

RESIST REMOVING METHOD AND APPARATUS

Background of The Invention

Field of the Invention

The present invention relates to a resist removing method, a resist removing apparatus and a semiconductor device manufactured by the method. More particularly, the present invention relates to a resist removing method and apparatus that directs a novel resist removal material onto a resist on a substrate.

Description of the Related Art

The resist removing process is a major process in preparing a semiconductor device. For example, after various processes for preparing the semiconductor device, e.g., an etching process (dry or wet) or an ion implantation process, a resist pattern, which is used as a mask on a semiconductor substrate, must be removed. Also, if the resist pattern is misaligned, it must be removed to form a new resist pattern. Various material layers, e.g., an oxide layer, an aluminum layer, a polysilicon layer, a silicide layer or a polyimide layer, may be present under a resist layer. Therefore, an important consideration for a resist removing process is to remove a resist layer completely, as quickly as possible, and without attacking an underlying layer.

One resist removing agent currently in wide use includes a basic amine such as hydroxylamine, diglycolamine, monoethanolamine or methylethanolamine, and a polar solvent such as water or alcohol, as its essential components.

Since such a conventional resist removing agent cannot remove polymer completely, a pre-removal step for removing polymer is further necessary. Polymer is a material produced by the reaction of components constituting the resist, such as carbon (C), hydrogen (H) or oxygen (O), and plasma when plasma etching or reactive ion etching (RIE) is performed using the resist pattern as a mask. In particular, when a

metal layer is formed under the resist pattern, an organometallic polymer is produced. If such a polymer or organometallic polymer is not removed, but remains in a contact hole or a via hole, for example, contact resistance increases and defects in the semiconductor devices may result. Thus, before using the resist removing agent, a polymer removing agent, e.g., a nitric acid (HNO_3) solution, must treat the substrate during the pre-removal step.

The conventional resist removing agent may attack the underlying layers. A typical example of an underlying layer liable to be attacked is a metal layer. The reason for the foregoing is because the resist removal agent is primarily composed of a basic solvent or water which easily corrodes the metal layer. Thus, a post-removal step for preventing the attack must be performed before executing a post-removal rinse step. In the post-removal step, isopropyl alcohol (IPA) is used, for example.

Therefore, since a nitric acid treatment step (pre-removal step) and an IPA treatment step (post-removal step) are usually also performed, the resist removal process becomes more complicated and processing time is prolonged, thereby lowering productivity. Also, since a pre-removal material, e.g., nitric acid and a post-removal material, e.g., IPA, are further required as well as the resist removal material, the manufacturing cost increases. In addition, since the various baths containing the nitric acid and IPA are required, a resist removing apparatus becomes undesirably bulky.

Summary of The Invention

An objective of the present invention is to provide a resist removing method that substantially overcomes one or more of the problems due to the limitations and disadvantages of the related art.

A second objective of the present invention is to provide a resist removing apparatus for use in the method.

Accordingly, to achieve the above ³ objectives and other objectives and advantages of the current invention, a resist removing method involves providing a substrate and forming a resist on the substrate. Then the substrate is contacted with a resist removing agent comprising N alkanol alkoxy alkanamide, to remove the resist from the substrate.

According to another aspect of the method invention, the substrate is contacted with a resist removing composition having N alkanol alkoxy alkanamide and an attack inhibitor. A polar material may be added to this composition.

According to an alternative aspect of the method invention, the resist removing composition includes alkanolamine and alkyl alkoxy alkanoate. Preferably, the composition includes an attack inhibitor and a polar material.

In another aspect of the invention, an apparatus for removing resist from a substrate includes a source of a resist removing agent comprising N alkanol alkoxy alkanamide. A supply unit is in flow communication with the source, through which the resist removing agent is supplied. A resist removing unit in flow communication with the supply unit, directs the resist removing agent into contact with a substrate disposed in the resist removing unit, whereby the resist is removed from the substrate.

In other aspects of the apparatus invention, the source is a source of a resist removing composition. The composition can be N alkanol alkoxy alkanamide and an attack inhibitor, or can be alkanolamine and alkyl alkoxy alkanoate. An attack inhibitor, or a polar material, or both, can be added to the composition supplied.

The resist removing method of the present invention can remove resist and polymer completely by a simple process in a short time without attacking the underlying layer of the resist. The apparatus can consequently be simpler and smaller.

Brief Description of The Drawings

FIG. 1 is a flow diagram, wherein the solid lines indicate a process of removing a resist using a resist removing agent or a resist removing composition according to

the present invention, and the dashed lines⁴ indicate the conventional steps eliminated by using the present invention;

FIG. 2 is a block diagram of a resist removing apparatus using a resist removing agent or a resist removing composition according to the present invention;

FIG. 3 is a diagram of a horizontal type resist removing apparatus using the resist removing composition according to the present invention;

FIG. 4 is a diagram of a vertical type resist removing apparatus using the resist removing composition according to the present invention; and

FIG. 5 is a graph illustrating the change in contents of components of the resist composition, measured by gas chromatography for 48 hours at intervals of 8 hours.

Description of the Preferred Embodiments

Hereinbelow, an amide compound, a resist removing agent and a resist removing composition and methods for preparing the same will be described. The present invention is directed to a method for removing a resist using the same and a resist removing apparatus used in the resist removing method, and these will be described in detail.

A new amide compound used in the present invention is an N alkanol alkoxy alkanamide. In detail, the N alkanol alkoxy alkanamide is represented by formula (1):



wherein R_1 is a hydrogen atom, a C_1 to C_5 hydrocarbon (i.e., a non-ring hydrocarbon with 1 to 5 carbon atoms), or an aromatic hydrocarbon having 1 to 3 rings; R_2 is a C_1 to C_5 hydrocarbon or an aromatic hydrocarbon having 1 to 3 rings; and R_3 and R_4 are each any of the C_1 to C_5 hydrocarbons, independent of each other. In the preferred embodiment, R_1 is a hydrogen atom, R_2 is $-CH_2CH_2-$, R_3 is $-CH_2CH_2-$, and R_4 is $-CH_3$.

The amide compound used in the present invention contains a hydroxy group ($-OH$) causing a nucleophilic reaction with a resist, and an alkoxy group ($-OR_4$)

causing a hydrophilic reaction with the hydroxy group (-OH). Consequently, a resist removing agent having the amide compound according to the present invention is very effective in removing a resist. Therefore, according to one embodiment of the present invention, the N alkanol alkoxy alkanamide compound itself constitutes a resist removing agent.

In another embodiment, a resist removing composition includes the N alkanol alkoxy alkanamide and an attack inhibitor. Also, the resist removing composition optionally further includes a polar material having a dipole moment of 3 or greater.

For example, in the resist removal composition, the content of the N alkanol alkoxy alkanamide may be 50 to 99.9 percent by weight (weight %) of the total weight of the composition, and the content of the attack inhibitor may be 0.01 to 30 weight %. In the preferred embodiment, the content of the N alkanol alkoxy alkanamide is 70 to 90 weight %, and the content of the attack inhibitor is 7 to 15 weight %. Further, the content of the polar material having a dipole moment of 3 or greater may be 0.01 to 30 weight %, and is preferably 3 to 20 weight %.

The N alkanol alkoxy alkanamide is a compound represented in the above described formula (1). The attack inhibitor is represented in the following formula (2):



wherein R_6 is a C_1 to C_5 hydrocarbon, a C_1 to C_5 hydrocarbon having a -COOH group, an aromatic hydrocarbon having 1 to 3 rings, or an aromatic hydrocarbon having 1 to 3 rings and a -COOH group in at least one ring. The integer n may have a value between and inclusive of 1 and 4. In the preferred embodiment, R_6 is a benzene ring and the attack inhibitor is catechol in which n is 2. Also, gallic acid is a widely known attack inhibitor represented by formula (2) that may be used within the present invention.

For the polar material having a dipole moment of 3 or greater, water, methanol or dimethyl sulfoxide may be employed. The polar material having a dipole moment of 3 or greater exhibits a high solubility with respect to cross-linked polymer and resist. In other words, the polymer strongly bonded on the side walls of the resist pattern and the surface of the exposed underlying layer can be effectively removed by such polar material. Also, resist removal itself is facilitated by such polar material.

Another embodiment of a resist removing composition used in the present invention includes alkanolamine, which is an amine compound, and alkyl alkoxy alkanoate, which is an ester compound. Also, optionally, an attack inhibitor or a polar material having a dipole moment of 3 or greater, or both may be further included.

For example, in this embodiment, the content of the alkanolamine is 10 to 70 weight % of the resist removing composition, and the content of the alkyl alkoxy alkanoate is 10 to 70 weight %. In the preferred embodiment the alkanolamine is 30 to 40 weight % and the alkyl alkoxy alkanoate is 30 to 40 weight %.

In this example, the content of the attack inhibitor is 0.01 to 30 weight % of the resist removing composition. In the preferred embodiment, the attack inhibitor is 7 to 15 weight %. In addition, the content of the polar material is 0.01 to 30 weight % of the resist removing composition. In the preferred embodiment, the polar material is 3 to 20 weight %.

The N alkanolamine suitable for use in the present invention is represented by the following formula (3):



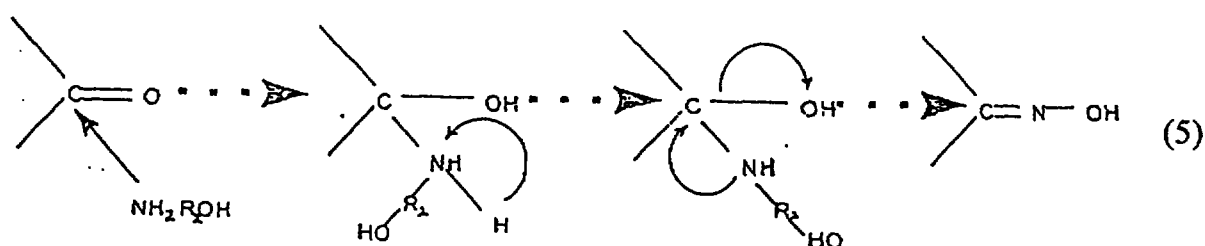
wherein R_1 is a hydrogen atom, a C_1 to C_5 hydrocarbon, or an aromatic hydrocarbon having 1 to 3 rings; and R_2 is a C_1 to C_5 hydrocarbon, or an aromatic hydrocarbon having 1 to 3 rings. In the preferred embodiment, R_1 is hydrogen and R_2 is monoethanolamine, i.e., $-CH_2CH_2-$.

The alkyl alkoxy alkanoate suitable⁷ for use in the present invention is represented by the following formula (4):



wherein R_3 , R_4 and R_5 are each any of the C_1 to C_5 hydrocarbons, independent of each other. The preferred alkyl alkoxy alkanoate is methyl methoxy propanate in which R_3 is $-CH_2CH_2-$, R_4 is $-CH_3$ and R_5 is $-CH_3$.

Now, the reaction mechanism of the composition according to the latest embodiment will be described. First, as shown in the following reaction formula (1), exfoliation of a resist occurs by the nucleophilic reaction mechanism of alkanolamine. Also, dissolution occurs by the nucleophilic reaction mechanism of a hydroxy group in the alkanolamine and the hydrophilic reaction mechanism of an alkoxy group in the alkyl alkoxy alkanoate. Also, the attack inhibitor effectively prevents the underlying layer, specifically a metal layer, from being attacked. Further, the polar material, e.g., water, maximizes the polymer removing action.



For convenience of explanation, the mechanism described in reaction formula (5) is for the case when R_1 is hydrogen.

To form the composition completely, the composition may be heated to a temperature between room temperature and about 120°C . In the preferred embodiment, the composition is heated to a temperature from about 80°C to about 90°C . The reason for the foregoing is to expedite the reaction by the components in reaction formula (5) that results in N alkanol alkoxy alkanamide. Alternatively, a

reaction catalyst, such as platinum, can be added in reaction formula (5), to promote a quicker reaction.

The resist removing compositions used in the present invention are expressed in the following Table 1. In Table 1, the contents of the preferred compositions are given in parentheses.

Table 1: Resist Removing Compositions

Composition for removing resist	N alkanol alkoxy alkanamide (weight %)	Alkanol amine (weight %)	Alkyl alkoxy alkanoate (weight %)	Attack inhibitor (weight %)	Polar material (weight %)
1	50 to 99.9			0.01 to 30	
2	50 to 99.9 (70 to 90)			0.01 to 30 (7 to 15)	0.01 to 30 (3 to 20)
3		10 to 70	10 to 70		
4		10 to 70 (30 to 40)	10 to 70 (30 to 40)	0.01 to 30	
5		10 to 70 (30 to 40)	10 to 70 (30 to 40)	0.01 to 30 (7 to 15)	0.01 to 30 (3 to 20)

The resist removing agent and resist removing compositions used in the present invention have excellent capability for removing the resist and the polymer which is an etching by-product. Also, they do not attack the layer underlying the resist, e.g., a metal layer. In addition, the above-described materials are cheaper than the components of the conventional resist removing compositions.

The N alkanol alkoxy alkanamide, the amide compound of the present invention, is prepared according to the following method of the present invention. First, the alkanolamine represented by the formula (3) as an amine compound, and

alkyl alkoxy alkanoate represented by the formula (4) as an ester compound, are mixed. The mixture ratio of the alkanolamine and the alkyl alkoxy alkanoate is 1:1 by weight. Next, the reaction of amine and ester is carried out to prepare N alkanol alkoxy alkanamide represented by the formula (1). To supply energy sufficient for this reaction, the temperature of the mixture is maintained at a temperature in the range from room temperature to about 120°C. In the preferred embodiment of the method, the mixture is heated to a temperature in the range from about 80°C to about 90°C.

The resist removing composition 1 or 2 demonstrated in the Table 1 is prepared by mixing the N alkanol alkoxy alkanamide prepared in the above manner with an attack inhibitor or a polar material, or both, in an appropriate ratio.

Also, the composition 1 or 2 may be prepared according to the following method. First, 10 to 70 weight % of alkanol amine, and 10 to 70 weight % of alkyl alkoxy alkanoate are mixed with 0 to 30 weight % of an attack inhibitor or 0 to 30 weight % of a polar material or both. Then, the temperature of the mixture is maintained at a temperature in the range from room temperature to about 120°C. In the preferred embodiment of this method, the mixture is heated to a temperature in the range from about 80°C to about 90°C. The duration of the reaction, i.e. the reaction time, is about 1 to about 24 hours, preferably about 1 to about 12 hours. After the heating is completed, the reactant is left alone for 1 to 7 hours to let the chemical reactants stabilize.

As a result, a composition is obtained which is substantially composed of N alkanol alkoxy alkanamide and the attack inhibitor or the polar material or both. Small amounts of unreacted alkanolamine and alkyl alkoxy alkanoate may remain.

The completion of the reaction can be verified visually or by gas chromatography. In visual verification, layer separation among components is observed to vanish as the reaction progresses. When the separate component layers are observed to completely vanish, the completion of the reaction is presumed. When the composition is analyzed using gas chromatography, the area percentile of N

alkanol alkoxy alkanamide exceeding 80 % implies completion of the reaction. Area percentile is defined as the area under a peak in the gas chromatography spectrum associated with a component, divided by the sum of the areas under all peaks of all components, and the quotient multiplied by 100.

In preparing the compositions 3 to 5, the components are mixed in the ratios listed in Table 1, and then allowed to react at a temperature in the range from room temperature to about 120°C for 1 to 24 hours. Typically, these compositions 3 to 5 are formed first, before using them in removing the resist. However, if it is possible to set the temperature to the above temperature range while the compositions 3 through 5 contact the resist, the above described separate reacting step can be omitted.

The method for removing the resist according to the present invention will be described with reference to the solid line steps in FIG. 1. Note that the conventional process is represented by both the solid line and the dashed line steps in FIG. 1. Various processes for completing a semiconductor device, for instance, an etching (dry or wet) process or an ion implantation process, are performed using a resist pattern as a mask. Subsequently, a substrate where the resist pattern is formed is allowed to contact a resist removing agent or composition listed in Table 1 in order to remove the resist or polymer or both (step 110). This is achieved by placing the resist removing agent or resist composition in a bath and then dipping the substrate into the bath. Alternatively, the resist removing agent or the resist removing composition may be sprayed onto the substrate as the substrate is moved through the spray.

The resist removing agent is formed, and the resist removing compositions 1 and 2 are mixed, and then can be brought immediately into contact with the substrate to remove the resist in the removal step. The compositions 3 to 5 shown in Table 1 are mixed first, and then also may be allowed to contact the substrate immediately; however, compositions 3 to 5 are preferably given time to react before performing the removal step. The reaction is performed at a temperature in the range from room temperature to about 120°C for 1 to 12 hours, and may be performed even without heating. In the preferred embodiment, the compositions do not contact the substrate

with the resist until an even further time has elapsed after the completion of the reaction, e.g., an additional 1 to 7 hours after the reaction is complete.

Using these compositions, the resist removal method of the present invention can be performed at a low temperature of 70°C or below, specifically, in the range from 45°C to 70°C. A contact time in the range from about 10 to about 30 minutes is preferred.

Alternatively, when the structures formed on the substrate have a high heat resistance, the unheated compositions 3 to 5 may be placed in a resist removal unit in contact with the substrate. Subsequently, the temperature of the resist removal unit can be adjusted to the temperature at which the amine and the ester can react, in the range of room temperature and above, to form the amide. Then, the reaction in which amide is formed by the composition, and the reaction in which resist is removed from the substrate, can occur concurrently. That is, in this case, a separate reaction step for the compositions 3 to 5 can be omitted before the removal step.

The resist removing material, i.e., the resist removing agent or resist removing composition, can be applied to a resist suitable for short wavelength exposure such as a resist for an ArF excimer laser (193 nm) as well as a resist for a conventional i-line (365 nm) source or a resist for a KrF excimer laser (248 nm).

After the resist is completely removed, the resist removing material and the dissolved resist remaining on the substrate are rinsed away (step 130). The rinsing step is performed using a rinsing solution, e.g., deionized water. If necessary, the rinsing step can be performed in two steps. Finally, the substrate is dried by a spin dry method using air as the drying agent or a drying method using isopropyl alcohol, for example, as the drying agent to remove the deionized water remaining on the substrate (step 140).

After the drying step 140, the substrate is transferred for subsequent processing. When a resist mask is formed in a subsequent step, the resist is later removed through the steps shown in FIG. 1 after the subsequent step is completed. The semiconductor

device is completed through such repeated unit fabrication processes and resist removal steps.

As shown in FIG. 1, since the resist removing material used in this invention has an excellent capability for removing the resist or polymer, the pre-removal step 100 (dashed lines) is not necessary, unlike the conventional art. Also, since the layer underlying the resist is prevented from being attacked, the post-removal step 120 (dashed lines) can be omitted, also unlike the conventional art. Thus, according to the present invention, the resist can be completely removed by a simpler process, compared to the conventional resist removing process. Therefore, the productivity of semiconductor devices can be significantly enhanced.

Also, as described above, since the resist removal process is simplified, the resist removing apparatus according to the present invention can be made smaller or more compact.

Referring to FIG. 2, a resist removing apparatus 200 according to the present invention simply includes a resist removal unit 210, a rinsing unit 220 and a drying unit 230. That is, the conventional pre-removal unit and post-removal unit are not necessary. Thus, the area occupied by the resist removing apparatus 200 can be significantly reduced, compared to the conventional art.

The resist removing unit of the present invention is in flow communication with a source of the resist removing material used in the method of the present invention.

In the case that the resist removing apparatus 200 employs a dipping method, the units 210, 220 and 230 each correspond to an independent bath. Thus, unlike the conventional art, a nitric acid (HNO_3) pre-removal treatment bath and an isopropyl alcohol (IPA) post-removal treatment bath are not necessary, thereby eliminating two baths and significantly reducing the area occupied by the resist removing apparatus 200.

A resist removing apparatus employing a spray method can be classified into a horizontal type and a vertical type.

Referring to FIG. 3, a horizontal type resist removing apparatus 300 employs a horizontal carrier means 340, e.g., a conveyor system, and is sectioned into a resist removing unit 310, a rinsing unit 320 and a drying unit 330. A source 360 of resist material contains either N alkanol alkoxy alkanamide or alkanolamine and alkyl alkoxy alkanoate. The source is in flow communication with the resist removing unit 310, for example, through a supply unit 370. Conventional sources 362 and 364 for a rinsing solution and drying agent, respectively, are also included, and may also be connected in flow communication with respective units 320 and 330, through the supply unit 370. Nozzles 312, 322 and 332 are installed in the units for spraying materials suitable for functions of the respective units. In particular, the nozzle 312 is installed in the resist removing unit 310. In operation, when a substrate is loaded into the resist removing unit 310, a resist removing material of the present invention is sprayed from the nozzle 312 to remove the resist. Then, the substrate is continuously conveyed horizontally, by the conveyor system 340, toward the rinsing unit 320. A rinsing solution is sprayed in the rinsing unit 320 through the nozzle 322. Finally, the substrate is conveyed to the drying unit 330 by the conveyor system 340 to then be dried by a drying agent, such as air or a drying chemical directed onto the substrate by nozzle 332. Since the horizontal type resist removing apparatus includes only three units, the size of the apparatus is significantly reduced.

Referring to FIG. 4, a vertical type resist removing apparatus 400 employs a vertically movable substrate support 440. The vertical type also includes a source 460 of the resist removing materials of the present invention and a supply unit 470 to supply the resist removing material. In the preferred embodiment, the substrate support 440 is rotatable. Also, the inside of the apparatus is constructed of three areas in a bedded structure, vertically displaced with respect to each other, and not independent chambers. That is, the units are composed of a drying area 430, a rinsing area 420, and a resist removing area 410 in vertical sequence. Sources 462 and 464 for the rinsing solution and a drying agent, respectively, may also be included and those materials may be delivered through the supply unit 470. In the example

embodiment, a single supply duct 450 provides the respective materials for all three units.

For example, when a substrate is loaded onto the substrate support 440, the support 440 first moves to an area where the resist removal is performed and resist removing material from the resist removing source 460 via the supply unit 470 is sprayed through the supply duct 450. In the preferred embodiment, the resist removing material is discharged to the outside through an exhaust duct (not shown). When the resist removal step is completed, the substrate support 440 moves the substrate to the rinsing unit 420 by descending. A rinsing solution is then sprayed into the rinsing unit 420 through the supply duct 450. Finally, the substrate is then carried to the drying unit 430 by the vertical movement of the substrate support 440 to be dried.

Although FIG. 4 shows that the drying unit 430, the rinsing unit 420 and the resist removing unit 410 are disposed vertically in sequence from bottom to top, these units may be vertically disposed in a reverse order.

Because the vertical type resist removing apparatus of the present invention also includes only three units, the size of the apparatus is significantly reduced compared to a conventional vertical type apparatus.

The further details of the present invention are described with reference to the following examples, but it is understood that the invention is not limited to these specific embodiments.

EXAMPLE I

Preparation of N Ethanol Methoxy Propanamide

In this example, 200 ml of monoethanolamine as an alkanolamine and 200 ml of methyl methoxy propanoate as an ester were mixed. Subsequently, the mixture was heated at 90°C for 5 hours. After heating, the reactant was restored to room temperature for 5 hours.

The resultant material was analyzed by gas chromatography to ascertain that the N ethanol methoxy propanamide product was obtained. In addition, the product was analyzed by proton nuclear magnetic resonance (^1H -NMR) spectrum giving relative amounts of components in parts per million (ppm). The NMR data for the product are as follows: 6.8 ppm (1H), 3.7 ppm (4H), 3.5 ppm (3H) and about 2.8 ppm (1H).

EXAMPLE II

Preparation of N,N T-butyl Ethanol Methoxy Propanamide

In this example, 200 ml of N,N t-butyl ethanolamine as an alkanolamine and 200 ml of methyl methoxy propanoate as an ester were mixed. Subsequently, the mixture was heated at 90°C for 5 hours. After heating, the reactant was restored to room temperature for 5 hours.

The resultant material was analyzed by gas chromatography to ascertain that the N,N t-butyl ethanol methoxy propanamide product was obtained.

EXAMPLE III

Evaluation of an Appropriate Temperature in Preparing N Ethanol Methoxy Propanamide

In this example, 200 ml of monoethanolamine as an alkanolamine and 200 ml of methyl methoxy propanoate as an ester were mixed. Subsequently, to ascertain the temperature suitable for the reaction of this amine and ester, the N ethanol methoxy propanamide was synthesized at different temperatures as shown in Table 2 and the time consumed for the synthesis to be complete was measured. The timing for completion of the synthesis was determined by the elapsed time until the area % of the amide (N ethanol methoxy propanamide) exceeds 80% as analyzed by gas chromatography.

Table 2: N ethanol methoxy propanamide Reaction Temperatures and Times

Reaction temperature (°C)	25	35	45	55	65	80	90
Reaction time (hr)	55	24	30	7	6	4	3

From the above result, it was understood that the reaction does occur at room temperature, and that the reaction occurs more rapidly at higher temperatures. However, in consideration of other processing conditions, it is preferable that the reaction temperature does not exceed 120°C. Thus, the temperature for preparing the amide compound according to the present invention is desirably between room temperature and about 120°C. In the preferred embodiment of the method, the reacting temperature is in the range from about 80°C to about 90°C.

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EXAMPLE IV

Preparation of Resist Removing Composition and
Evaluation of Same to Remove the Resist

As shown in Table 3, seven (7) resist removing compositions were prepared with monoethanolamine (MEA), methyl methoxy propanoate (MMP), catechol and water of different contents. Subsequently, the compositions were heated at 80°C for 5 hours. Next, the resultant material was placed at room temperature for 6 hours to complete the compositions.

Table 3: Resist Removing Performance of Several Compositions

Item	MEA(ml)	MMP(ml)	Catechol (g)	Water (ml)	Observations
1	50	350	60	100	○
2	100	300	60	100	○
3	150	250	60	100	⊙
4	200	200	60	100	⊙
5	250	150	60	100	⊙
6	300	100	60	100	○
7	350	50	60	100	○

(○ : good, ⊙: better, ⊙: best)

The resist to be removed using the above-described resist removing composition was prepared in the following manner on each of 7 sheets of substrates. First, BoroPhosphoSilicate Glass (BPSG) layers were formed to a thickness of 5000 Å. Then, a titanium layer and a titanium nitride layer were formed to a thickness of 200 Å each, and heated. Next, an aluminum layer was deposited to a thickness of 6000 Å and then flowed. A titanium nitride layer as a capping layer was formed on the aluminum layer and then an interlevel dielectric layer was formed to a thickness of 10000 Å. Then, a resist was coated on the interlevel dielectric layer and photolithography was performed to form a resist pattern defining a via hole. The

resist pattern was baked and then the interlevel dielectric layer was etched, using the resist pattern as a mask, by a buffered oxide etchant to form a via hole exposing the aluminum layer.

After forming the via hole, the 7 substrates were dipped into respective 7 baths containing the respective 7 compositions listed in Table 3. The temperatures of the baths were maintained at 60°C. After being submerged for 20 minutes, the substrates were rinsed with water for 5 minutes and dried, and then the substrates were examined using scanning electron microscopy (SEM). The substrates were graded as good, better, best based on the SEM observations, and the grades are indicated in Table 3 using symbols. The state of the substrate is characterized by the relative amounts of remaining polymer and remaining photoresist. The good state is the state similar to that using a conventional resist removing composition known to those skilled in the art. The better state is improved compared to the conventional case; and the best state is significantly improved compared to the conventional case.

EXAMPLE V

Evaluation of Appropriate Processing Time

To verify appropriate processing time, the composition corresponding to item number 4 shown in Table 3 was used, and the resist was removed at different processing times as listed in Table 4. The other processing conditions were the same as those in Example IV. The removal state of the resist and the attacked states of an aluminum layer and a silicon layer were observed using SEM. The symbols in Table 4 representing the removal state are the same as in Table 3. In Table 4 an “” indicates the underlying layer is not attacked.

From the results shown in Table 4, it was observed that an appropriate reaction time for removing the resist includes times from 10 to 30 minutes.

Table 4: Resist Removing Performance By Time

Item	MEA (ml)	MM P (ml)	Catechol (g)	Water (ml)	Time (min)	Observations of resist removing capability	Attacked or not (Al, Si)
1	200	200	60	100	10	○	×
2	200	200	60	100	15	⊙	×
3	200	200	60	100	20	⊙	×
4	200	200	60	100	25	⊙	×
5	200	200	60	100	30	⊙	×

(⊙: better, ○: best)

EXAMPLE VI

Evaluation of Appropriate Processing Temperature

To verify appropriate processing temperature, the composition corresponding to item number 4 shown in Table 3 was used, and the resist was removed at different processing temperatures as listed in Table 5. The other processing conditions were the same as those in Example 4. The removal state of the resist and the attacked states of an aluminum layer and a silicon layer were observed using SEM. Again, the 𐄂 indicates the underlying layer does not show the effects of attack, and a circle indicates the underlying layer does show the effects of attack.

From the result shown in Table 5, it was observed that an appropriate reaction temperature for removing the resist was in the lower temperature range from about 45°C to about 70°C, because the underlying layer was not attacked noticeably in that range.

Table 5: Resist Removing Performance By Temperature

Item	MEA (ml)	MMP (ml)	Catechol (g)	Water (ml)	Temperature (°C)	Observations of resist removing capability	Attacked or not (Al, Si)
1	200	200	60	100	45	⊙	×
2	200	200	60	100	50	⊙	×
3	200	200	60	100	55	⊙	×
4	200	200	60	100	60	⊙	×
5	200	200	60	100	65	⊙	×
6	200	200	60	100	70	⊙	×

EXAMPLE VII

Comparison of Resist Removing Capability

In this example, the via hole was formed using the resist pattern in the same manner as that of Example 4, the resist was removed with the composition corresponding to item number 4 shown in Table 3, the processing time was 20 minutes, and the reaction temperature was 60°C. The resultant material was observed using SEM, and the observation results are shown in FIG. 3.

In a comparative example, the resist was removed using a conventional resist removing composition, with other conditions being the same as those in the above described examples, and then the resultant material was observed using SEM. The observation results are shown in FIG. 4.

When the SEM photographs shown in FIGs. 3 and 4 are compared, one can see the resist was completely removed when the resist removing composition according to the present invention was used, while the resist partially remains when the conventional resist removing composition was used. Also, although the underlying aluminum layer was not attacked in the present invention, the aluminum layer was attacked partially in the case of using the conventional resist removing composition.

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EXAMPLE VIII

Consumption of Components of Resist Removing Composition

The amount of components of the resist removing compositions were analyzed by gas chromatography during resist removal for the composition corresponding to item number 4 shown in Table 3 at 8 hour intervals. The analysis results are shown in FIG. 5, in which -■- is the area % of amide, -Δ- is the area % of monoethanolamine, and -□ is the area % of methyl methoxy propanoate, respectively. From the results shown in FIG. 5, it was observed that the area % of amide was constant at about 80 % even after 48 hours had elapsed. Also, the area % of monoethanolamine was constant at 3.4. The area % of methyl methoxy propanoate was reduced from 0.9 to 0.5 after 24 hours elapsed, until it became essentially 0 after 40 hours.

Considering that the main active component of the composition according to the present invention is amide, little change in the content of the amide even after 48 hours implies that the composition according to the present invention is not quickly consumed in the process and can be used for a long time. This means that the composition according to the present invention can enhance the productivity and can reduce the manufacturing cost significantly, unlike the conventional resist removing composition which must be replaced every 24 hours.

The amide compound according to the present invention has an excellent capability for removing a resist. Thus, the resist removing agent having the amide compound or resist removing composition according to the present invention has an excellent capability for removing a resist and can effectively remove polymer and organometallic polymer. Also, the layer underlying the resist may not be attacked. Therefore, when the resist removing agent or resist removing composition according to the present invention is used, it is not necessary to perform a pre-removal step for removing the polymer and a post-removal step for preventing the underlying layer from being attacked. Thus, the resist removing process can be simplified and the processing time can be reduced. Also, the temperature required for removing the

resist can be set to a lower temperature. ²² Further, the resist removing apparatus can be simplified and made more compact.

It will be apparent to those skilled in the art that various modifications and variations of the present invention can be made without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this invention provided they come within the scope of the appended claims and their equivalents.

What Is Claimed Is:

1. A resist removing method comprising:
providing a substrate;
forming a resist on the substrate; and
contacting the substrate with a resist removing agent comprising N alkanol alkoxy alkanamide, to remove the resist from the substrate.

2. The method according to claim 1, wherein, during said contacting, the N alkanol alkoxy alkanamide is of the formula (1):



wherein:

R_1 is hydrogen, a C_1 to C_5 hydrocarbon, or an aromatic hydrocarbon having 1 to 3 rings,

R_2 is a C_1 to C_5 hydrocarbon or aromatic hydrocarbon having 1 to 3 rings, and

R_3 and R_4 are, independently, a C_1 to C_5 hydrocarbon.

3. The method according to claim 2, wherein, during said contacting:

R_1 is hydrogen,

R_2 is $-CH_2CH_2-$,

R_3 is $-CH_2CH_2-$, and

R_4 is $-CH_3$.

4. The method according to claim 1, further comprising:

rinsing the substrate; and

drying the substrate.



5. The method according to claim 1, wherein said contacting is performed at a temperature in a range from about 45°C to about 70°C.

6. The method according to claim 1, wherein said contacting is performed for a time in a range from about 10 minutes to about 30 minutes.

7. A resist removing method comprising:
providing a substrate;
forming a resist on the substrate; and
contacting the substrate with a resist removing composition comprising N alkanol alkoxy alkanamide and an attack inhibitor, to remove the resist from the substrate.

8. The method according to claim 7, wherein, during said contacting, the N alkanol alkoxy alkanamide is of the formula (1):



wherein:

R_1 is hydrogen, a C_1 to C_5 hydrocarbon, or an aromatic hydrocarbon having 1 to 3 rings,

R_2 is a C_1 to C_5 hydrocarbon or an aromatic hydrocarbon having 1 to 3 rings,
and

R_3 and R_4 are, independently, a C_1 to C_5 hydrocarbon.

9. The method according to claim 7, wherein, during said contacting, the attack inhibitor is a compound of the formula (2):





wherein:

R_6 is a C_1 to C_5 hydrocarbon, a C_1 to C_5 hydrocarbon having a $-COOH$ group, an aromatic hydrocarbon having 1 to 3 rings, or an aromatic hydrocarbon having 1 to 3 rings and a $-COOH$ group, and

n is an integer from 1 to 4.

10. The method according to claim 7, wherein, during said contacting:
the N alkanol alkoxy alkanamide is in a range from about 50 to about 99.9 weight % of the composition, and
the attack inhibitor is in a range from about 0.01 to about 30 weight % of the resist removing composition.

11. The method according to claim 7, further comprising mixing a polar material having a dipole moment not less than about 3 into the resist removing composition, prior to completion of said contacting.

12. The method according to claim 11, wherein, during said mixing, the polar material is in a range from about 0.01 to about 30 weight % of the resist removing composition.

13. The method according to claim 7, further comprising:
rinsing the substrate; and
drying the substrate.

14. The method according to claim 7, wherein said contacting is performed at a temperature in a range from about $45^{\circ}C$ to about $70^{\circ}C$.

15. The method according to claim 7, wherein said contacting is performed for a time in a range from about 10 minutes to about 30 minutes.



16. A resist removing method comprising:
providing a substrate;
forming a resist on the substrate; and
contacting the substrate with a resist removing composition comprising
alkanolamine and alkyl alkoxy alkanoate, to remove the resist from the substrate.

17. The method according to 16, wherein, during said contacting, the
alkanolamine is of the formula (3):



wherein:

R_1 is hydrogen, a C_1 to C_5 hydrocarbon, or an aromatic hydrocarbon having 1 to 3 rings, and

R_2 is a C_1 to C_5 hydrocarbon or an aromatic hydrocarbon having 1 to 3 rings.

18. The method according to claim 16, wherein, during said contacting, the
alkyl alkoxy alkanoate is of the formula (4):



wherein R_3 , R_4 and R_5 are, independently, a C_1 to C_5 hydrocarbon.

19. The method according to claim 16, wherein, during said contacting:
the alkanolamine is in a range from about 10 to about 70 weight % of the
composition, and

the alkyl alkoxy alkanoate is in a range from about 10 to about 70 weight % of
the composition.



20. The method according to claim 17, wherein, during said contacting:

R_1 is hydrogen, and

R_2 is $-\text{CH}_2\text{CH}_2-$.

21. The method according to claim 18, wherein, during said contacting:

R_3 is $-\text{CH}_2\text{CH}_2-$,

R_4 is $-\text{CH}_3$, and

R_5 is $-\text{CH}_3$.

22. The method according to claim 16, further comprising mixing an attack inhibitor into the resist removing composition, prior to completion of said contacting.

23. The method according to claim 22, wherein, during said mixing, the attack inhibitor is a compound of the formula (2):



wherein

R_6 is a C_1 to C_5 hydrocarbon, a C_1 to C_5 hydrocarbon having a $-\text{COOH}$ group, an aromatic hydrocarbon having 1 to 3 rings, or an aromatic hydrocarbon having 1 to 3 rings and a $-\text{COOH}$ group, and

n is an integer from 1 to 4.

24. The method according to claim 22, wherein, during said mixing the attack inhibitor is in a range from about 0.01 to about 30 weight % of the resist removing composition.



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25. The method according to claim 16, further comprising mixing a polar material with a dipole moment not less than about 3 into the resist removing composition, prior to completion of said contacting.

26. The method according to claim 25, wherein, during said mixing, the polar material is in a range from about 0.01 to about 30 weight % of the resist removing composition.

27. The method according to claim 16, wherein said contacting is performed at a temperature in a range from about room temperature to about 120°C.

28. The method according to claim 16, wherein said contacting is performed for a time in a range from about 10 minutes to about 30 minutes.

29. The method according to claim 16, further comprising heating the resist removing composition at a temperature in a range from about room temperature to about 120°C, before said contacting.

30. The method according to claim 29, wherein said contacting is performed at a temperature in a range from about 45°C to about 70°C.

31. The method according to claim 16, further comprising:
rinsing the substrate; and
drying the substrate.

32. A resist removing method comprising:
providing a substrate;
forming a resist on the substrate; and



contacting the substrate with a resist removing composition to remove the resist from the substrate, the resist removing composition comprising

alkanolamine in a range from about 10 to about 70 weight % of the composition,

alkyl alkoxy alkanoate in a range from about 10 to about 70 weight % of the composition,

an attack inhibitor in a range from about 0.01 to about 30 weight % of the composition, and

a polar material with a dipole moment not less than about 3, in a range from about 0.01 to about 30 weight % of the composition.

33. The method according to claim 32, further comprising heating the resist removing composition at a temperature in a range from about room temperature to about 120°C, before said contacting,

wherein the contacting is performed at a temperature in a range from about 45°C to about 70°C.

34. The method according to claim 32, wherein said contacting is performed at a temperature in a range from about room temperature to about 120°C.

35. The method according to claim 33, wherein said contacting is performed for a time in a range from about 10 minutes to about 30 minutes.

36. The method according to claim 34, wherein said contacting is performed for a time in a range from about 10 minutes to about 30 minutes.

37. An apparatus for removing resist from a substrate comprising:
a source of a resist removing agent comprising N alkanol alkoxy alkanamide;



a supply unit in flow communication with the source, through which the resist removing agent is supplied; and

a resist removing unit in flow communication with the supply unit, for directing the resist removing agent into contact with a substrate disposed in the resist removing unit, whereby the resist is removed from the substrate.



38. An apparatus for removing resist from a substrate comprising:
a source of a resist removing composition comprising N alkanol alkoxy alkanamide and an attack inhibitor;
a supply unit in flow communication with the source, through which the resist removing composition is supplied; and
a resist removing unit in flow communication with the supply unit, for directing the resist removing composition into contact with a substrate disposed in the resist removing unit, whereby the resist is removed from the substrate.
39. An apparatus for removing resist from a substrate comprising:
a source of a resist removing composition comprising alkanolamine and alkyl alkoxy alkanoate;
a supply unit in flow communication with the source, through which the resist removing composition is supplied; and
a resist removing unit in flow communication with the supply unit, for directing the resist removing composition into contact with a substrate disposed in the resist removing unit, whereby the resist is removed from the substrate.
40. An apparatus for removing resist from a substrate comprising:
a source of a resist removing composition comprising
 alkanolamine in a range from about 10 to about 70 weight % of the composition,
 alkyl alkoxy alkanoate in a range from about 10 to about 70 weight % of the composition,
 an attack inhibitor in a range from about 0.01 to about 30 weight % of the composition, and
 a polar material with a dipole moment not less than about 3, in a range from about 0.01 to about 30 weight % of the composition;



a supply unit in flow communication with the source, through which the resist removing composition is supplied; and

a resist removing unit in flow communication with the supply unit, for directing the resist removing composition into contact with a substrate disposed in the resist removing unit, whereby the resist is removed from the substrate.

41. The apparatus according to claim 37, 38, 39 or 40, further comprising:

a source of a rinsing solution;

a rinsing unit connected to the resist removing unit and in flow communication with the source of rinsing solution, for rinsing a substrate disposed in the rinsing unit with the rinsing solution after the resist is removed;

a source of a drying agent; and

a drying unit connected to the rinsing unit and in flow communication with the source of drying agent, for drying the rinsing solution which remains on a substrate disposed in the drying unit with the drying agent.

42. The apparatus according to claim 41, wherein:

the resist removing unit comprises a removing bath;

the rinsing unit comprises a rinsing bath different than the removing bath; and

the drying unit comprises a drying bath different from both the removing bath and the rinsing bath.

43. The apparatus according to claim 41, further comprising an integral carrier connected to the resist removing unit, the rinsing unit and the drying unit, for horizontally carrying the substrate from the resist removing unit to the drying unit through the rinsing unit, wherein:

the resist removing unit further comprises a first nozzle in flow communication with the supply unit, for spraying onto the substrate one of the resist removal agent and the resist removal composition,



the rinsing unit further comprises a second nozzle in flow communication with the source of rinsing solution through the supply unit, for spraying the rinsing solution onto the substrate, and

the drying unit further comprises a third nozzle in flow communication with the source of drying agent through the supply unit, for spraying the drying agent onto the substrate.

44. The apparatus according to claim 41, further comprising:

a vertical substrate support which carries the substrate among the resist removing unit, the rinsing unit and the drying unit by vertical movement; and

a supply duct in flow communication, through the supply unit, with the source of rinsing solution, the source of drying agent, and with a source of a resist removing material, for successively spraying the resist removing material, the rinsing solution, and the drying agent toward the substrate,

wherein each of the resist removal unit and the rinsing unit and the drying unit is displaced vertically with respect to one another, and

wherein the resist removing material is one of the resist removing agent and the resist removing composition.