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Original Article

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Exposure to Volatile Organic Compounds and Possibility of Exposure to By-product Volatile Organic Compounds in Photolithography Processes in Semiconductor Manufacturing Factories

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Objectives: The purpose of this study was to measure the concentration of volatile organic compound (VOC)s originated from the chemicals used and/or derived from the original parental chemicals in the photolithography processes of semiconductor manufacturing factories.

Methods: A total of four photolithography processes in 4 Fabs at three different semiconductor manufacturing factories in Korea were selected for this study. This study investigated the types of chemicals used and generated during the photolithography process of each Fab, and the concentration levels of VOCs for each Fab.

Results: A variety of organic compounds such as ketone, alcohol, and acetate compounds as well as aromatic compounds were used as solvents and developing agents in the processes. Also, the generation of by-products, such as toluene and phenol, was identified through a thermal decomposition experiment performed on a photoresist. The VOC concentration levels in the processes were lower than 5% of the threshold limit value (TLV)s. However, the air contaminated with chemical substances generated during the processes was re-circulated through the ventilation system, thereby affecting the airborne VOC concentrations in the photolithography processes.

Conclusion: Tens of organic compounds were being used in the photolithography processes, though the types of chemical used varied with the factory. Also, by-products, such as aromatic compounds, could be generated during photoresist patterning by exposure to light. Although the airborne VOC concentrations resulting from the processes were lower than 5% of the TLVs, employees still could be exposed directly or indirectly to various types of VOCs.

Key Words: Semiconductor, Photolithography, Wafer fabrication, Chemical substances, Volatile organic compounds

Introduction

Semiconductor devices are made through various fabrication

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processes during which electronic circuits are gradually created on and within the surface of highly purified semiconducting materials called "wafers" [1-3]. The entire manufacturing process is performed in highly complex facilities that are well known as "Fabs." The wafer fabrication process consists of several unit processes, such as diffusion, photolithography, etching, ion implantation, and deposition, which use various chemical substances in order to create a circuit pattern on a wafer [2-5]. Photolithography is a technique of writing a circuit pattern on a silicon wafer. The photolithography process is one of the

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most complex processes in semiconductor manufacturing. The process is composed of a series of sub-processes, such as photoresist coating, light exposure, and development [5-9]. A variety of organic compounds are used as solvents, developing agents, and thinners in the process [2,4]. This puts employees at risk of being exposed to these compounds during the process. According to the literature, by-products also can be released during the photolithography process. A US patent (No. 7358597: ultraviolet [UV]-activated dielectric layer) describes that irradiating dielectric material with UV light causes the photosensitive moieties to cleave from the "backbone" and become volatile and/ or low molecular-weight species, such as benzene and phenyl sulfide [10].

Some cases of malignant lymphohematopoietic disorders were reported from the semiconductor industry. Studies to evaluate work-relatedness have been conducted by researchers of the Occupational Safety & Health Research Institute (OSHRI) of the Korea Occupational Safety & Health Agency (KOSHA) [11-13], where this study was also conducted to assess the work-relatedness.

All semiconductor devices are produced in clean room facilities that are strictly controlled to avoid the generation of particles. But many chemical substances are used at each process and by-products can be generated during these processes. Studies on the semiconductor industry until now have mainly focused on some of the chemical substances used in the industry. However, a comprehensive study on worker exposure to the chemical substances that can be generated during the fabrication processes has not yet been reported. The purpose of this study was to measure the concentration of volatile organic compound (VOC)s originated from the chemical used and/or derived from the original parental chemicals in the photolithography processes of semiconductor manufacturing factories.

Materials and Methods

A total of four photolithography processes in 4 Fabs (one process for 5 inch wafer Fab, two for 8 inch wafer Fabs, and one for 12 inch wafer Fab) at three different semiconductor manufacturing factories in Korea were selected for this study in 2009. Because the semiconductor industry has made progress with the development of fabrication techniques for larger-sized wafers, which have improved productivity, we selected those Fabs that used these new techniques.

This study consists of an investigation into the possibility of worker exposure to organic compounds in photolithography processes and an evaluation of VOC concentrations in the air that resulted from these processes. The possibility of worker exposure to organic compounds was investigated through a review of the chemical substances used in the processes and an experiment to identify the by-products generated during the processes.

Identification of chemical substances used in each Fab

The types of chemical substances used in the four photolithography processes of the three semiconductor manufacturing factories in 2009 were reviewed. Survey sheets were distributed to each company's supervisor in charge of chemical management. All the companies in this study had a database for the chemicals used in each Fab. The authors also reviewed Material Safety Data Sheet (MSDS)s for mixture compounds such as photoresists as well as lists of chemical substances submitted by the supervisors. In Korea, all employers must provide MS-DSs for all chemical substances to workers.

Estimation of the decomposition products caused by light exposure

As mentioned in the introduction, by-products such as benzene can be produced during photolithography processes [10]. Decomposition products under light exposure during the photolithography process were identified indirectly through a thermal decomposition experiment performed on a photoresist, which generally consists of a Novolak resin, organic solvents, and a photosensitive material. There will be differences between the decomposition products produced by radiant energy and by thermal energy. The authors evaluated possible exposure to by-products by the method available in the laboratory. The purpose of this experiment was to assess whether the by-products derived from photolithography processes could be included in the VOCs detected in photolithography.

The photoresist used for the thermal decomposition experiment consisted of a cresol-formaldehyde resin (15-20%), a phenol polymer (1-10%), methyl-3-methoxypropionate as a solvent, and a photoactive compound (1-10%, the chemical name of which is a trade secret). The exact content of each component was a trade secret. The thermal decomposition experiment was conducted in a fume hood facility. An Erlenmeyer flask, personal air samplers (Gilian model, LFS-113DC, Sensidyne Inc., Clearwater, FL, USA), and a hot plate were used for the experiment. 5 mL of the photoresist was added to a flask and the initial temperature of the hot plate was set to 150°C in order to evaporate the organic solvent (methyl-3-methoxypropionate). The hot plate was then heated up to the final temperature of 420°C. The samples were collected at two different times: once during the ascent from 150°C to 420°C and another at the final

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temperature of 420°C. Sampling was made for 20 min at a flow rate of 0.2 L/min on the head space of the Erlenmeyer flask. Charcoal tubes were used to collect the organic vapors generated during the thermal decomposition experiment. The samples collected during the thermal decomposition experiment were analyzed by a gas chromatography-mass spectrometer (Gas Chromatography-Mass Spectrometer [GC-MS], Agilent model 6890N-5973N, Agilent Technologies, Santa Clara, CA, USA). The authors referred to the NIOSH analytical method No. 1501 for sample preparation [14].

Exposure monitoring for VOCs

The concentrations of VOCs in the air caused by the photolithography processes were evaluated by a sorbent tube/thermal desorption/chromatography-mass spectrometer system (ST/ TD/GC-MS). In this study, VOCs were evaluated with the threshold limit value (TLV)s of the American Conference of Governmental Industrial Hygienists (ACGIH). Tenax tubes were used as sorbent tubes to collect VOCs from the air. Tenax tubes are appropriate to collect samples of wide-ranging organic compounds such as aromatic compounds, aliphatic compounds, acetates, ethers, alcohols, and ketones. Sampling for VOCs in the photolithography processes was conducted for about six hours at a flow rate of 0.1 L/min using personal air samplers (Gilian model, LFS-113DC, Sensidyne Inc., Clearwater, FL, USA). There were many limitations in using the personal air sampling method in the semiconductor manufacturing factories due to the difficulty in attaching samplers within the breathing zone and the hindrance to worker's operation. Therefore, the area sampling method (fixed-location sampling) at worker's work area (work station) was applied to collect VOCs. The photolithography process consisted of 4-7 bays according to the semiconductor manufacturing factory. The number of workers (operators of photolithography instrument) per bay was 2-5 according to the factory. The number of samples collected at worker's work area was 1-3 by bay.

The samples were analyzed by a gas chromatographymass spectrometer (GC-MS, Agilent model 6890N-5973N, Agilent Technologies, Santa Clara, CA, USA) with reference of the International Organization for Standardization standard of 16017-1 for the sampling and analysis of VOCs [15]. Nondetectable values were substituted as "L (limit of detection)/2" for estimating the average concentration [16].

Results

Types of chemical used in the photolithography process

The photolithography process consists of a series of sub-processes, such as photoresist coating, adhesion promoter coating, pre/post baking, light exposure, and development. The wafer is coated with a photosensitive material called a "photoresist." The photoresist-coated wafer is then pre-baked at 90 to 120°C to create a firm bond with the photoresist and drive off excess photoresist solvent. After prebaking, the photoresist is exposed to a pattern of intense light. Optical lithography typically uses UV light. A post-exposure bake at 60 to 120°C is performed to solidify the pattern before development. The photoresist layer then is exposed to a chemical, known as the developer, in which either the irradiated or the non-irradiated photoresist is soluble [8,17].

Table 1 shows the composition of the photoresist used in the photolithography processes of the three semiconductor manufacturing factories. A photoresist consists of resins, organic solvents, photoactive compounds, and additives. Resins are used to provide mechanical strength to the photoresist and the solvents serve to lower the viscosity of the photoresist so that it can be uniformly applied to the surface of wafers. Sensitizers are compounds, such as diazonapthaquinones, that undergo a chemical change upon exposure to radiant energy, such as UV light [8]. Several types of organic resin including Novolak resin, which is most commonly used for photoresists, were used in the process. A variety of organic solvents, such as ethyl benzene, ethyl lactate, n-butyl acetate, and propylene glycol monomethyl ether (PGME), were used as solvents of photoresists. Sometimes wafers were primed with an adhesive, such as hexamethyldisilazane (HMDS). Glycol ethers have been a popular solvent for carrying HMDS, although some manufacturers have switched to alternative solvents such as xylene, n-butyl acetate, acetone, and 1,1,1-trichloroethane [4]. Also, organic compounds, such as ketone, alcohol, acetate, ether, and amine compounds as well as aromatic compounds, were used as solvents, developing agents, and thinners in this process (Table 2). Tens of chemicals were being used in the photolithography processes, though the types of chemical differed among the semiconductor manufacturing factories. Therefore, employees could be exposed to all of these chemicals during the photolithography processes.

Thermal decomposition products of photoresists

Workers could be exposed to the UV light-induced decomposition products of the photoresist during the photolithography

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Resins	Solvents	Others				
Acrylate polymer	1-Methoxy-2-propyl acetate	Photoactive compound (photo acid generator, photo sensitizer)				
Cyclized polyisoprene	2-Ethoxyethanol	Surfactant				
Cresol-formaldehyde resin	2-Heptanone Additives					
Novolak resin	2-Methoxy-1-methylethyl acetate					
Polyhydroxy styrene derivative	2-Methoxy-1-propanol • Chemical names are trade secrets.					
Polyvinyl phenol derivative	2-Methoxypropyl acetate					
Hydrogensiloxane polymer	Cresol					
Triethylenetetramine formaldehyde- phenol copolymer	Cyclohexanone					
Polymethacrylate derivative	Ethyl alcohol					
	Ethyl benzene					
	Ethyl lactate					
	gamma-Butyrolactone					
	Isopropyl alcohol					
	Methyl-2-hydroxyisobutyrate					
	Methyl-3-methoxypropionate					
	n-Butyl acetate					
	Propylene glycol monomethyl ether					
	Propylene glycol monomethyl ether acetate					
	Propylene glycol-dimethyl ether					
	Xylene					

Table 1. Composition of a photoresist used in photolithography processes (in 2009)

process. Fig. 1 shows a GC-MS chromatogram for a sample collected during the thermal decomposition experiment. Aromatic compounds, such as benzene, toluene, xylene, phenol, and cresol, were detected by GC-MS. Table 3 shows the GC-MS peak area based on the thermal decomposition products of the photoresist. The peak area indicates an instrumental response from the GC-MS. Therefore, it shows rough information regarding the contents of the thermal decomposition products, but does not indicate precise amounts of the thermal decomposition products can vary according to the photoresist components, such as the resin, solvent, and photoactive compound.

Though the samples were collected at two different times as described in the section on materials and methods, the analysis result for sample collected at the final temperature stage are presented. The authors identified the evaporation of all solvents in a photoresist during the experiment and were able to confirm that the components in Table 3 and Fig. 1 were derived from the thermal decomposition of a photoresist.

Results of exposure monitoring for VOCs

Table 4 shows the concentration of VOCs in the air from four photolithography processes in the three semiconductor manufacturing factories. Among the detected VOC components, only VOCs that had the TLVs of the ACGIH were evaluated in this study. For example, methyl-3-methoxy propionate, a component of raw materials, was detected but not evaluated.

VOCs, such as isopropyl alcohol (IPA), PGME, and toluene, were detected by the thermal desorption/gas chromatography-mass spectrometer system (TD/GC-MS). Most of the VOC concentration levels were lower than 0.1 ppm except for IPA, PGME, and xylene, which were used as solvents in the photolithography processes. Though the maximum concentrations of IPA, PGME, and xylene were more than 0.1 ppm, Park SH et al. Safety and Health at Work || Vol. 2, No. 3, SEP. 30, 2011

Developing step	Stripping step*	Thinners (general purpose)
Aliphatic hydrocarbons	1-Methoxy-2-propanol	N,N-Dimethyl acetamide
Ethyl-3-ethoxypropionate	1-Methoxy-2-propyl acetate	Ethyl lactate
gamma-Butyrolactone	1-Methyl-2-pyrrolidinone	Ethyl-3-ethoxypropionate
N-Methyl-2-pyrrolidone	2-(2-Aminoethoxy) ethanol	gamma-Butyrolactone
Propylene glycol monomethylether acetate	Catechol	Methoxy propanol
Polyamide acid	Ethanolamine	Methyl-3-methoxypropionate
Tetramethylammonium hydroxide	Hydroxyl Amine	n-Butyl acetate
Xylene	n-Butyl acetate	Propylene glycol monomethyl ether
		Propylene glycol monomethyl ether acetate
		Xylene

*The stripping step is classified as part of the etching process, but in some cases the step is located in the photolithography process.

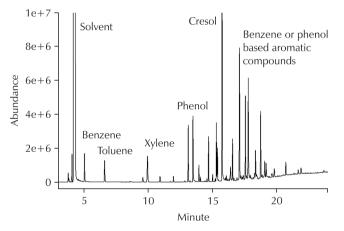


Fig. 1. GC-MS chromatogram for a sample collected during the decomposition experiment. GC-MS: gas chromatography-mass spectrometer.

the concentrations of IPA (TLV, 200 ppm), PGME (TLV, 100 ppm), and xylene (TLV, 100 ppm) were lower than 5% of the ACGIH TLVs [18].

Table 5 shows the airborne VOC concentrations from the outdoor environments of the Fabs. The airborne concentrations of n-hexane, benzene, and toluene inside the Fab locations were not different from those in the outdoor Fab environments. The airborne concentrations of chemical substances used at each indoor Fab location, such as IPA, PGME, butyl acetate, and xylene, except for n-hexane, benzene, and toluene, were higher than those in the outdoor Fab environments.

 Table 3. Result of GC-MS analysis for a sample collected during the decomposition experiment

Chemicals detected by GC-MS	GC-MS Peak area (%)
Acetone	1.4
Benzene	2.1
Toluene	1.8
Ethyl benzene	0.5
Xylene	3.6
1-Methylethyl benzene or its isomers	4.1
Phenol	5.1
1,2,3-Trimethyl benzene or its isomers	1.2
Benzofuran	0.3
1-Methyl-2-(1-methylethyl) benzene or its isomers	3.0
Cresol	20.9
1,2-Diethyl benzene or its isomers	2.6
2,3-Dimethyl phenol or its isomers	26.1
2,4,6-Trimethyl phenol or its isomers	11.0
Others	16.2

GC-MS: gas chromatography-mass spectrometer.

(unit: ppm)

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Table 4. Airborne VOC concentrations in the photolithography processes(unit: ppm)								
	IPA	Hexane	Benzene	PGME	Toluene	Butyl acetate	Ethyl benzene	Xylene
No. of samples	8	40	40	40	40	40	40	40
Detected samples	8	6	5	24	38	17	26	27
LOD	0.0024	0.0001	0.0001	0.0066	0.0008	0.0025	0.0007	0.0007
Min	0.0086	0.0002	0.0002	0.0142	0.0014	0.0046	0.0019	0.0014
Max	0.6548	0.0005	0.0003	0.1145	0.0064	0.0301	0.0204	0.1180
GM	0.0637	*	*	0.0175	0.0026	0.0040	0.0014	0.0026
TLV-TWA	200	50	0.5	100	20	150	100	100

Table 4 Airborne VOC concentrations in the photolithography processes

VOC: volatile organic compound, IPA: Isopropyl alcohol, PGME: propylene glycol monomethyl ether, No: number, LOD: limit of detection, GM: geometric mean, TLV-TWA: threshold limit value-time weighted average.

*The detected samples were too small to calculate GM.

	IPA	n-Hexane	Benzene	PGME	Toluene	Butyl acetate	Ethyl benzene	Xylene
No. of samples	4	19	19	19	19	19	19	19
Detected samples	3	2	4	0	17	0	8	9
LOD	0.0024	0.0001	0.0001	0.0066	0.0008	0.0025	0.0007	0.0007
Min	0.0074	0.0004	0.0002	-	0.0016	-	0.0015	0.0023
Max	0.0100	0.0007	0.0003	-	0.0041	-	0.0033	0.0072

VOC: volatile organic compound, GM: geometric mean, IPA: Isopropyl alcohol, PGME: propylene glycol monomethyl ether, No: number, LOD: limit of detection.

Discussion

Characteristics of chemical substances used in photolithography processes

The tested photolithography processes used tens of chemical substances, including photoresists, which consisted of resins, organic solvents, a photo-sensitive compound, and additives. Notably, various types of organic compound, such as ketones, alcohols, acetates, ethers, amines, and aromatic compounds, were used as solvents, developing agents, and thinners in the process. Therefore, employees could be exposed to these chemicals during the photolithography processes. Many chemical substances that were used in the photolithography processes do not have occupational exposure limits. Workers should be well informed of the hazards and control measures for these chemical substances because they may use the substances carelessly due to the absence of exposure limits.

Possibility of decomposition products

According to US patents, sensitizers in photoresists undergo

chemical changes upon exposure to radiant energy, such as UV light, and irradiating dielectric material with UV light causes the photosensitive moieties to cleave from the backbone and become volatile and/or low molecular weight species, such as benzene and phenyl sulfide [8-10].

This study investigated decomposition products indirectly through experiments using thermal energy instead of radiant energy due to the difficulty of experimenting with UV light. Various types of aromatic compound, such as benzene, toluene, phenol, and cresol, were identified through a thermal decomposition experiment involving a photoresist which consisted of Novolak resin (cresol-formaldehyde resin), methyl-3methoxypropionate, a phenol polymer, and a photosensitive material. The chemical name of the photosensitive material is a trade secret (semiconductor manufacturing companies keep photosensitive material information as trade secrets). A photoresist comprising Novolak resin, an organic solvent, and a photosensitive material is the most common type of positive photoresist.

It seems that the aromatic compounds identified through

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this experiment were closely associated with the Novolak resin and the photosensitive material. The Novolak resin and diazonaphthoquinone, a common type of photosensitive material, both have structural aromatic compounds [9,19,20].

There will be differences between the decomposition products by radiant energy and those by thermal energy due to the differing amounts of energy applied to the photoresist. However, when judging from the results of literature reviews and the thermal decomposition experiment, workers that have contact with photolithography processes could be exposed to aromatic compounds, such as benzene, toluene, phenol, and cresol, during the patterning of photoresists by exposure to light. Meanwhile polar compounds, gas-phase compounds and/or non-volatile compounds might be included among the decomposition products but this study did not cover those compounds.

Airborne VOC concentration levels due to photolithography processes

Though tens of chemical substances are directly used in photolithography processes and their decomposition products can be generated during the patterning of photoresists by exposure to light, the airborne VOC concentration levels due to photolithography processes were lower than 5% of the ACGIH TLVs.

It seems that these low VOC levels were closely associated with the ventilation systems in the respective Fabs. Most of the wafer fabrication facilities were equipped with local ventilation systems and all the processes in each Fab were equipped with total ventilation systems. Therefore, the chemical substances generated at the wafer fabrication facilities for photolithography processes are primarily removed through local ventilation systems and are additionally removed through total ventilation systems. Air circulation systems (total ventilation system) of a vertical laminar airflow type are used in the clean rooms of semiconductor manufacturing factories. Air passes from an overhead plenum above the filter (high-efficiency particulate air, filters or ultra-low particulate air, filters), through the filter, vertically downward through the clean room, and through an apertured floor in the clean room into an air-receiving plenum [21]. The flow rate of the vertical laminar airflow in the clean room is generally 0.2-0.4 m/sec. The air exposed to the photolithography process, however, is re-circulated with about 20-30% outdoor air. Therefore, air that is contaminated with chemical substances in spite of low concentration levels is re-circulated through the total ventilation systems. That is, if chemical substances generated from some facilities are exposed to the air in the process, the substances are mixed with the total air in the process location and re-circulated over time.

Meanwhile, there are some limitations of this study. It was difficult to discern the effects of byproducts upon the airborne VOCs concentrations. Therefore, further study on byproducts is required. Also, though the Tenax tubes, which were used to collect airborne VOCs in this study, are apt to collect wide-ranging VOCs, there may have been a limitation in sample collection for very light organic compounds that were less than 5 (C5) in the carbon number.

In conclusion, tens of chemical substances were used during the photolithography processes. Decomposition products, such as aromatic compounds, also could be generated during the patterning of photoresists by exposure to light. Although the airborne VOC concentration levels in the photolithography processes were lower than 5% of the ACGIH TLVs, employees working with photolithography processes could be exposed directly or indirectly to various VOCs.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

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