlyhexanol	124	104	−16.1
6	not identified (aromatic compound including nitrogen)	28	24	−14.3
7	cyclic siloxane (nonamer)	45	61	35.6
8	dibutylphthalate, DBP	133	151	13.5
9	cyclic siloxane (decamer)	138	165	19.6
10	cyclic siloxane (undecamer)	246	175	−28.9
11	decomposition residue of polyglycol	70	41	−41.4
12	cyclic siloxane (dodecamer)	68	45	−33.8
13	dioctylphthalate, DOP	617	274	−55.6
	Total	1654	1242	−24.9

(pg/cm2)

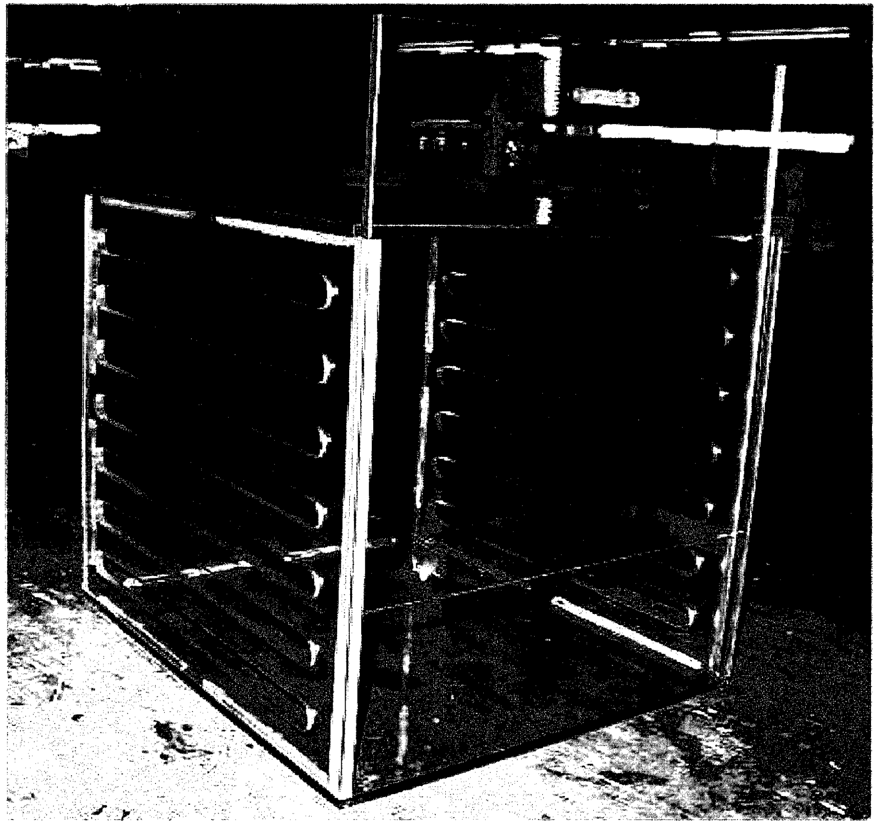

Fig.1 Wafer Cassette Made of DC Plate

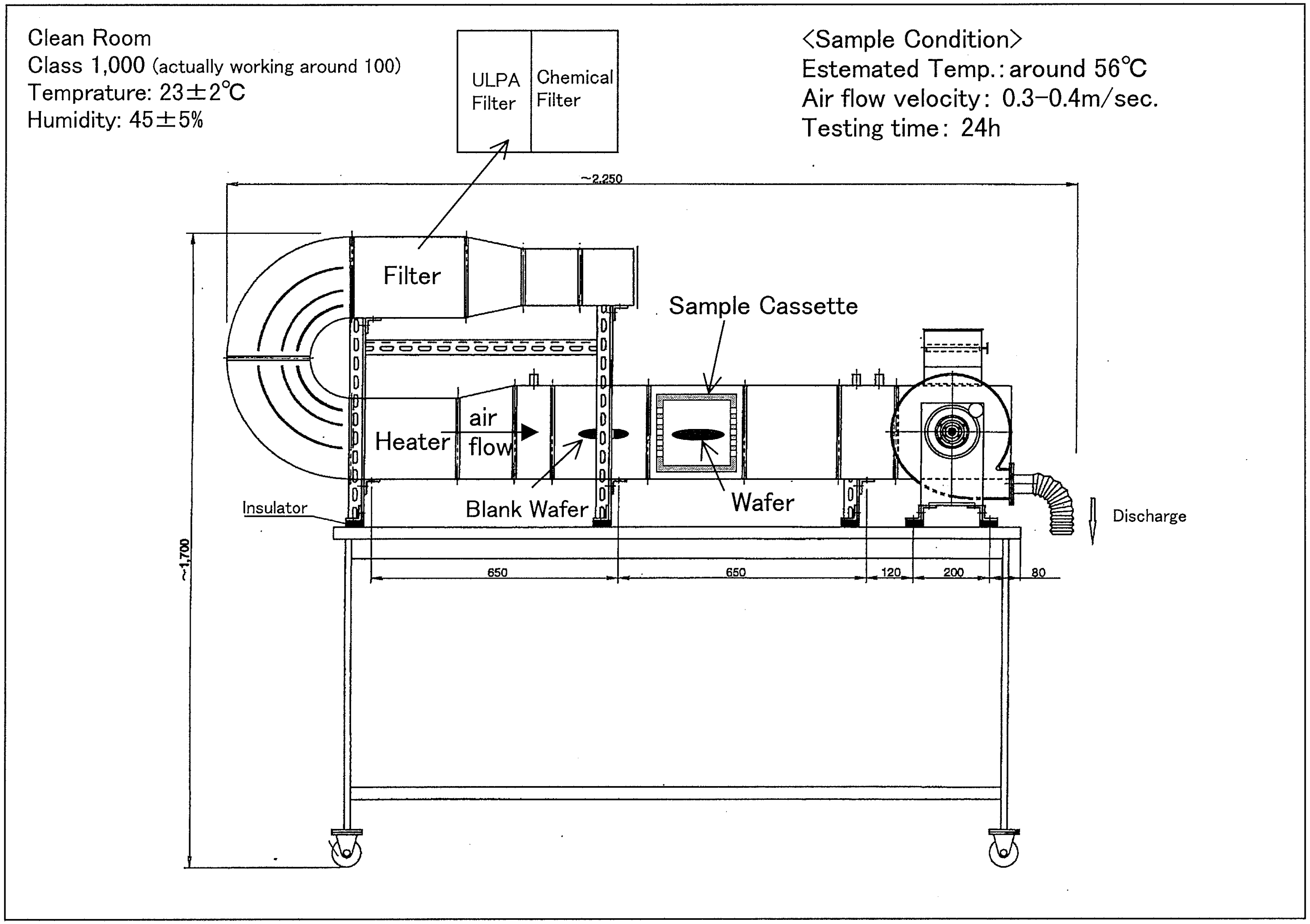

Fig.2 Apparatus