

PATENT SPECIFICATION

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(54) METHODS FOR PHOTORESIST DEVELOPMENT

(71) We, ALLIED CHEMICAL CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of Columbia Road & Park Avenue, Morris Township, Morris County, New Jersey 07960, United States of America, do hereby declare the invention for which we pray that a patent may be granted, to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to methods for differentially removing uncross-linked photoresist portions from a photoresist layer on a substrate, especially a semiconductor or metal substrate.

A photolithography process is presently being employed in semiconductor fabrication to remove selected portions of a photoresist layer on a semiconductor wafer. For example, selected portions of a silicon wafer are stripped of a silicon dioxide protective layer by the photolithography process.

In this photolithography process, a photoresist, a polymer whose structure changes upon exposure to light, and especially ultra violet light, is coated on the wafer. Light, passing through a mask of the desired pattern place on the wafer, exposes selected portions of the photoresist to crosslink the polymer in those portions. With certain photoresists, the exposed portions are less crosslinked, but, the present invention is directed toward developing photoresists in which the exposed portions are more cross-linked.

A solvent, generally xylene, and sometimes toluene, is used to remove the photoresist. The xylene removes the unexposed portions of polymer. To avoid substantial dissolving of the cross-linked exposed portions of polymer, a rinse or "stop" is used to halt the action of the xylene, typically n-butyl acetate. Heating then further sets the cross-linked polymer and dries off remaining solvents. Thus, a "window" is created in the unexposed portions of photoresist to uncover portions of substrate. In subsequent treatment, the uncovered portions of substrate through which a "window" now appears are etched to remove the protective silicon dioxide coating and uncover the underlying silicon. The exposed portions of photoresist are then stripped from the substrate with a second solvent and the wafer is prepared for further processing making use of the pattern of etched surface portions at which the silicon is uncovered.

In general, xylene has been a satisfactory developing solution for photoresist. However, on occasions, xylene produces an uneven or ragged edge between the exposed and unexposed areas either because of inadequate dissolving of the uncross-linked photoresist or because the xylene has begun to dissolve cross-linked areas of photoresist. Since, if left long enough on the wafer, xylene will dissolve cross-linked areas, the rapid application of a stop is required. Xylene also leaves a film on both the developed photoresist and on the bare wafer. Xylene does not always evaporate quickly and completely from the wafer after the desired developing is completed.

In some developing processes, the wafers are spun on a chuck at speeds from about 1500 to about 15,000 rpm, such that most of the xylene is spun off with dissolved photoresist.

However, many operations still dip the wafers in the xylene, causing a potential large concentration of xylene after the uncross-linked photoresist is removed, which must evaporate off. If the wafer is then quickly dipped in the stop, most of the xylene is removed before it can attack the cross-linked areas of photoresist. However, the necessity of two steps in rapid succession permits at least the possibility of certain wafers being ruined from too long a time in the stop solution. Many preferred fluorocarbon developing solutions also include organic materials with higher boiling points. Fluorocarbon 113 trichlorofluoromethane is also a preferred fluorocarbon. Either the

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because of delay in applying the stop.

Xylene also poses potential disposal problems in that xylene is photosensitive and quite flammable. Thus, other photoresist developing solutions have been sought which provide differential dissolving of uncross-linked photoresist at as good or better level than xylene, but without the necessity of a rapid stop treatment or the potential problems of flammability or photosensitivity posed by xylene.

The present invention provides a method of developing a photoresist layer on a surface of an article exposed portions of the photoresist layer being more cross-linked than the remaining, unexposed, portions, comprising contacting the photoresist layer with a liquid developer solution comprising 50 to 100 weight % of at least one aliphatic halogenated hydrocarbon solvent selected from methylene chloride, trichloromonofluoromethane (fluorocarbon 11), tetrachlorodifluoroethanes (fluorocarbon 112), trichlorotrifluoroethanes (fluorocarbon 113), dichlorotetrafluoroethanes (fluorocarbon 114) and mixtures of two or more thereof, and from 0 to 50 weight % of a normally liquid, unhalogenated organic material miscible with or capable of dissolving said halogenated hydrocarbon solvent, at a temperature and for a period of time sufficient to remove the remaining unexposed portions of photoresist without removing the selected, more highly cross-linked, exposed, portions of photoresist.

The handling properties of certain of the halocarbons are improved by the addition of up to 50% by weight and preferably up to 25% by weight of a normally liquid unhalogenated organic material. Exemplary unhalogenated organic materials include cyclohexanol, cyclohexanone, ethylene glycol monobutyl ether, Stoddard solvent, xylene, cyclic and acyclic hydrocarbons with 5 to 10 carbon atoms and isopropyl alcohol and mixtures of two or more thereof. These and other unhalogenated organic materials can be selected for desired evaporation rates, boiling points and/or miscibility with particular halocarbon solvents. As shown in the Examples hereinafter, many of these unhalogenated organic materials in critical amounts also speed up development.

The method may include contacting the surface with the solvent and unhalogenated organic materials for a time sufficient to dissolve areas of uncross-linked photoresist. This may be done, for example, by pouring, dripping or spraying solvent onto the photoresist-covered surface while the surface is being spun on a chuck, or, also for example, by dipping a semiconductor wafer coated with photoresist in the solvent. The method also includes stopping development either by total evaporation or spinning off of the solvent and organic material, if any, or by dilution of the remaining solvent and organic material by a "stop" such as n-butyl acetate which is either applied with the solvent and unhalogenated organic material or is added after the desired period of development.

Developing solutions are applied to photoresist-coated silicon or other semiconductor wafers by conventional techniques. For example, the wafers are spun at about 3,000 rpm, although speeds as low as about 1500 rpm or as high as about 10,000 or even about 15,000 rpm are suitable. The developing solutions are poured, sprayed or dropped onto the wafers, such that developing solution with dissolved photoresist is spun off of the wafer. Spinning devices for such applications are well known in the art.

Alternatively, the developing solutions are made up into baths, into which the photoresist-coated wafers are dipped. As is conventional, a second dip of "stop" such as n-butyl acetate may follow the initial dip. Alternatively, n-butyl acetate may, according to the present invention, be incorporated into the photoresist developer or may be dispensed with entirely with certain compositions.

The developing solutions of the present invention include at least one halocarbon solvent as described herein, comprising at least 50% and preferably at least 75% and most preferably at least 90% of the developing solution. A normally liquid unhalogenated organic material may comprise up to 50%, and preferably up to 25%, and most preferably up to 10% of the developing solution. Additionally, in some developing solutions, a stop such as n-butyl acetate comprises up to 25% and preferably up to 10% of the developing solution.

The preferred halocarbons for use in the invention are those which are liquid at normal room temperature or at temperatures slightly above room temperature, and atmospheric pressure.

Fluorocarbon 11, trichloromonofluoromethane is among the preferred solvents and is liquid at room temperature with a boiling point about 23.8°C (74.8°F). Fluorocarbon 11 has a higher vapor pressure than many of the other suitable halocarbons, and therefore it may evaporate off in some applications before dissolving off the uncross-linked photoresist. In order to raise the flash point at which too rapid evaporation takes place above room temperature and preferably above 30°C, many preferred fluorocarbon 11 developing solutions also include organic materials with higher boiling points.

Fluorocarbon 113, trichlorotrifluoroethane, is also a preferred fluorocarbon. Either the

1,1,2-trichloro-1,2,2-trifluoroethane isomer, the 1,1,1-trichloro-2,2,2-trifluoroethane isomer or mixtures may be used. The vapor pressure of fluorocarbon 113 is lower at room temperature than the vapor pressure of fluorocarbon 11 and thus fluorocarbon 113 normally does not require higher boiling organic materials. However, in some preferred

embodiments, developing solution having fluorocarbon 113 include organic materials as cosolvents which add to the dissolving power of fluorocarbon 113 for uncross-linked photoresist. Additionally, fluorocarbon 113 can be combined with other halocarbon solvents, such as fluorocarbon 11 or methylene chloride.

Other fluorocarbons are also suitable halocarbons for use as solvents in the developing solutions. Fluorocarbon 112, tetrachlorodifluoroethane, either the symmetrical or asymmetrical isomer or a mixture thereof, is a suitable primary ingredient in the developing solutions, even though fluorocarbon 112 is normally solid at room temperature. In developing solutions including fluorocarbons 112, either another halocarbon or other organic materials, thoroughly dissolve the fluorocarbon 112 and permit the developing solution to be liquid. The organic material should be a good solvent for the fluorocarbon 112 and, preferably, also for the uncross-linked photoresist.

Fluorocarbon 14, dichlorotetrafluoroethane may also be suitable with proper addition of other or the above described halocarbons or organic materials, or both. Either isomer or mixture of isomers can be used.

Methylene chloride is also a useful solvent in the present developing solutions. Many of the useful solutions include methylene chloride in combination with one of the above fluorinated halocarbons. Additionally, developing solutions with methylene chloride and organic materials such as alkanes, are among the preferred embodiments. Methylene chloride may also be used alone or with other organic materials.

Several highly preferred embodiments of the invention include methylene chloride as the predominant material with an alkane having 6-10 carbons or an alkanol having 2-5 carbons being also present. Binary compositions of about 95-99.5 weight % methylene chloride and 0.5-5 weight % of an alkanol having 2-5 carbons are good developers. About 2 weight % lower alkanol is most preferred. Binary compositions of about 1-30 weight % heptane and about 70-99 weight % methylene chloride are very good developers. About 2-25 weight % heptane and about 75-98 weight % methylene chloride is more preferred. Binary compositions of about 57-89 weight % methylene chloride and about 11-43 weight % hexane are also good developers, with about 67-83 weight % methylene chloride and about 17-33 weight % hexane being preferred. In general, about 1-43 weight % alkane having 6-8 carbons and about 57-99 weight % methylene chloride is preferred.

Ternary mixture of methylene chloride, a lower alcohol and a fluorocarbon are also preferred. These ternary mixtures generally contain about 0.5-6 weight % alkanol (2-5 carbons) about 1-11 weight % fluorocarbon 112, 11 or 113 and the balance (about 83-98.5 weight %) methylene chloride. More preferred are mixtures of about 3-10 weight % alcohol (2-5 carbons), about 2-5 weight % of fluorocarbon 112, 11 or 113 and the balance (about 85-95 weight %) methylene chloride. The preferred alcohols are isopropanol, n-pentanol, ethanol, t-butanol, and mixtures thereof and the preferred fluorocarbon is 112 ($C_2Cl_4F_2$) with 11 (CCl_3F) being next.

With methylene chloride, alkanes having 6-10 carbons are preferred, with about 70-95 weight % methylene chloride and about 5-30 weight % alkane having 6-8 carbons being exemplary. Other suitable cosolvents for various halocarbon solvents include alcohols such as cyclohexanol, isopropanol, n-butanol and n-hexanol. Other suitable cosolvents include ketones such as cyclohexanone. Standard mixtures of organic solvents, such as Stoddard solvent (a petroleum distillation cut) or ethylene glycol monobutyl ether may also be used as cosolvents in the developing solutions. Although not preferred in large quantities, xylene may be a cosolvent with one or more of the halogenated hydrocarbon solvents in the present developing solutions.

Some criteria for selecting suitable unhalogenated organic materials are that the particular halocarbon or mixture of halocarbons be miscible with or soluble in the unhalogenated organic material in quantities used, and unreactive with the halocarbon.

Additionally, the unhalogenated organic materials are selected to improve the properties of the halocarbon. Thus, since fluorocarbon 11 has a high vapor pressure at room temperature, higher boiling unhalogenated organic material acting as vaporization suppressants may be added to fluorocarbon 11.

Other of the fluorocarbons do not dissolve particular uncross-linked photoresists as readily as fluorocarbon 11, so that cosolvents for uncross-linked photoresist may be added. Preferably, the unhalogenated organic material will itself spin off the water surface with ease and evaporate off under drying oven conditions.

Still other of the halocarbons, particularly fluorocarbon 112, are themselves solid at room temperature, but dissolve readily in the organic material. For such halocarbons, the organic

material is desirably a solvent for both the halocarbon and the uncross-linked photoresist.

Examples of suitable developing solution compositions are given in Examples 1-108. Each of the indicated solutions have been found or would be expected to give good developing properties with sharp lines between developed and undeveloped photoresist areas, with the exposed areas remaining on the wafer and the unexposed areas being removed by the developing solution.

It should be understood, however, that other standard organic solvents or mixtures thereof may be used as the unhalogenated organic material in the present invention based upon a selection of a suitable cosolvent according to the desired properties of preventing too rapid evaporation with solvents such as fluorocarbon 11, or increasing dissolving power with solvents such as fluorocarbon 113.

It should also be appreciated that the solvent used need not contain highly purified materials. When separated from other halocarbons by distillation, the solvent may contain more than one suitable halocarbon, and particularly fluorocarbon. In particular, fluorocarbons such as fluorocarbon 113, that is 1,1,2-trichloro 1,2,2-trifluoroethane need not, and normally is not, separated from its isomer, fluorocarbon 113a, 1,1,1-trichloro, 2,2,2-trifluoroethane. It also may contain fractions of other fluorocarbons with slightly higher or lower boiling points.

A "stop" such as n-butyl acetate may be applied after the developing solution to remove the halocarbon solvent and unhalogenated organic material from the area of cross-linked photoresist, to prevent dissolving the cross-linked areas of photoresist. In general, the solutions of the present invention do not attack cross-linked areas of photoresist as easily as does xylene. Accordingly, the rapid application of "stop" is not as critical as with xylene. Furthermore, some of the solutions of the present invention, and especially the solutions where fluorocarbon 11 is the sole or primary halocarbon solvent, do not require a "stop" at all. However, with other fluorocarbons and where higher boiling unhalogenated organic materials such as cyclohexanone and cyclohexanol are applied with fluorocarbon 11, it may still be desirable to rinse with n-butyl acetate.

A suitable alternative is to include up to 25%, usually from 5% to 25% and preferably up to 10% of the n-butyl acetate in the developing solution. As the developing continues, the halocarbon solvent and unhalogenated organic materials will spin off or evaporate off to a greater extent than the n-butyl acetate, such that after a desired period of time, the n-butyl acetate will comprise a much larger proportion of the liquid on the wafer surface, causing further dissolving of photoresist to substantially cease. Thus, with certain developing solutions the necessity of a separate stop step may be eliminated by adding n-butyl acetate to the developing solution or by dispensing with it altogether. With certain other developing solutions, a separate n-butyl acetate rinse or drip onto the spinning wafer may be employed.

A wide variety of photoresist materials are available on the market. Many prepolymers which differentially cross-link in response to light are used. Exemplary photoresist polymers include polyisoprene photoresists, e.g. as used in the present examples. It should be appreciated that these are "negative" photoresists with the exposed portions being the more cross-linked portions.

Existing photoresists are frequently formulated with a small amount of solvent such as xylene incorporated therein. In those photoresists, the prepolymer or uncross-linked polymer is soluble in xylene and hence xylene is a suitable developing solution. The developing solutions of the present invention have been found satisfactory when used on xylene-based photoresist, but would work at least as well on photo-resists based upon any of the halocarbon solvents as described herein.

EXAMPLE 1-5

A silicon wafer was coated with a layer of photoresist approximately 1 micron thick, the photoresist used being Kodak 747 ("Kodak" is a registered trademark of the Eastman Kodak Company). Similar results are achieved with Waycoat IC and Waycoat HR-100 from Philip A. Hunt Chemical Corp. ("Waycoat" being their registered trademark). The wafer was then exposed to light using a micro negative and a 600 watt bulb including some ultraviolet light. The wafers were then placed upon chucks and rotated at about 3,000 rpms for about a minute. During this spinning, a few milliliters of the developing solution were poured onto the spinning wafer for about 10 seconds. Subsequently, n-butyl acetate was poured onto the wafer for about 10 seconds. This test was repeated with 5 developing solutions which included, by weight percentage:

- 1) 70% methylene chloride, 10% fluorocarbon 113 and 20% heptane;
- 2) 50% methylene chloride, 25% cyclohexane and 25% heptane;
- 3) 70% methylene chloride, 10% fluorocarbon 113 and 20% hexane;
- 4) 70% methylene chloride, 20% heptane and 10% isopropyl alcohol;
- 5) 70% methylene chloride, 15% fluorocarbon 113 and 15% hexane.

Wafers to which the above 5 developing solutions were applied for 10 seconds, followed by a 10 second application of n-butyl acetate, all exhibited good resolution between exposed and unexposed portions.

EXAMPLES 6-10

Silicon wafers coated with Waycoat IC or Waycoat HR-100, both photoresists from Philip A. Hunt, were totally unexposed and prebaked at 90°C for twenty minutes. They were then immersed in the five solutions of Examples 1-5, without agitation, and checked at 7 seconds, 15 seconds, 30 seconds, 60 seconds and 120 seconds for complete removal of photoresist. In Examples 6 and 10 the solutions of Examples 1 and 5, respectively, were observed to remove all photoresist within 15 seconds. In Examples 7 and 9 the solutions of Examples 2 and 4, respectively, were observed to remove all photoresist within 30 seconds. In Example 8, the solution of Example 3 was observed to remove almost all of the photoresist in 60 seconds and the remainder by 120 seconds.

When totally exposed photoresist is used, none of the above five solutions or any of the solutions of the comparisons and examples that follow caused appreciable weight loss, evidencing good selectivity.

EXAMPLES 11-85*Methylene chloride and solutions thereof*

The procedure of Examples 6-10 was followed using methylene chloride or methylene chloride-containing solutions shown in Table 1 as the developer and producing complete removal of unexposed photoresist in the time shown. Where a + follows the time, almost all of the unexposed photoresist was removed within the time shown.

Comparison with xylene

The procedure of Examples 6-10 was repeated with xylene as the developer. Appreciable amounts of photoresist remained on the wafer after 120 seconds and a liquid film remained where the photoresist was removed.

EXAMPLES 86-108*Fluorocarbon solutions*

The procedure of Examples 6-10 is repeated for the fluorocarbon-containing solutions of Table 2. Rapid removal of unexposed photoresist without a liquid film residue is achieved in each case. The numbers indicate weight % except as indicated in Example 100 and 107.

TABLE 1

5	Example	Methylene Chloride Weight %	Nonhalogenated Material Weight %	Fluorocarbon Weight %	Time (Seconds)	5
	11	100			120+	
	12	98	isopropanol-2		60	
	13	98	n-pentanol-2		60	
10	14	98	ethanol-2		60	10
	15	98	t-butanol-2		60	
			<i>isopropanol</i>	<i>fluorocarbon 11</i>		
	16	96	2	2	60	
15	17	95	3	2	30	15
	18	94	4	2	60+	
	19	94.5	2.0	3.5	60+	
	20	94.0	2.5	3.5	30	
	21	93.5	3.0	3.5	30	
20	22	93.0	3.5	3.5	15	20
	23	92.5	4.0	3.5	30	
	24	91.5	5.0	3.5	30	
	25	90.5	6.0	3.5	60	
	26	94.9	0.6	5.5	60+	
25	27	93.3	1.2	5.5	60	25
	28	92.7	1.8	5.5	30	
	29	92.1	2.4	5.5	60	
	30	86	2	11	60+	
	31	85	4	11	60	
30	32	83	6	11	60+	30
			<i>isopropanol</i>	<i>fluorocarbon 112</i>		
	33	96	3.0	1.0	60	
	34	97.5	0	2.5	60	
35	35	96.5	1.0	2.5	60	35
	36	94	2.0	4.0	30	

TABLE 1 (continued)

5	Example	Methylene Chloride Weight %	Nonhalogenated Material Weight %	Fluorocarbon Weight %	Time (Seconds)	5
			<i>isopropanol</i>	<i>fluorocarbon 112</i>		
	37	93.5	2.5	4.0	15	
	38	93	3.0	4.0	15	
10	39	92.5	3.5	4.0	30	10
	40	94	1.0	5.0	15	
	41	93	2.0	5.0	7	
	42	91.5	3.5	5.0	7	
	43	91	4.0	5.0	15	
15	44	93	1.0	6.0	30	15
	45	91.5	2.5	6.0	7	
	46	90.5	3.5	6.0	7	
	47	90	4.0	6.0	15	
	48	89	5.0	6.0	30	
20	49	88.5	5.5	6.0	60	20
	50	92	0.5	7.5	30	
	51	91.0	1.5	7.5	15	
	52	90	2.5	7.5	7	
	53	89	3.5	7.5	7	
25	54	88.5	4.0	7.5	7	25
	55	87.5	5.0	7.5	30	
	56	91.5	0	8.5	30	
	57	89.5	2.0	8.5	15	
	58	89.0	2.5	8.5	7	
30	59	88	3.5	8.5	7	30
	60	87.5	4.0	8.5	7	
	61	86.5	5.0	8.5	15	
	62	88	2.0	10.0	30	
35	63	87.5	2.5	10.0	7	35

TABLE 1 (continued)

5	Example	Methylene Chloride Weight %	Nonhalogenated Material Weight %	Fluorocarbon Weight %	Time (Seconds)	5
	64	86.5	<i>isopropanol</i>	<i>fluorocarbon 112</i>	7	
	65	86	3.5	10.0	30	
10			4.0	10.0		10
	66	89	<i>hexane</i>		60	
	67	83	11	-	30	
	68	75	17	-	7	
15	69	71	25	-	7	15
	70	67	29	-	7	
	71	57	33	-	60	
			43	-		
20	72	70	<i>hexane</i>	<i>fluorocarbon 113</i>	30	20
	73	70	20	10	30	
	74	67	15	15	15	
	75	63	19	14	7	
	76	66	24	13	7	
25	77	60	27	7	7	25
	78	55	27	13	15	
			34	11		
	79	70	<i>heptane</i>	-	30	
30	80	75	30	-	7	30
	81	80	25	-	7	
	82	90	20	-	7	
	83	95	10	-	7	
	84	98	5	-	7	
35	85	99	2	-	15	35
			1	-		

Each of the solutions of Examples 11-85 produce negligible weight loss of wafers coated with unexposed photoresist after 30 minutes.

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TABLE 2

Example	Fluorocarbons				Other Materials	
	11	112	113	114		
5						5
86	50				xylene 25, heptane 25	
87	75				pentane 20, methylene chloride 5	
10						10
88	90				octane 10	
89	95				decane 5	
15						15
90	98				nonane 2	
91	95				cyclohexanone 5	
20	95				cyclohexanol 5	
92						20
93		90			methylene chloride 10	
94			80		cyclohexanone 20	
25			90		cyclohexanol 10	
95						25
96			95		xylene 5	
30				80	ethylene glycol mono-butyl ether 20	
97						30
98				95	Stoddard solvent 5	
35				90	t-butanol 10	
99						35
100 by mole %			39.1		methylene chloride 51.6 cyclopentane 9.3 (an azeotrope, see U.S. Patent No. 3,607,767)	
40			40		methylene chloride 50 cyclopentane 6, n-pentane 4	
101						40
45			10		heptane 20, methylene chloride 70	
102						45
103			10		hexane 20, methylene chloride 70	
50			15		hexane 15, methylene chloride 70	
104						50
105	85				ethylene glycol monobutyl ether 15	
55						55
106	90				Stoddard solvent 10	
107 by mole %			33.1		methylene chloride 55.3, methanol 11.6 (an azeotrope, see U.S. Patent No. 3,400,077)	
60						60
108			97		isopropanol 3 (an azeotrope, see U.S. Patent No. 3,340,199)	

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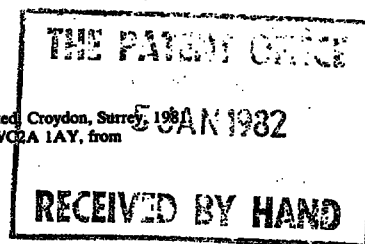
EXAMPLES 109-112

The procedure of Examples 6-10 was repeated with pure trichloromonofluoromethane (fluorocarbon 11) as the developer. Photoresist was completely removed within 120 seconds. By themselves, each of fluorocarbons 112 and 113 took over 10 minutes to completely remove the photoresist. With minor amounts of methylene chloride and/or unhalogenated materials added to form solutions, these fluorocarbons became better developers. Fluorocarbon 14 performed similarly.

WHAT WE CLAIM IS:-

1. A method of developing a photoresist layer on a surface of an article, exposed portions of the photoresist layer being more highly cross-linked than the remaining unexposed portions, which method comprises contacting the photoresist layer with a liquid developer solution comprising 50 to 100 weight % of at least one aliphatic halogenated hydrocarbon selected from methylene chloride, trichloromonofluoromethane, tetrachlorodifluoroethanes, trichlorotrifluoroethanes, dichlorotetrafluoroethanes and mixtures of two or more thereof, and from 0 to 50 weight % of a normally liquid, unhalogenated organic material miscible with or capable of dissolving said halogenated hydrocarbon, at a temperature and for a period of time sufficient to remove the remaining, unexposed, portions of photoresist without removing the more highly cross-linked, exposed, portions of photoresist.
2. A method as claimed in claim 1 wherein said developer contains unhalogenated organic material selected from cyclohexanol, cyclohexanone, ethylene glycol monobutyl ether, Stoddard solvent, xylene, other cyclic and acyclic hydrocarbons with 5 to 10 carbon atoms, isopropyl alcohol and mixtures of two or more thereof.
3. A method as claimed in claim 1 wherein said halogenated hydrocarbon comprises methylene chloride.
4. A method as claimed in claim 1, 2 or 3, wherein said developer comprises from 75 to 100 % by weight of the halogenated hydrocarbon.
5. A method as claimed in claim 4, wherein said developer comprises from 90 to 100% by weight of the halogenated hydrocarbon.
6. A method as claimed in any preceding claim, wherein said developer includes by weight 5-25 % n-butyl acetate as a stop.
7. A method as claimed in claim 1, wherein said developer contains unhalogenated organic material selected from alkanes having 6-10 carbon atoms.
8. A method as claimed in claim 7, wherein said developer comprises 70-99 weight % methylene chloride and 1-30 weight % heptane.
9. A method as claimed in claim 1, wherein said developer comprises 83-98.5 weight % methylene chloride, 0.5-6 weight % of an alkanol having 2-5 carbon atoms and 1-11 weight % of a fluorocarbon selected from tetrachlorodifluoroethanes, trichloromonofluoromethane and trichlorotrifluoroethanes.
10. A method as claimed in any preceding claim, wherein the photoresist is present as a coating on a semiconductor wafer, and the photoresist-coated wafer is spun at from 1500 to 15,000 r.p.m. while the developer is contacted with the photoresist.
11. A method as claimed in any preceding claim, wherein the photoresist is of a material which is developable by xylene.
12. A method as claimed in any one of claims 1 to 11, wherein the more highly cross-linked portions of the photoresist comprise polyisoprene.
13. A method as claimed in claim 1, substantially as described in any one of Examples 1 to 108.
14. An article having a surface bearing a photoresist layer developed by a method claimed in any preceding claim.
15. A semi-conductor wafer bearing a coating of a photoresist developed by a method claimed in any one of claims 1 to 13.

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EXAMPLES 109-112

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WHAT WE CLAIM IS:-

1. A method of developing a photoresist layer on a surface of an article, exposed portions of the photoresist layer being more highly cross-linked than the remaining unexposed portions, which method comprises contacting the photoresist layer with a liquid developer solution comprising 50 to 100 weight % of at least one aliphatic halogenated hydrocarbon selected from methylene chloride, trichloromonofluoromethane, tetrachlorodifluoroethanes, trichlorotrifluoroethanes, dichlorotetrafluoroethanes and mixtures of two or more thereof, and from 0 to 50 weight % of a normally liquid, unhalogenated organic material miscible with or capable of dissolving said halogenated hydrocarbon, at a temperature and for a period of time sufficient to remove the remaining, unexposed, portions of photoresist without removing the more highly cross-linked, exposed, portions of photoresist.
2. A method as claimed in claim 1 wherein said developer contains unhalogenated organic material selected from cyclohexanol, cyclohexanone, ethylene glycol monobutyl ether, Stoddard solvent, xylene, other cyclic and acyclic hydrocarbons with 5 to 10 carbon atoms, isopropyl alcohol and mixtures of two or more thereof.
3. A method as claimed in claim 1 wherein said halogenated hydrocarbon comprises methylene chloride.
4. A method as claimed in claim 1, 2 or 3, wherein said developer comprises from 75 to 100 % by weight of the halogenated hydrocarbon.
5. A method as claimed in claim 4, wherein said developer comprises from 90 to 100% by weight of the halogenated hydrocarbon.
6. A method as claimed in any preceding claim, wherein said developer includes by weight 5-25 % n-butyl acetate as a stop.
7. A method as claimed in claim 1, wherein said developer contains unhalogenated organic material selected from alkanes having 6-10 carbon atoms.
8. A method as claimed in claim 7, wherein said developer comprises 70-99 weight % methylene chloride and 1-30 weight % heptane.
9. A method as claimed in claim 1, wherein said developer comprises 83-98.5 weight % methylene chloride, 0.5-6 weight % of an alcohol having 2-5 carbon atoms and 1-11 weight % of a fluorocarbon selected from tetrachlorodifluoroethanes, trichloromonofluoromethane and trichlorotrifluoroethanes.
10. A method as claimed in any preceding claim, wherein the photoresist is present as a coating on a semiconductor wafer, and the photoresist-coated wafer is spun at from 1500 to 15,000 r.p.m. while the developer is contacted with the photoresist.
11. A method as claimed in any preceding claim, wherein the photoresist is of a material which is developable by xylene.
12. A method as claimed in any one of claims 1 to 11, wherein the more highly cross-linked portions of the photoresist comprise polyisoprene.
13. A method as claimed in claim 1, substantially as described in any one of Examples 1 to 108.
14. An article having a surface bearing a photoresist layer developed by a method claimed in any preceding claim.
15. A semi-conductor wafer bearing a coating of a photoresist developed by a method claimed in any one of claims 1 to 13.

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