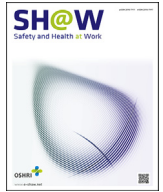




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Original article

## Possibility of Benzene Exposure in Workers of a Semiconductor Industry Based on the Patent Resources, 1990–2010

Sangjun Choi<sup>1,\*</sup>, Donguk Park<sup>2</sup>, Yunkyung Park<sup>3</sup><sup>1</sup> Department of Preventive Medicine, College of Medicine, The Catholic University of Korea, Seoul, 06591, Republic of Korea<sup>2</sup> Department of Environmental Health, Korea National Open University, Seoul, 03087, Republic of Korea<sup>3</sup> Department of Occupational Health, Daegu Catholic University, Gyeongbuk, 38430, Republic of Korea

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## ABSTRACT

**Background:** This study aimed to assess the possibility of benzene exposure in workers of a Korean semiconductor manufacturing company by reviewing the issued patents.

**Methods:** A systematic patent search was conducted with the Google “Advanced Patent Search” engine using the keywords “semiconductor” and “benzene” combined with all of the words accessed on January 24, 2016.

**Results:** As a result of the search, we reviewed 75 patent documents filed by a Korean semiconductor manufacturing company from 1994 to 2010. From 22 patents, we found that benzene could have been used as one of the carbon sources in chemical vapor deposition for capacitor; as diamond-like carbon for solar cell, graphene formation, or etching for transition metal thin film; and as a solvent for dielectric film, silicon oxide layer, nanomaterials, photoresist, rise for immersion lithography, electrophotography, and quantum dot ink.

**Conclusion:** Considering the date of patent filing, it is possible that workers in the chemical vapor deposition, immersion lithography, and graphene formation processes could be exposed to benzene from 1996 to 2010.

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## 1. Introduction

Cases of cancer occurrence in the semiconductor industry have been reported in several countries, including the United Kingdom [1–3], the United States [4–6], and Taiwan [7]. In South Korea, since a young female worker died of leukemia in 2007 after working at a semiconductor manufacturing process in Samsung’s Giheung plant, there has been controversy over the causes of cancer among semiconductor workers [8–13].

Since 2007, the Korean Non-Governmental Organization named Supporters for the Health and Rights of People in the Semiconductor Industry has collected data on the cases of cancers or rare diseases and supported workers’ claims for compensation. Park et al. analyzed the occupational characteristics of 55 semiconductor workers with cancer or rare diseases who claimed their benefits from the Workers’ Compensation and Welfare Service (COMWEL) [14]. Lymphohematopoietic (LHP) disorders including

leukemia (n = 14), aplastic anemia (n = 6), and non-Hodgkin lymphoma (n = 4) accounted for 43% of all disease. Among 55 applicants, only 10 were compensated by the COMWEL and 8 were compensated through civil litigation. Among 2,468 claimants, 519 (21%) were awarded compensation for occupational cancer including lung, malignant mesothelioma, LHP, and liver cancers between 2000 and 2012 in South Korea [15].

Under the Industrial Accident Compensation Insurance (IACI) Act, to receive compensation for occupational diseases, exposure to harmful factors suspected of causing the disease must be identified [16]. Patients with chronic diseases, such as cancer, usually experience difficulties in claiming compensations because the retrospective exposure should be investigated and confirmed. In the high-tech sectors, especially in the semiconductor industry, identifying the past exposure history has been a major challenge for occupational health professionals due to the rapid changes in processes and handling materials [17]. In addition, it is more

\* Corresponding author. Department of Preventive Medicine, College of Medicine, The Catholic University of Korea, 222 Banpo-daero, Seocho-gu, Seoul, 06591, Republic of Korea.

E-mail address: [junilane@gmail.com](mailto:junilane@gmail.com) (S. Choi).

difficult to identify past exposures as the information on the materials used in the semiconductor industry are not usually divulged to protect their trade secrets [18]. On the contrary, companies in the high technology sector have exclusive intellectual property rights through patent applications, which can be used to identify technological trends and related substances used at the time of filing. The possibility of benzene exposure in semiconductor workers as a major risk factor for LHP cancers [19] remains controversial [20–22], which is mostly reported among Korean semiconductor companies. Therefore, this study aimed to assess the possibility of benzene use in Korean semiconductor manufacturing companies by reviewing the issued patents.

## 2. Materials and methods

### 2.1. Patent search

A systematic patent search was conducted with the Google “Advanced Patent Search” engine using the keywords “semiconductor” and “benzene” combined with all of the words accessed on January 24, 2016. The search period was set from January 1, 1990 to December 31, 2010 based on the filing date. As Samsung Electronics was Korea’s semiconductor manufacturing company where most cases of leukemia were reported, patent search was performed with the original assignee limited to “Samsung Electronics Co. Ltd.” or coapplicants including “Samsung Electronics Co. Ltd.”

### 2.2. Patent selection and data analysis

We searched 77 patents and collected the original patent documents. A total of 75 patent documents were reviewed except 2 of 77 patent data. One was excluded because the applicant was not Samsung Electronics, whereas the other was duplicated. Among the patent contents, the patent number, patent office, filing year, publication year, title of the patent, and sentence containing “benzene” in the text were entered in the spreadsheet.

### 2.3. Assessment of the benzene exposure possibility

The full text of the included patents was reviewed by two authors (S.C. and D.P.). In case of discrepancies in data interpretation, it was resolved through consensus. To evaluate the possibility of benzene exposure in each of the included patents, we designed a scoring system with four parameters, which were related to environmental exposure. These items were chemical type, where used, handling condition, and probability to be used benzene. We attributed different weights to each item’s characteristics. The greater the sum of the scores, the more likely the patent document suggests that semiconductor workers may be exposed to benzene in the past. The weight scale of each item is shown in Table 1.

In terms of chemical type, if “benzene” or an empirical formula of benzene ( $C_6H_6$ ) was found in a patent document, 2 points were given. When aromatic compounds with a benzene ring were used or there was no mention of benzene, “1” points and “0 point” were given, respectively.

When benzene or aromatic compounds with benzene rings were used directly as raw materials in the semiconductor manufacturing process, 3 points (the highest score) were given. As benzene or benzene compounds were used as a raw material of an accessory used in a semiconductor manufacturing process (e.g., an insulation film), it was classified as indirect use and “2 points” were given. One point was given when benzene or benzene compounds were used regardless of the semiconductor manufacturing process. If use of benzene or benzene compounds did not seem probable, a 0 rating was provided. In terms of handling condition, when it was

**Table 1**

Scoring parameters, defined classification, and associated scores for evaluating the possibility of benzene exposure

Parameter	Classification	Score
Chemical type	Benzene	2
	Aromatic compounds containing benzene ring	1
	Uncertain or not found benzene compounds	0
Where used	Direct use in semiconductor manufacturing process	3
	Indirect use in semiconductor manufacturing process	2
	Unrelated to semiconductor manufacturing process	1
	Uncertain or not found benzene compounds	0
Handling condition	Used as a gas phase	3
	Used as a liquid phase	2
	Uncertain	1
	Not found benzene or benzene compounds	0
Probability to be used benzene	Most likely	2
	May or may not	1
	Unlikely	0
Total*		10

\* The maximum sum of scores evaluated by four parameters.

clearly confirmed that benzene or benzene compounds were used in the gaseous or liquid state, 3 and 2 points were given, respectively. However, when it is difficult to confirm, it is classified as “uncertain” and 1 point was given. With regard to the probability of benzene use, in consideration of the evaluation results of the three items described previously, 2 points were only given if benzene was clearly used. One point was assigned if benzene could be used as one of several alternatives and zero if benzene was not used.

## 3. Results

### 3.1. Basic characteristics of 75 patents reviewed

A total of 75 patent documents were reviewed and evaluated for the possibility of benzene exposure with several items as previously described in Table 1. The detailed evaluation results and reference information of the patent documents reviewed can be found in Supplementary Table S1, and the main review results are summarized in Table 2.

Of the 75 patents, US patents accounted for 89% (67) and 67% (50) were filed between 2006 and 2010. The patent contents were classified into nine invention fields: capacitor (4), chemical vapor deposition (CVD) (1), cleaning (2), etching (1), gas detecting sensor (1), insulator (15), organic semiconductor (28), patterning (18), and quantum dot (5). As a result of the review, we found that benzene and aromatic compounds were possibly used in 22 patents and 48 patents, respectively. As a result of the score evaluation, the total score of 22 patents for which the possibility of using benzene was confirmed was 6 points or more, and the highest score for 3 documents (P2, P3, and P46) was 9 points.

### 3.2. Benzene use characteristics of 22 patents

Table 3 shows the main characteristics of 22 patent documents in which the possibility of using benzene was found. Benzene use was divided into the following categories: raw material as a carbon source (P2, P3, P24, P27, P29, P40, P46, P64, and P75) and an invention-related solvent (P1, P5, P12, P31, P35, P41, P45, P51, P52, P55, P66, P67, and P73).

**Table 2**  
Summary of the main review results for 75 patent documents

Item	Relevant chemical type			Total
	Benzene	Aromatic compounds containing benzene ring	Uncertain or not found benzene	
Patent office	Europe	2	3	5
	United States	20	42	67
	WIPO*		3	3
Filing year	1994–1999	2	1	3
	2000–2005	7	15	22
	2006–2010	13	32	50
Fields of invention	Capacitor	2	1	4
	Chemical vapor deposition	1		1
	Cleaning		2	2
	Etching	1		1
	Gas detecting sensor	1		1
	Insulator	3	12	15
	Organic semiconductor	11	16	28
	Patterning	2	13	18
Probability to be used benzene	Quantum dot	1	4	5
	Most likely	3		3
	May or may not	19		19
Score†	Unlikely		48	53
	0			5
	4			14
	5			30
	6	1	4	5
	7	8		8
8	10		10	
9	3		3	
<b>Total</b>	<b>22</b>	<b>48</b>	<b>5</b>	<b>75</b>

\* World Intellectual Property Organization.

† The total sum of scores evaluated by the method described in Table 1.

### 3.2.1. Raw material as a carbon source

According to P2 and P3, benzene is used as one of the source gases for plasma CVD to form a silicon carbide layer, a constituent in a capacitor in a semiconductor memory device. In the P40 filed in 2006, benzene was used as a hydrocarbon-containing liquid monomer vaporized as a carbon source in the plasma CVD process. For graphene formation by CVD method (P64 and P75), benzene could also be injected into a chamber containing a graphitization catalyst film used as a carbon source.

In three patent documents related to thin film transistor (TFT), benzene could be used as a gas for the etching process (P46) or as an aromatic backbone of a crystalline organic binder (P27 and P29).

For solar cell manufacturing (P24), when the protective layer including diamond-like carbon (DLC) is formed by arc deposition, benzene can be used as a raw material.

### 3.2.2. Invention-related solvent

Among 13 patent documents, it was confirmed that benzene may have been used as a solvent in the manufacturing process of semiconductor-related products including surface acoustic wave (SAW) sensor (P1), dielectric film (P5 and P31), silicon oxide layer (P52), nanomaterials (P41, P45, P55, and P67), solar cell electrode (P12), photoresist (PR) copolymer (P51), rinse for immersion lithography (P66), electrophotographic photoreceptor (P73), and quantum dot ink (P35).

In P1 filed in 2003, benzene was used as a mixture with 25 weight % of ethanol to develop a sensitive film for SAW gas sensors with lower limit of detection (LOD) to detect airborne molecular contaminants (AMCs), including benzene in semiconductor fab processes.

In P5 and P31, which are related to dielectric films of semiconductor devices, benzene was used as a solvent in the preparation of different siloxane-based monomers to make insulating films with low dielectric constants.

In the case of P52, benzene can be used as one of the aromatic solvents used to manufacture spin-on glass, a precursor for forming a silicon oxide layer.

Benzene could also be used as a solvent in the manufacture of various nanomaterials used in the semiconductor field. Nanofibers can be formed by electrospinning of conductive organic material-based nanowires. Based on P41, benzene could be used as a solvent for dissolving conductive organic polymers in electrospinning process. Benzene could also be used as a solvent in the process of attaching the monomer for binding nanometal to the nanometal rod (P55), the synthesizing carbon nanotube (CNT) (P45), and removing the particulate materials for the transparent CNT electrode manufacturing (P67).

For solar cell electrode manufacturing, benzene was one of solvents used to disperse the organic material for forming bonding with metal oxide (P12). With regard to the photolithography process, benzene could be used as a solvent for the synthesis of copolymers in preparing the PR for ArF excimer laser lithography (P51) and rinsing immersion layer in immersion lithography (P66).

In the field of electrophotography technology, photoreceptor can be formed by laminating a charge generation layer and a charge transport layer on a conductive substrate. Benzene could be selected as a solvent for coating liquid of charge generation layer and charge transport layer (P73). In the case of inkjet printing (P35), benzene could also be used as a composition of quantum dot ink about 60% to 95% by weight.

## 4. Discussion

Since a young female worker who worked at a semiconductor manufacturing site in Samsung Electronics died of leukemia in 2007 [11], Korean researchers have been investigating the possibility of exposure to benzene, the causative agent of leukemia. Occupational Safety and Health Research Institute of the Korea

**Table 3**  
 Characteristics of 22 patent documents with contents relevant to benzene use

Patent document	Patent office	Filing date	Title	Field of invention	Usage for benzene	Score <sup>a</sup>	Major contents regarding benzene use
P2	United States	September 21, 1998	Semiconductor memory device having capacitive storage therefor	Capacitor in semiconductor device	Source gas for plasma chemical vapor deposition	9	<p><i>It is still further preferable that the silicon carbide (SiC) layer is formed by a plasma chemical vapor deposition (CVD) method where a mixed gas of silane (SiH<sub>4</sub>) and propane (C<sub>3</sub>H<sub>8</sub>) or of silane (SiH<sub>4</sub>) and <b>benzene</b> (C<sub>6</sub>H<sub>6</sub>) is used, and by adding phosphine (PH<sub>3</sub>) or arsenic hydride (AsH<sub>3</sub>) thereto, and that impurities therein are activated through heat treatment at 800 °C for 10–30 seconds under an argon (Ar) atmosphere or by depositing and then reflowing an insulating material on the entire substrate resulting from the second electrode formation step</i></p> <p><i>Method (a) phosphine (PH<sub>3</sub>) or arsenic hydride (AsH<sub>3</sub>) for lowering the intrinsic resistivity is injected into a plasma where silane (SiH<sub>4</sub>) and propane (C<sub>3</sub>H<sub>8</sub>), or silane (SiH<sub>4</sub>) and benzene (C<sub>6</sub>H<sub>6</sub>) are used as source gas, and then are deposited by a CVD method, to thereby form a first SiC layer of an amorphous state where impurities are doped.</i></p>
P3	United States	February 23, 1996	Method for manufacturing a semiconductor memory device having capacitive storage	Capacitor in semiconductor device	Source gas for plasma chemical vapor deposition	9	Same as above, P2

P46	United States	July 28, 2000	Etching gas mixture for transition metal thin film and method for etching transition metal thin film using the same	Etching	Etching gas for transition metal thin film	9	<i>What is claimed is: 1. A method for etching a transition metal thin film, comprising the steps of: (a) loading a semiconductor substrate having the transition metal thin film in a reaction chamber, wherein the transition metal thin film is a ferroelectric capacitor electrode film selected from the group consisting of Ru, Ir, Rh, Pt, and Ni; and (b) injecting into the reaction chamber an etching gas mixture comprising a first gas which is one selected from the group consisting of halogen gas, halide gas, halogen gas mixture, halide gas mixture and gas mixture of halogen and halide, and a second gas which is one selected from the group consisting of carbon oxide gas, hydrocarbon gas, and nitrogen-containing gas, to form a volatile metal halide through a reaction between the transition metal thin film and the etching gas mixture, thereby etching the transition metal thin film and converting the film into an organic metal halide, a metal amine halide, or a metal nitrosohalide, wherein the hydrocarbon gas comprises one selected from the group consisting of <b>benzene</b>, cyclopentadiene, toluene and butadiene.</i>
P5	United States	November 24, 2004	Method for forming interlayer dielectric film for semiconductor device using polyhedral molecular silsesquioxane	Insulator	Solvent usable in the invention	8	<i>Preparation of polyhedral molecular silsesquioxanes: 80 g of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and fuming H<sub>2</sub>SO<sub>4</sub> containing 15% SO<sub>3</sub> were mixed with 200 ml of <b>benzene</b> in a dry flask, and the resulting mixture was vigorously stirred.</i>
P24	United States	March 3, 2010	Solar cell and method for manufacturing the same	Organic semiconductor	Carbon source for arc deposition	8	<i>When the protective layer including diamond-like carbon is formed by arc deposition, the raw material may include a hydrocarbon such as methane (CH<sub>4</sub>), acetylene (C<sub>2</sub>H<sub>2</sub>), and <b>benzene</b> (C<sub>6</sub>H<sub>6</sub>), a solid-phase graphite or a combination thereof.</i>

(continued on next page)

Table 3 (continued)

Patent document	Patent office	Filing date	Title	Field of invention	Usage for benzene	Score <sup>a</sup>	Major contents regarding benzene use
P31	United States	January 5, 2009	Multifunctional cyclic silicate compound, siloxane-based polymer prepared from the compound and process of producing insulating film using the polymer	Insulator	Solvent usable in the invention	8	Synthesis of a multifunctional cyclic silicate compound: To a well-dried flask are introduced 31.5 mmol (25.0 g) of octaphenyl tetracyclosiloxane and 37.4 mmol (5.0 g) of aluminum chloride and dissolved in <b>benzene</b> . Then, bubbling with HCl gas is performed until solution is saturated, and the reaction is continued at room temperature for 12 h.
P40	United States	March 23, 2006	Method of forming carbon polymer film using plasma CVD	Chemical vapor deposition	Source gas for plasma chemical vapor deposition	8	The liquid monomer is cyclic hydrocarbon in an embodiment. The cyclic hydrocarbon may be substituted or non-substituted <b>benzene</b> . Further, the substituted or non-substituted benzene may be $C_6H_6-nRn$ (wherein n, 0, 1, 2, 3); R may be independently $-CH_3$ or $-C_2H_5$ .
P41	United States	January 30, 2010	Nanofiber composite, method of manufacturing the same, and field effect transistor including the same	Organic semiconductor	Solvent usable in the invention	8	The solvent dissolving the high molecular weight material may include chloroform, chlorobenzene, tetrahydrofuran, toluene, acetone, ethanol, methanol, dimethylformamide, dimethylsulfoxide, <b>benzene</b> , dioxane, cyclohexane, acetic acid, and water.
P45	United States	November 18, 2005	Method of synthesizing carbon nanotubes (CNT)	Organic semiconductor	Solvent usable in the invention	8	In an example embodiment, the organic compound is one of xylene, <b>benzene</b> , and ether, which acts as a solvent for the organometallic compound and a carbon supplying source.
P51	United States	March 25, 2002	Photosensitive polymers and resist compositions comprising the photosensitive polymers	Patterning semiconductor device	Solvent usable in the invention	8	Synthesis of copolymer example 1: 9.8 g maleic anhydride (0.1 mol) and 41.7 g 4-O-acetyl3,6-di-O-(t-butyl dimethylsilyl)-D-glucal (0.1 mol) are dissolved in tetrahydrofuran (THF), <b>benzene</b> , dioxane, or ethylacetate of 0.1–3 times on the basis of the weight of the whole monomers.

P52	United States	January 23, 2007	Method for forming a silicon oxide layer using spin-on glass (SOG)	Insulator	Solvent usable in the invention	8	Both inorganic and organic solvents may be used in preparing the spin-on glass (SOG) compositions, and aromatic, aliphatic or ether-type solvents, such as toluene, <b>benzene</b> , xylene, dibutylether, diethylether, THF (tetrahydrofuran), PGME (propylene glycol methoxy ether), PGMEA (propylene glycol monomethyl ether acetate) and hexane (and other cycloalky compounds) have been found useful.
P64	United States	October 8, 2009	Method for chemical modification of a graphene edge, graphene with a chemically modified edge and devices including the graphene	Organic semiconductor	Source gas for graphene formation	8	In an embodiment, the gaseous carbon source may consist essentially of carbon monoxide, ethane, ethylene, ethanol, acetylene, propane, butane, butadiene, pentane, pentene, cyclopentadiene, hexane, cyclohexane, <b>benzene</b> , toluene, or the like or a combination thereof. The carbon atoms of the carbon source may bond to each other to form a stable fused planar hexagonal shape with an extended pi-electron system, thus forming the graphene sheet.

(continued on next page)

Table 3 (continued)

Patent document	Patent office	Filing date	Title	Field of invention	Usage for benzene	Score*	Major contents regarding benzene use
P66	United States	March 11, 2003	Immersion lithography methods using carbon dioxide	Patterning semiconductor device	Solvent usable in the invention	8	<i>In some embodiments, the immersion rinse composition comprises liquid or supercritical carbon dioxide and a co-solvent. Exemplary co-solvents that could be used include, but are not limited to, alcohols (e.g., methanol, ethanol, and isopropanol); fluorinated and other halogenated solvents (e.g., chlorotrifluoromethane, trichlorofluoromethane, perfluoropropane, chlorodifluoromethane, and sulfur hexafluoride); amines (e.g., N-methyl pyrrolidone); amides (e.g., dimethyl acetamide); aromatic solvents (e.g., <b>benzene</b>, toluene, and xylenes); esters (e.g., ethyl acetate, dibasic esters, and lactate esters); ethers (e.g., diethyl ether, tetrahydrofuran, and glycol ethers); aliphatic hydrocarbons (e.g., methane, ethane, propane, ammonium butane, n-pentane, and hexanes); oxides (e.g., nitrous oxide); olefins (e.g., ethylene and propylene); natural hydrocarbons (e.g., isoprenes, terpenes, and d-limonene); ketones (e.g., acetone and methyl ethyl ketone); organosilicones; alkyl pyrrolidones (e.g., N-methylpyrrolidone); paraffins (e.g., isoparaffin); petroleum-based solvents and solvent mixtures; and any other compatible solvent or mixture that is available and suitable.</i>
P1	United States	December 3, 2003	Sensitive substance and surface acoustic wave gas sensor using the same	Gas detecting sensor	Experimental reagent for development of sensitive film	7	<i>A variety of monitoring systems have been proposed for monitoring airborne molecular contaminants (AMCs), such as acetone, ethanol, <b>benzene</b>, toluene or dichloroethane, in a semiconductor fabricating apparatus. The <b>benzene</b>-ethanol mixture stabilizes the viscosity and is preferably comprised of about 75 weight % of <b>benzene</b> and about 25 weight % of ethanol.</i>



P12	Europe	August 21, 2006	Semiconductor electrode, fabrication method thereof and solar cell comprising the same	Organic semiconductor	Solvent usable in the invention	7	Treatment using organic material having electron-donating group: examples of the solvent usable in the present invention include, but are not limited to, pentane, hexane, <b>benzene</b> , toluene, xylene, dichloromethane, or chloroform.
P27	United States	April 4, 2008	Organic thin film transistor and method of manufacturing the same	Organic semiconductor	Components of the crystalline organic binder	7	The organic thin film transistor as set forth in claim 2, wherein the aromatic backbone of the crystalline organic binder is selected from a group consisting of <b>benzene</b> , naphthalene, anthracene, tetracene, and n-phenylene (wherein n is about 2-about 6).
P29	Europe	June 13, 2008	Organic thin film transistor and method of manufacturing the same	Organic semiconductor	Components of the crystalline organic binder	7	Same as above, P27
P55	United States	November 21, 2008	Monomer for binding nano-metal, conductive polymer composite and method of preparing the conductive polymer composite	Organic semiconductor	Solvent usable in the invention	7	Examples of the solvent useful in the exemplary embodiments include dimethylformamide ("DMF"), isopropyl alcohol, tetrahydrofuran ("THF"), <b>benzene</b> , toluene, methanol, ethanol, and N-methylpyrrolidone ("NMP"), which may be used alone or in mixtures thereof.
P67	United States	June 22, 2007	Transparent CNT electrode with net-like CNT film and preparation method thereof	Organic semiconductor	Solvent usable in the invention	7	Removal of particulate materials from carbon nanotube (CNT) composition-injected thin film by treatment with the organic solvent can use one or more organic solvents selected from the group consisting of toluene, cyclohexane, <b>benzene</b> , chloroform, and a combination thereof.

(continued on next page)

Table 3 (continued)

Patent document	Patent office	Filing date	Title	Field of invention	Usage for benzene	Score*	Major contents regarding benzene use
P73	United States	December 25, 2000	Electrophotographic photoreceptors	Organic semiconductor	Solvent usable in the invention	7	<i>Solvents useful herein include benzoic hydrocarbons such as <b>benzene</b>, xylene, ligroin, monochlorobenzene, and dichlorobenzene; ketones such as acetone, methylethylketone, and cyclohexanone; alcohols such as methanol, ethanol, and isopropanol; esters such as ethyl acetate and methylcellosolve; aliphatic halogenized hydrocarbons such as carbon tetrachloride, chloroform, dichlormethane, dichlorethane and trichlorethylene; ethers such as tetrahydrofuran, dioxane, dioxolane and ethylene glycol monomethyl ether; amides such as N,N-dimethylformamide and N,N-dimethylacetamide; and sulfoxides such as dimethyl sulfoxide.</i>
P75	United States	November 12, 2010	Graphene laminate and method of preparing the same	Organic semiconductor	Source gas for graphene formation	7	<i>In the graphene sheet formation process disclosed above, the vapor-phase carbon source may be any of a variety of materials that supply carbon and are present in a vapor phase at a temperature of 300° C or higher. The vapor-phase carbon source may be any carbon-containing compound. For example, the vapor-phase carbon source may include at least one of carbon monoxide, ethane, ethylene, ethanol, acetylene, propane, propylene, butane, butadiene, pentane, pentene, cyclopentadiene, hexane, cyclohexane, <b>benzene</b>, or toluene.</i>
P35	United States	April 25, 2008	Quantum dot ink composition for inkjet printing and electronic device using the same	Quantum dot	Solvent usable as a constituent of the quantum dot ink	6	<i>The solvent as a constituent of the quantum dot ink composition may be selected from the group consisting of chloroform, chlorobenzene, cyclohexane, hexane, heptane, octane, hexadecane, undecane, decane, dodecane, xylene, toluene, <b>benzene</b>, octadecane, tetradecane, butyl ether, ethanol, and mixtures thereof, but is not necessarily limited thereto.</i>

\* The total sum of scores evaluated by the method described in Table 1.

Occupational Safety and Health Agency conducted a work environmental assessment of the semiconductor company in 2008 and reported that airborne benzene concentration was below 1 ppb of LOD [8,20]. In 2009, a research team led by Seoul National University reported that benzene contained 0.08 to 8.91 ppm by weight as a result of investigating six PRs used by Samsung Electronics [23]. However, Samsung Electronics claimed that PR does not contain benzene and that impurities in the solvent used in the analysis were detected. In 2009, Park et al. [21] reported that benzene was detected as a result of a pyrolysis experiment during the ascent from 150°C to 420°C for a PR containing cresol-formaldehyde resin. Jang et al. [22] also confirmed that benzene was detected in nine products as a result of the thermal decomposition experiments at 110°C, which is similar to the photolithography operating temperature conditions for 51 PRs. Although it has been reported that benzene can be generated by thermal decomposition of PRs, it has never been confirmed that benzene or benzene-containing products are used in the semiconductor manufacturing process.

It is very difficult to confirm that carcinogens such as benzene have been used in the past in semiconductor manufacturing operations. First, the semiconductor industry is a rapidly developing technology, and thus the process and materials used are rapidly changing. Second, it is extremely difficult to obtain a detailed information on the substance used by the company due to trade secret infringements. Traditional industrial hygiene research methods have had limitations in assessing the likelihood of past exposure to benzene by semiconductor manufacturing workers. In this study, we evaluated the exposure possibility of benzene by investigating the previous patents of semiconductor manufacturing company. To more objectively assess the possibility of benzene exposure, a scoring system using exposure-related parameters was used. The scoring technique is used to qualitatively or semi-quantitatively evaluate the hazard and exposure of chemicals [24–26]. All 22 patent documents that recorded the use of benzene were evaluated with more than 6 points (Table 2). The higher the score, the higher the likelihood of benzene exposure for workers in the semiconductor manufacturing process.

Of the 75 patents reviewed, benzene could be used as a carbon source in nine patents filed from 1996 to 2010. In particular, benzene can be used as a carbon source in the CVD process for the production of amorphous silicon carbide layers (P2 and P3), carbon polymer film (P40), and graphene (P64 and P75). The CVD process is widely used in the semiconductor industry as a deposition process for forming a thin film by injecting source gas into a substrate surface in a reaction chamber. Various source gases can be used in CVD. In the case of amorphous layer production (P2 and P3), a mixed gas of silane and propane or of silane and benzene can be used, and phosphine or arsenic hydride is injected to react at 800°C. P2 and P3 differ only in the patent filing date, and the contents of the invention are almost the same.

With regard to P40, when a hydrocarbon polymer that can be used as a hard mask is prepared by plasma CVD, benzene or benzene substituted by a methyl or ethyl group can be used as a liquid monomer. In particular, when a liquid monomer having a boiling point of 150°C or less and high vapor pressure, such as benzene and toluene, is used, steam injection is easy to perform because cracking through a polymerization reaction does not occur inside the tank used for storing the liquid.

Graphene, a two-dimensional monolayer of carbon atoms arranged in hexagonal lattices, has received much attention due to its excellent electronic, mechanical, and optical properties. P64 and P75 show that graphene can be produced by plasma CVD by injecting carbonization catalysts such as nickel, copper, and platinum and carbon source gases including benzene into the chamber.

The carbon sources that can be used in addition to benzene include carbon monoxide, ethane, ethylene, ethanol, acetylene, propane, butane, butadiene, pentane, pentene, cyclopentadiene, hexane, cyclohexane, or toluene. Benzene is one of the most popular and effective liquid precursors for graphene synthesis [27]. Using benzene as a liquid carbon precursor at about 300 °C can effectively grow the graphene [28–30]. Gadipelli et al. [31] reported that benzene and methanol were most suitable for graphene production, as a result of testing using liquid carbon sources such as methanol, ethanol, benzene, hexane, toluene, acetic acid, and acetone. Dai et al. [32] described that the synthesis of graphene using a liquid precursor is more advantageous than using a gas precursor because most of the organic compounds are easily found in a liquid phase at room temperatures and a liquid precursor is more flexible and is tailored to the electronic properties of graphene by doping nitrogen or boron.

P46 is an invention related to the application of dry etching to TFT. In the background of the invention, when patterning a transition metal thin film by low-pressure high-density plasma etching, an etching by-product having a low boiling point is generated and redeposition on the pattern wall may occur. To solve this problem, the inventors proposed a method of forming a metal halide by injecting halogen gas and forming a volatile metal halide by injecting secondary gas, which is one of the gases selected from the group consisting of carbon oxide gas, hydrocarbon gas including benzene, and nitrogen gas. In addition to benzene, cyclopentadiene, toluene, and butadiene may be used as a hydrocarbon gas. However, the experiment conducted for the invention in P46 used a mixture of carbon oxide gas and chlorine gas, and no benzene. In another study related to ruthenium (Ru) thin film [33], a plasma etching method using methanol has been proposed because an etch damage occurs when a corrosive gas such as chlorine is used, but no research data using benzene has been published. P27 and P29 regarded as organic TFT had different application dates and patent offices, but the invention was almost the same. According to the two patent documents, benzene, naphthalene, anthracene, and tetracene can be used as an aromatic backbone to form a crystalline organic binder layer that is a component of organic TFT.

DLC film is amorphous materials applicable to protective coating of solar cells due to its high hardness and excellent chemical stability and optical properties [34]. DLC films can be deposited with a variety of hydrocarbon gases or vapors. It was indicated in the P24 patent that methane, acetylene, or benzene can be used. In the studies comparing the properties of DLC films deposited using methane and benzene, the possibility of using benzene was confirmed [35,36].

In 13 patent documents, benzene can also be used as a solvent in a semiconductor-related manufacturing process or an invention experiment. Benzene was definitely used in the invention experiments of three patents (P1, P5, and P31), and the remaining 10 patents indicated that benzene among various chemicals could be selected as a solvent. Frequently mentioned major solvents more usable than benzene are acetone, chloroform, ethanol, isopropyl alcohol, hexane, methanol, DMF, PGME, PGMEA, THF, toluene, and xylene. In 2014, the most frequently found chemicals were PGMEA, cyclohexanone, and PGME, as a result of material safety data sheet investigations of chemicals handled by two semiconductor manufacturing companies in Korea [18]. Substances detected at low concentrations in the air of semiconductor manufacturing processes in Korea were isopropyl alcohol, butyl acetate, PGMEA, PGME, and xylene [20,21]. As mentioned earlier, detection of benzene was confirmed only in the study of PR pyrolysis experiments [21,22].

Several limitations should be considered when interpreting the results of this study.

First, the use of benzene in the patent content does not directly imply that workers are handling and exposed to benzene in actual product production. However, unlike the general research report, the patent has intellectual technology protection, which has strong practical aspects; thus, it will provide a basis for providing a reasonable estimate of the probability of benzene use in actual production.

Second, the use of benzene does not necessarily mean that handling workers have been exposed. In particular, the degree of automation of the process may be a very important variable in determining the possibility of chemical exposure of semiconductor process workers. Based on the statement of COMWEL regarding registered workers and the report of the Samsung Electronic Research Institute, Park et al. [14] reported that 4 inches of wafers were used until the end of 2004 in the oldest production line; thus, it can be assumed that most of the processes were manually handled by fabrication workers who were employed before 2005. The use of benzene in the invention of P1's SAW gas sensor is not directly related to the semiconductor manufacturing process but provides very interesting information regarding the possibility of benzene exposure in workers in the semiconductor fabrication process. It was described in the background of the P1 invention that a monitoring system capable of detecting low concentration of AMCs in a short time is required to maintain a high level of cleanliness in a semiconductor clean room. Acetone, ethanol, benzene, toluene, and dichloroethane were selected as AMCs targeted for the development of SAW sensors with lower LOD than the existing monitoring systems. In Fig. 3 of P1, the experimental results showed that the LOD of benzene was  $3.6 \text{ mg/m}^3$  ( $=1.1 \text{ ppm}$  @  $25^\circ\text{C}$ ,  $1 \text{ atm}$ ) and suggested  $1/25$  lower sensitivity than the best LOD ( $92 \text{ mg/m}^3$ ) of the previous study [37]. The Korean occupational exposure limit value of benzene was revised from  $10 \text{ ppm}$  to  $1 \text{ ppm}$  in 2002 [38]. Since 2003, the number of workplaces with an airborne concentration of benzene exceeding  $1 \text{ ppm}$  has dramatically decreased in Korea [39]. Considering the time when the patent P1 was filed in 2003 and the fact that patents filed until 2003 describe the possibility of benzene use (P2, P3, P46, P51, P66, and P73), workers in semiconductor fab process could be exposed to benzene at a concentration of  $1 \text{ ppm}$  or more until 2003.

## 5. Conclusions

As a result of reviewing 75 patents filed from 1994 to 2010, we found that benzene could have been used as one of the carbon sources in CVD for capacitor, DLC for solar cell, graphene formation, or etching for transition metal thin film from 9 patents. Moreover, benzene could be used as a solvent for dielectric film, silicon oxide layer, nanomaterials, PR, rinse for immersion lithography, electro-photography, and quantum dot ink in 13 patents. Considering the date of filing patent, it is possible that workers in the CVD, immersion lithography, and graphene formation processes could be exposed to benzene from 1996 to 2010.

## Conflicts of interest

All authors have no conflicts of interest to declare.

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## Appendix A. Supplementary data

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