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(54) Title: RESIN COMPOSITION FOR FORMING FINE PATTERNS, METHOD FOR FABRICATING SEMICONDUCTOR DEVICE USING THE COMPOSITION AND SEMICONDUCTOR DEVICE FABRICATED BY THE METHOD

(57) Abstract: Disclosed herein is a resin composition for forming fine patterns that enables reduction in width of an engraved portion in a photoresist pattern during lithography in semiconductor device fabrication. Further, disclosed herein is a method for fabricating a semiconductor device by using the composition. The resin composition comprises a) a polymer having aromatic hydroxyl groups in which all or a part of the hydroxyl groups are substituted with a water-soluble group; and b) water or an aqueous mixture of water-miscible solvent wherein the composition is applied to a photoresist pattern to form a coating film and the water-soluble group is removed by an acid catalyst supplied from the photoresist pattern, to selectively leave insoluble regions in the coating film.

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Description

RESIN COMPOSITION FOR FORMING FINE PATTERNS, METHOD FOR FABRICATING SEMICONDUCTOR DEVICE USING THE COMPOSITION AND SEMICONDUCTOR DEVICE FABRICATED BY THE METHOD

Technical Field

- [1] The present invention relates to a resin composition for forming fine patterns that enables reduction in width of an engraved portion in a photoresist pattern during lithography in semiconductor device fabrication and a method for fabricating a semiconductor device by using the composition.

[2]

Background Art

- [3] In the microelectronics industry as well as in other industries associated with microscopic structures (*e.g.*, micromachines, magnetoresistive heads, etc.), there has been continuous demand for reduction in size of structures. In particular, in the microelectronics industry, there has been demand to provide greater amount of circuitry in a chip having a predetermined size based on the reduction in feature size of micro-electronic devices.
- [4] Lithographic techniques are essential for obtaining reduction in sizes of patterns. The manufacture of microscopic structures in lithography must be made in view of not only directly imaging patterns on a substrate, but also producing masks used in such imaging.
- [5] Typical lithographic processes involve formation of a patterned resist layer by patternwise exposing a radiation-sensitive resist to an imaging radiation. The image is subsequently developed by contacting the exposed resist layer with a material (typically an aqueous alkaline developer) to selectively remove portions of the resist layer to reveal the desired pattern. The pattern is subsequently transferred to an underlying material by etching the material in openings of the patterned resist layer. After the transfer is complete, the remaining resist layer is removed.
- [6] Lithographic techniques require irradiation with light of shorter wavelength and development of high-resolution resist materials depending on the characteristics of the light. However, improvements of exposure systems are needed to shorten the wavelength of light, thus incurring considerable costs. In addition, it is not easy to develop resist materials in response to short-wavelength light for exposure.
- [7] In particular, conventional lithographic techniques have limitations in improving the

degree of integration through micropatterning due to limited wavelength of light for exposure. Some attempts to overcome these limitations have been proposed. For example, Japanese Patent No. 3,071,401 suggests a micropattern-forming material which uses a water-soluble resin causing a crosslinking reaction with a resist in the presence of an acid to form a crosslinked film at the interface between a resist pattern and the micropattern-forming material by the acid supplied from the resist pattern and to strip the uncrosslinked portions.

- [8] However, when the material is used to form a pattern, the resist pattern may be deformed by the action of an internal stress resulting from volume shrinkage of the resin during the crosslinking reaction. There is thus a demand for a micropattern-forming material with a new type of mechanism that is capable of overcoming the limitations of conventional materials utilizing crosslinking mechanisms.

[9]

Disclosure of Invention

Technical Problem

- [10] In an attempt to solve the problems of prior arts, it is one object of the present invention to provide a resin composition for forming fine patterns with a new type of mechanism that enables formation of fine patterns without limitation in wavelength of exposure light sources.

- [11] It is another object of the present invention to provide a method for fabricating a semiconductor device using the resin composition.

- [12] It is yet another object of the present invention to provide a semiconductor device fabricated by the method.

[13]

Technical Solution

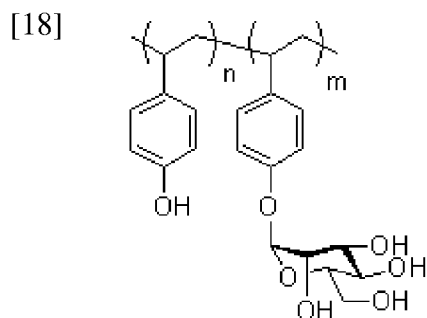
- [14] In accordance with one aspect of the present invention, there is provided a resin composition for forming fine patterns, the resin composition comprising: a) a polymer having aromatic hydroxyl groups in which all or a part of the hydroxyl groups are substituted with a water-soluble group; and b) water or an aqueous mixture of water-miscible solvent whereby the composition is applied to a photoresist pattern to form a coating film and the water-soluble group is removed by an acid catalyst supplied from the photoresist pattern, to selectively make insoluble regions in the coating film.

- [15] The polymer may be a novolac-type polymer, hydroxystyrene-type polymer or naphthol-type polymer, or a mixture thereof in which all or a part of the hydroxyl groups of the aromatic rings are substituted with a water-soluble group.

- [16] The water-soluble group may be at least one selected from the group consisting of carbohydrates, nucleic acids, proteins, amino acids, ketones having an amine or

hydroxyl group, aldehydes having an amine or hydroxyl group, and derivatives thereof.

[17] The polymer may be represented by Formula 1 below:



(1)

[19] wherein the ratio n/m is 0 to 999 and the sum $n+m$ is 2 to 30,000.

[20] The composition may comprise 1 to 50 parts by weight of the polymer and 50 to 99 parts by weight of the solvent.

[21] The composition may further comprise at least one additive selected from acid diffusers, acid generators, acid quenchers and surfactants.

[22] In accordance with another aspect of the present invention, there is provided a method for fabricating a semiconductor device, the method comprising the steps of: forming a first photoresist pattern containing an acid catalyst on a semiconductor substrate; coating the first photoresist pattern with the resin composition to form a coating film; allowing the acid catalyst contained in the first photoresist to be supplied to the coating film to make insoluble regions in the coating film; developing and stripping the coating film with a developing solvent to form a second photoresist pattern; and etching the semiconductor substrate using the second photoresist pattern as a mask.

[23] The supply of acid catalyst from the first photoresist pattern may be promoted by heating the first photoresist pattern.

[24] The developing solvent may be water or an aqueous mixture of water-miscible solvent.

[25] In accordance with yet another aspect of the present invention, there is provided a semiconductor device fabricated by the method.

[26]

Advantageous Effects

[27] According to the present invention, patterns can be formed without limitation of exposure light wavelength by using fine photoresist patterns.

[28] It is possible to reduce the size of an L/S or hole pattern. In addition, when a semiconductor device is fabricated using the fine patterns as a mask, finer patterns can be achieved, as compared to patterns obtained from conventional exposure light sources.

[29] Accordingly, the use of the present invention enables formation of semiconductor devices including finer L/S and hole patterns.

[30]

Brief Description of the Drawings

[31] The above and other objects, features and other advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

[32] FIG. 1 is a diagram schematically showing a lithographic process using a resin composition for forming fine patterns according to the present invention; and

[33] FIG. 2 is a cross-sectional view illustrating a state in which a predetermined region insoluble in a developing solution is selectively formed in a coating film by a chemical reaction of a fine pattern forming resin composition contained in the coating film according to the present invention.

[34]

Best Mode for Carrying Out the Invention

[35] Detailed description will be made of preferred embodiments of the present invention with reference to the accompanying drawings. However, various changes and modifications may be made to the preferred embodiments of the invention and the invention is not to be construed as being limited to the embodiments.

[36] The resin composition of the present invention comprises a) a polymer having aromatic hydroxyl groups in which all or a part of the hydroxyl groups are substituted with a water-soluble group; and b) water or an aqueous mixture of water-miscible solvent.

[37] The polymer is preferably a novolac-type polymer, hydroxystyrene-type polymer or naphthol-type polymer, or a mixture thereof in which all or a part of the hydroxyl groups of the aromatic rings are substituted with a water-soluble group.

[38] The solvent contained in the resin composition must be capable of dissolving the polymer, but be incapable of dissolving a photoresist layer. Taking into consideration this fact, preferred is water or an aqueous mixture of water-miscible solvent.

[39] The examples of the water-soluble solvent include isopropyl alcohol, 1-butanol, ethanol and methanol. The ratio of water to the water-soluble solvent may be in the range of 1 : 99 to 99 : 1 (w/w).

[40] The water-soluble group is at least one selected from the group consisting of carbohydrates, nucleic acids, proteins, amino acids, ketones containing an amine or hydroxyl group, aldehydes containing an amine or hydroxyl group, and derivatives thereof.

[41] The resin composition may consist of 1 to 50 parts by weight of the polymer and 50

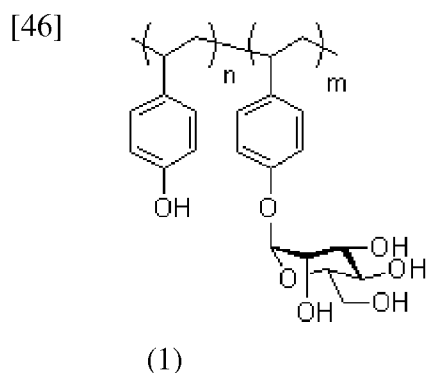
to 99 parts by weight of the solvent. The contents out of the range defined above disadvantageously cause an excessively high or low viscosity upon spin coating, thus making it difficult to control a film thickness.

[42] After the resin composition is applied to on a photoresist pattern to form a coating film, when an acid catalyst present within the photoresist pattern is supplied into the coating film, water-soluble groups within the coating film are removed by the acid catalyst. As a result, predetermined regions insoluble in a developing solvent such as water or an aqueous mixture of water-miscible solvent are selectively produced in the coating film.

[43] In this case, the acid catalyst diffused from the photoresist pattern is supplied into the coating film. Thus, removal reactions of water-soluble groups selectively occur in predetermined regions being in contact with the photoresist pattern and in regions to which the diffusing acid catalyst can reach. The moieties, where the water-soluble groups are removed, become insoluble in the solvent. The coating film includes both soluble and insoluble regions in developing solvents, thus achieving a selective solubility to the developing solvents.

[44] Accordingly, when the resin composition is used during a lithographic process in semiconductor device fabrication, the unreacted portions of the coating film are dissolved in and stripped by the developing solvent having a selective solubility dependent upon chemical reaction of the resin composition of coating film, thereby enabling reduction in width of an engraved portion of photoresist pattern.

[45] As the polymer contained in the resin composition, there may be used a polymer represented by Formula 1 below:



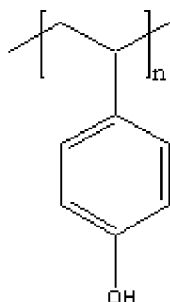
[47] wherein the ratio n/m is 0 to 999 and the sum $n+m$ is 2 to 30,000.

[48] The n/m value of zero indicates that hydroxyl groups of side chain aromatic groups in polyhydroxystyrene are completely substituted with glucose groups. Meanwhile, the n/m value exceeding 999 disadvantageously involves considerable reduction in solubility to the solvent of the present invention.

[49] The glucose group of the polymer represented by Formula 1 is removed in the presence of an acid catalyst to generate polyhydroxystyrene represented by Formula 2

below:

[50]



(2)

[51] wherein n is 2 to 30,000

[52] The polyhydroxystyrene is insoluble in the developing solvent used to develop the coating film which is formed by coating a photoresist pattern with the resin composition of the present invention. Accordingly, after the removal of glucose groups in the presence of an acid catalyst, predetermined regions insoluble in the developing solution are made in the coating film. At this time, the acid catalyst from the photoresist pattern is diffused into the coating film. Thus, the removal reaction of water-soluble groups selectively occurs in predetermined regions of the coating film being in contact with the photoresist pattern and in regions to which the diffusing acid catalyst can reach. The moieties, in which the water-soluble groups are removed, become insoluble in the solvent. The coating film includes both soluble regions and insoluble regions, thus achieving a selective solubility.

[53] The resin composition may further comprise at least one selected from acid diffusers, acid generators, acid quenchers and surfactants.

[54] The acid diffuser elevates a diffusion ratio of acid which is supplied from a photoresist pattern to the coating film including the resin composition and enables the chemical reaction of polymer to occur from the surface of the coating to a larger depth thereof. As a result, the width of the engraved portion of photoresist pattern is reduced, thus achieving fine patterns.

[55] The acid generator generates an acid upon heating or exposing to light. The acid generator contained in the composition enables occurrence of an acid within the composition upon heating, regardless of the acid catalyst diffused from the photoresist pattern.

[56] The acid quencher eliminates the acid catalyst diffused from the photoresist pattern, thus controlling the rate of chemical reaction with the polymer in the coating film.

[57] The content of the acid diffuser, acid generator and acid quencher may be 0.1 to 100 parts by weight, based on the total weight of the polymer.

[58] The surfactant controls coatability and gap-filling property of the resin composition.

[59] The content of the surfactant may be 0.01 to 0.5 parts by weight, based on the total

weight of the resin composition.

- [60] A method for fabricating a semiconductor device by using the resin composition according to the present invention comprises the steps of: forming a first photoresist pattern containing an acid catalyst on a semiconductor substrate; coating the first photoresist pattern with the resin composition of the present invention to form a coating film; allowing the acid catalyst contained in the first photoresist pattern to be supplied to the coating film to make insoluble regions in the coating film; developing and stripping the coating film with a developing solvent to form a second photoresist pattern; and etching the semiconductor substrate using the second photoresist pattern as a mask.
- [61] The photoresist that may be used in semiconductor device fabrication according to the present invention may be a KrF or ArF photoresist.
- [62] The supply of acid catalyst from the first photoresist pattern may be promoted by heating the first photoresist pattern.
- [63] The developing solvent may be water or an aqueous mixture of water-miscible solvent.
- [64] A lithographic process to form fine patterns by using the resin composition according to the present invention will be described in detail as follows.
- [65] An organic anti-reflective coating is coated on a silicon wafer. A photoresist is then coated thereon. The photoresist is exposed to light using exposure equipment, followed by developing, to form a line and space (L/S) pattern or a hole pattern. The resin composition is coated on the pattern to form a coating film. The coating film is heated to facilitate diffusion of an acid catalyst in the photoresist pattern. At this time, there arise removal reactions of water-soluble groups within the polymer contained in the coating film being in contact with the photoresist pattern. This mechanism is schematically shown FIG. 2.
- [66] That is, when the resin composition is coated on the photoresist pattern formed on the semiconductor substrate, followed by heating, the acid catalyst within the photoresist pattern diffuses into the coating film. The acid catalyst induces a chemical reaction of the polymer in the coating film. As a result, insoluble regions exhibiting insolubility to a developing solvent are selectively left in the coating film. At this time, the heating temperature and time are determined by varying the kind of photoresist used and desired thickness of the insoluble regions in the coating film.
- [67] The unreacted portions of coating film are dissolved in the developing solvent, followed by stripping, to form a second photoresist pattern having a reduced width of engraved portion.
- [68]

Mode for the Invention

[69] The present invention will be better understood from the following examples. These examples are not to be construed as limiting the scope of the invention.

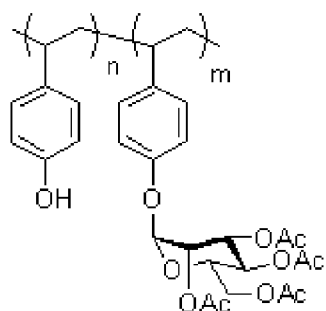
[70]

[71] EXAMPLES

[72] Synthesis Example

[73] 10 g of polyhydroxystyrene (available from Dupont), 45 g of 2,3,4,6-tetra-O-acetyl-mannopyranosyl-trichloroacetimidate, 2 g of trimethylsilyltriflate, 5 g of 0.4 nm molecular sieve and 300 mL of acetonitrile were put in a flask of 500 mL. Then, the mixture was stirred at 0°C for 2 hours. Triethylamine was added thereto, thereby neutralizing the solution. After the temperature was allowed to warm to room temperature, the solvent was evaporated, and was distilled using a vacuum distiller. The residues was purified by chromatography (methylenechloride and methanol (2 : 1)). The solvents were distilled off under reduced pressure, and dried under vacuum to yield a polymer (n/m = 1.1, weight average molecular weight: 18,000, 35.5 g) represent by Formula 3 below:

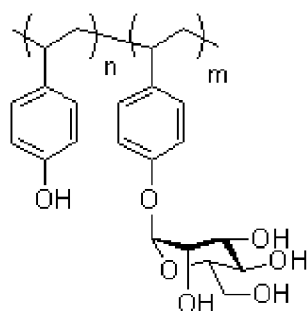
[74]



(3)

[75] Next, 20 g of the polymer of Formula 3 was put in a flask of 500 mL, and was dissolved in 300 mL of tetrahydrofuran (THF). A 25% solution of sodium methanolate (NaOMe) in methanol (MeOH) was added thereto. After stirring at 0°C for 2 hours, the reaction mixture was filtered under reduced pressure. The obtained solid was washed twice with THF and was dried under vacuum to yield a polymer (n/m = 1.1, 12.0 g) represent by Formula 1 below:

[76]



(1)

[77]

[78] Example 1

[79] An organic anti-reflective coating was coated on a silicon wafer, and a KrF photoresist was coated thereon. The resulting structure was subjected to exposure to light using exposure equipment (ASML, XT: 1,400, NA 0.93), followed by developing. A substrate bearing an L/S pattern with 200 nm of an initial critical dimension (CD_0) was obtained.

[80] Next, a resin composition comprising 10 g of the polymer prepared in Synthesis Example and 90 g of water was coated on the pattern, followed by heating at 110°C for 1 min.

[81] The photoresist was developed by dipping in water for 1 min. The critical dimension (CD_1) of the substrate was measured using a field emission scanning electron microscope (FE-SEM). The result is shown in Table 1.

[82]

[83] Example 2

[84] A substrate was produced in the same manner as in Example 1, except that the heating was conducted at 130°C. The critical dimension (CD_1) of the produced substrate was measured. The result is shown in Table 1.

[85]

[86] Example 3

[87] A substrate was produced in the same manner as in Example 1, except that the heating was conducted at 150°C. The critical dimension (CD_1) of the produced substrate was measured. The result is shown in Table 1.

[88] Table 1

[Table 1]

[Table]

Example No.	Heating temperature (°C)	CD_0 (nm)	CD_1 (nm)
1	110	200	189
2	130	200	178
3	150	200	169

[89]

[90] From Table 1, it could be confirmed that the resin composition of the present invention enables considerable reduction in width of the ungraved portion in photoresist pattern.

[91] In Examples of the present invention, a KrF photoresist was used as a photoresist material. However, the present invention is not limited to the photoresist material.

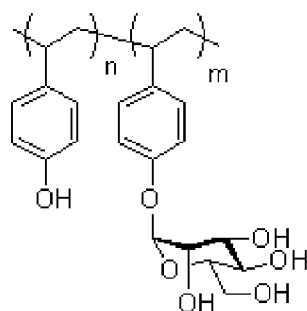
Meanwhile, an L/S pattern was used as a photoresist pattern. However, the present invention is not limited to the pattern and is applicable to various patterns including a hole pattern.

[92] Although the present invention has been described herein in detail with reference to its preferred embodiments, those skilled in the art will appreciate that these embodiments do not serve to limit the invention and that various changes and modifications may be made thereto without departing from the spirit and scope of the invention as defined in the appended claims.

[93]

Claims

- [1] A resin composition for forming fine patterns, the resin composition comprising:
 a) a polymer having aromatic hydroxyl groups in which all or a part of the hydroxyl groups are substituted with a water-soluble group; and
 b) water or an aqueous mixture of water-miscible solvent
 whereby the composition is applied to a photoresist pattern to form a coating film and the water-soluble group is removed by an acid catalyst supplied from the photoresist pattern, to selectively make insoluble regions in the coating film.
- [2] The composition according to claim 1, wherein the polymer is a novolac-type polymer, hydroxystyrene-type polymer or naphthol-type polymer, or a mixture thereof in which all or a part of the hydroxyl groups of the aromatic rings are substituted with a water-soluble group.
- [3] The composition according to claim 1, wherein the water-soluble group is at least one selected from the group consisting of carbohydrates, nucleic acids, proteins, amino acids, ketones having an amine or hydroxyl group, aldehydes having an amine or hydroxyl group, and derivatives thereof.
- [4] The composition according to claim 1, wherein the polymer is represented by Formula 1 below:



(1)

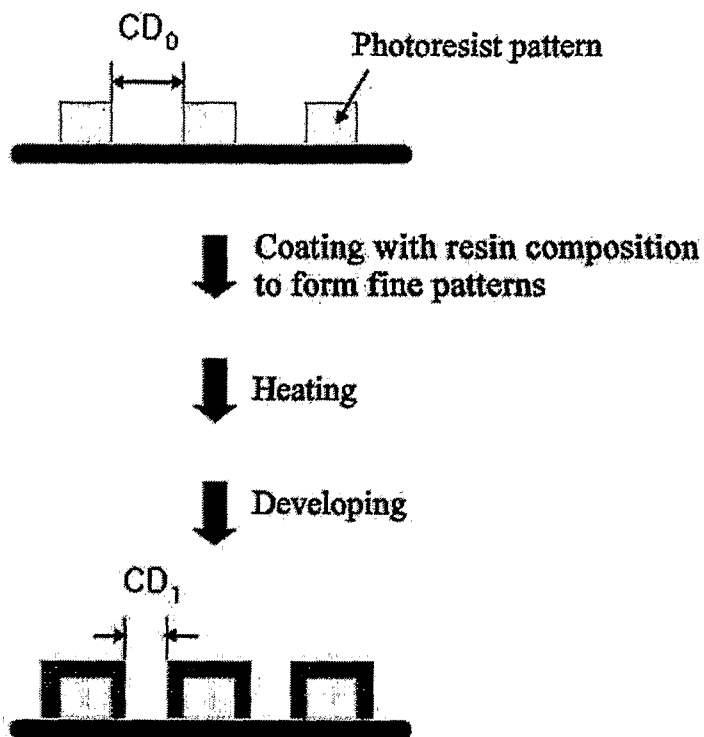
wherein the ratio n/m is 0 to 999 and the sum $n+m$ is 2 to 30,000.

- [5] The composition according to claim 1, wherein the composition comprises 1 to 50 parts by weight of the polymer and 50 to 99 parts by weight of the solvent.
- [6] The composition according to claim 1, further comprising at least one additive selected from acid diffusers, acid generators, acid quenchers and surfactants.
- [7] A method for fabricating a semiconductor device, the method comprising the steps of:
 forming a first photoresist pattern containing an acid catalyst on a semiconductor substrate;
 coating the first photoresist pattern with the resin composition according to any one of claims 1 to 6 to form a coating film;

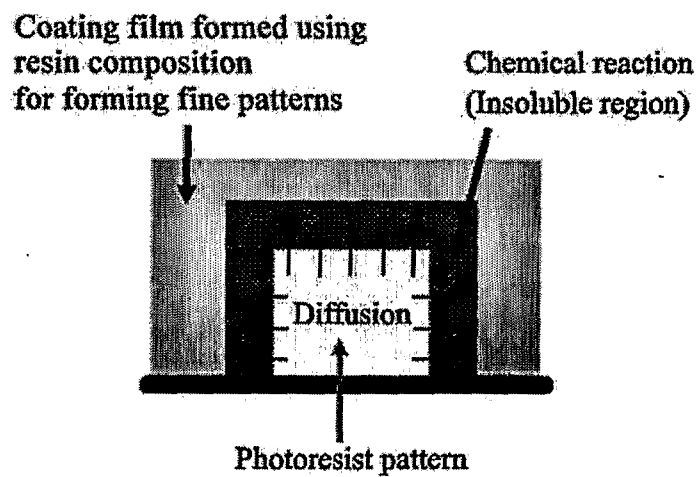
allowing the acid catalyst contained in the first photoresist to be supplied to the coating film to make insoluble regions in the coating film;
developing and stripping the coating film with a developing solvent to form a second photoresist pattern; and
etching the semiconductor substrate using the second photoresist pattern as a mask.

- [8] The method according to claim 7, wherein the supply of the acid catalyst from the first photoresist pattern is promoted by heating the first photoresist pattern.
- [9] The method according to claim 7, wherein the developing solvent is water or an aqueous mixture of water-miscible solvent.
- [10] A semiconductor device fabricated by the method according to claim 7.

[Fig. 1]



[Fig. 2]



INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2007/003809**A. CLASSIFICATION OF SUBJECT MATTER****G03F 7/004(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 8 : G03F 7/004

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean Utility models and Applications for Utility models since 1975

Japanese Utility models and Applications for Utility models since 1975

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKIPASS(KIPO internal only)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2004072098 A1 (FUJITSU LIMITED) 15 April 2004 See the whole document, especially abstract; [0038]-[0052]; Figures 1, 2.	1-10
X	US 20040121259 A1 (FUJITSU LIMITED) 24 June 2004 See the whole document, especially abstract; [0030]-[0047], [0063]-[0088].	1-10
A	US 2004029047 A1 (RENESAS TECH CORP.) 12 February 2004 See the whole document, especially abstract; [0054]-[0058].	1-10
A	US 2003175624 A1 (FUJITSU LIMITED) 18 September 2003 See abstract.	1-10

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Date of the actual completion of the international search

01 NOVEMBER 2007 (01.11.2007)

Date of mailing of the international search report

01 NOVEMBER 2007 (01.11.2007)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2007/003809

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