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(54) Title: NOVEL RESIST MATERIAL

(57) Abstract: The present invention relates to the use of fullerols having the formula $C_{2x}(OH)_n$ where x is at least 10 and n is at least 2 as resist materials. The invention also includes within its scope methods of patterning a fullerol-based resist layer.

# NOVEL RESIST MATERIAL

The present invention relates to a resist material, particularly but not exclusively an electron beam resist material, and to a method for forming a finely patterned resist layer on a substrate surface using the resist material.

As is well known, the manufacturing process of various kinds of electronic or semiconductor devices such as ICs, LSIs and the like involves a fine patterning of a resist layer on the surface of a substrate material such as a semiconductor silicon wafer. This fine patterning process has traditionally been conducted by the photolithographic method in which the substrate surface is uniformly coated with a positive or negative tone photoresist composition to form a thin layer of the photoresist composition and selectively irradiating with actinic rays (such as ultraviolet light) through a photomask followed by a development treatment to selectively dissolve away the photoresist layer in the areas exposed or unexposed, respectively, to the actinic rays leaving a patterned resist layer on the substrate surface. The thus obtained patterned resist layer is utilized as a mask in the subsequent treatment on the substrate surface such as etching.

The fabrication of structures with dimensions of the order of nanometers is an area of considerable interest since it enables the realisation of electronic and optical devices which exploit novel phenomena such as quantum confinement effects and also allows greater component packing density. As a result, the resist layer is required to have an ever increasing fineness which can by accomplished only by using actinic rays having a shorter wavelength than the conventional ultraviolet light. Accordingly, it is now the case that,

in place of the conventional ultraviolet light, electron beams (e-beams), excimer laser beams and X-rays are used as the short-wavelength actinic rays. Needless to say the minimum size obtainable is primarily determined by the performance of the resist material and the wavelength of the actinic rays.

Various materials have been proposed as suitable resist materials. These include organic resinous materials such as methacrylic resin-based, polystyrene-based and novolac resin based materials. In the case of negative tone resists based on polymer crosslinking, there is an inherent resolution limit of about 10 nm, which is the approximate radius of a single polymer molecule. Other materials have been investigated, including low molecular weight organic molecules (Yoshiiwa M, et. al., Appl. Phys. Lett. 69 (1996) 2605) and inorganic substances such as metal fluorides (Fujita J, et. al., Appl. Phys. Lett. 66 (1995) 3064). $C_{60}$ (fullerene) demonstrates negative tone behaviour, but has low sensitivity (critical dose about $1x10^{-2}$ $C/cm^2$). Various methanofullerene derivatives were subsequently shown to be useful e-beam resist materials by the present inventors, Appl. Phys. Lett. volume 72, page 1302 (1998) and US6,117,617.

It is also known to apply a technique called "chemical amplification" to the polymeric resist materials. A chemically amplified resist material is generally a multi-component formulation in which there is a main polymeric component, such as a novolac resin which contributes towards properties such as resistance of the material to etching and its mechanical stability and one or more additional components which impart desired properties to the resist and a sensitizer. By definition, the chemical amplification occurs

through a catalytic process involving the sensitizer which results in a single irradiation event causing exposure of multiple resist molecules. In a typical example the resist comprises a polymer and a photoacid generator (PAG) as sensitizer. The PAG releases a proton in the presence of radiation (light or e-beam). This proton then reacts with the polymer to cause it to lose a dissolution inhibiting functional group. In the process, a second proton is generated which can then react with a further molecule. The speed of the reaction can be controlled, for example, by heating the resist film to drive the reaction. After heating, the reacted polymer molecules are soluble in a developer whilst the unreacted polymer is not (i.e. positive tone resist). In this way the sensitivity of the material to actinic radiation is greatly increased, as small numbers of irradiation events give rise to a large number of exposure events.

In other chemical amplification schemes, irradiation results in cross-linking of the exposed resist material, thereby creating a negative tone resist. The resist material may be self cross-linking or a cross linking molecule may be included. Chemical amplification of polymeric-based resists is disclosed in US5,968,712, US5,529,885, US5,981,139 and US6,607,870 the disclosure of which references is incorporated herein by reference.

It will be understood that, due to the nature of the resist materials, the standard technique for forming a uniform film of the resist material on a substrate is by dissolution in a solvent and spin coating. Mention has already been made of the use of a developer to remove exposed (or unexposed) resist material after irradiation. Typical solvents used for these purposes are organic (e.g. esters, acetates, glycol ethers, xylene) and often halogenated

(e.g. chloroform, monochlorobenzene). Such solvents are unsatisfactory for cost, health and/or environmental considerations.

It is an object of the present invention in one aspect to provide a novel photoresist material which obviates or mitigates one or more disadvantages associated with prior art resist materials.

In a first aspect, the invention resides in the use of a fullerol as a resist material.

By fullerol (sometimes referred to as fullerenol or hydroxylated fullerene) is meant any fullerene derivative having at least two hydroxy groups covalently linked to the cage carbons. Preferably, there are no more than 30 such hydroxy groups. Preferably, there are at least 18 such hydroxy groups particularly for aqueous usage. Most preferably, there are from 22 to 26 such hydroxy groups. Where a non-aqueous solvent (e.g. DMSO) is required, there are preferably from 6 to 10 hydroxy groups.

By fullerene is meant any closed carbon cage molecule of formula $C_{2x}$ where x is at least 10. Thus the compounds of the present invention can conveniently be represented by the formula $C_{2x}(OH)_n$ where x is at least 10 (preferably 17) and n is at least 2. Values of x less than 10 are theoretically impossible. Compounds of formulae $C_{50}(OH)_n$, $C_{60}(OH)_n$ and $C_{70}(OH)_n$ are particularly useful, especially $C_{60}(OH)_n$. Compounds having $x < 30$ are inherently unstable and will decompose spontaneously. Hence x is preferably at least 30.

According to a second aspect of the invention there is provided a method for the formation of a patterned resist layer on a substrate surface by patternwise irradiation with actinic radiation comprising the steps of:-

(i) forming a coating layer comprising a fullerol on the substrate surface,

(ii) irradiating the coating layer patternwise, and

(iii) removing unirradiated areas of the coating layer.

Step (i) may be achieved by application of the fullerol in solution, followed by removal of the solvent. Solvent may be removed by heating, a process which is commonly referred to as a soft pre-bake. Convenient coating techniques include spin coating (preferred), dipping and roller coating. Other conventional coating techniques include vacuum sublimation. When spin coating, it will be appreciated that the solids content of the coating solution can be adjusted to provide a desired film thickness based upon the specific spinning equipment utilized, and parameters such as the viscosity of the solution, the speed of the spinner and the amount of time allowed for spinning. The thickness of the film is not particularly limited and may be from about 10 nm or less up to about 500 nm. A particularly preferred film thickness is from about 10 nm to about 200 nm.

The nature of the substrate is not particularly limited, but in the preparation of electronic components, the substrate will normally be a silicon or silicon dioxide wafer for the production of microprocessors and other integrated circuit components. Aluminum-aluminum oxide, gallium arsenide and silicon nitride wafers can also serve as substrate.

Surprisingly, the inventors have found that fullerol can successfully be cast using water as solvent. The preferred concentration of fullerol in the casting solution will depend to some extent on the desired thickness of the final film. For very thin films a concentration of from 1 to 5 mg/ml can be used. For relatively thicker films, a concentration of from about 5 to 120 mg/ml is preferred.

In certain embodiments it may be desirable to use an organic solvent (e.g. DMSO) in one or both of steps (i) and (iii) , in which case the fullerol is preferably $C2_x(OH)_n$ with n being from 6 to 10.

Step (iii) is conveniently achieved by selectively dissolving the unirradiated areas of the coating layer in a solvent. The inventors have found that water can also be used as the solvent in step (iii). It will therefore be appreciated that in a preferred embodiment of the invention water is used as the solvent in both steps (i) and (iii), thereby obviating the need for any organic solvents in the method.

Preferably, when the solvent used in step (i) is water, the coating solution of step (i) additionally comprises a surfactant. It has been found that the use of a surfactant assists in formation of the coating layer and results in higher sensitivity of the layer to actinic radiation. A preferred surfactant is aminopropyl terminated polydimethyldisiloxane. Other useful surfactants include sodium dodecyl benzene sulfonate and sodium lauryl ether sulphate. Only trace quantities of the surfactant are required (e.g. 5 $\mu$l or less of polydimethyldisiloxane added to 100 $\mu$l of an aqueous solution of 37 mg/ml of fullerol is sufficient).

Preferably, the fullerol is chemically amplified. That is, the coating layer formed in step (i) preferably includes at least one additional component (sensitizer) which increases the sensitivity of the exposed layer to the actinic radiation of step (ii). It will be appreciated that when the coating layer is formed from solution, the additional component(s) is/are also in solution. In a preferred embodiment, the additional components are a photo acid generator and a cross-linker.

Suitable PAGs are described in US6,607,870 the disclosure of which is incorporated herein by reference) and include non-ionic, organic acid generators. Specific non-ionic organic acid generators include halogenated non-ionic compounds such as, for example, 1,1-bis[p-chlorophenyl]-2,2,2-trichloroethane (DDT); 1,1-bis[p-methoxyphenyl]-2,2,2-trichloroethane; 1,2,5,6,9,10-hexabromocyclododecane; 1,10-dibromodecane; 1,1-bis[p-chlorophenyl]2,2-dichloroethane; 4,4'-dichloro-2-(trichloromethyl)benzhydrol or 1,1-bis(chlorophenyl) 2-2,2-trichloroethanol; hexachlorodimethylsulfone; 2-chloro-6-(trichloromethyl)pyridine; O,O-diethyl-O-(3,5,6-trichloro-2-pyridyl)phosphorothioate; 1,2,3,4,5,6-hexachlorocyclohexane; N(1,1-bis[p-chlorophenyl]-2,2,2-trichloroethylacetamide; tris[2,3-dibromopropyl]isocyanurate; 2,2-bis[p-chlorophenyl]-1,1-dichloroethylene. Suitable photoacid generators are also disclosed in European Patent Application Nos. 0164248 and 0232972. Especially preferred is triphenylsulphonium triflate. In addition to PAGs photoinitiators such as triarylsulfonium hexafluoroantiminate salts or triarylsulfonium hexafluorophosphate salts may be used.

Amine-based crosslinkers are preferred. Suitable amine-containing crosslinkers include urea-formaldehyde, melamine-formaldehyde, benzoguanamine-formaldehyde, glycoluril-formaldehyde resins and combinations thereof. Other suitable amine-based crosslinkers include the melamines manufactured by American Cyanamid Company such as Cymel(TM)300, 301, 303, 350, 370, 380, 1116 and 1130; benzoguanamine resins such as Cymel(TM)1123 and 1125; glycoluril resins Cymel(TM)1170, 1171, 1172; and urea-based resins Beetle(TM)60, 65 and 80. A large number of similar amine-based compounds are presently commercially available from various suppliers. As known to those in the art, polymeric amine-based resins may be prepared by the reaction of acrylamide or methacrylamide copolymers with formaldehyde in an alcohol-containing solution, or alternatively by the copolymerization of N-alkoxymethyl acrylamide or methacrylamide with other suitable monomers.

Of the above crosslinkers, the melamines are preferred, and particularly preferred are hexaalkoxymethylmelamines such as the above identified Cymel(TM) resins, especially Cymel(TM) 350.

In addition to the amine-based crosslinkers, epoxide crosslinkers can also be used. Where water is used as a solvent, Erisys Ga-240 by CVC is suitable. For non aqueous solvents, there are many choices including epoxy novolacs such as DEN439 by Dow.

The preferred mass ratio of fullerol to sensitiser is from about 1:0.1 to about 1:1. The preferred ratio of fullerol by mass to cross linker by volume is from about 1:0.5 to about 1:5.

Step (ii) is preferably conducted using electron beam energy, although EUV, X-rays and excimer laser beams may also be used. The patternwise irradiation may be achieved by scanning the actinic ray source according to the required pattern, or by using a mask formed to the pattern over the substrate.

The method may include the additional step, between steps (ii) and (iii) of a post exposure bake, in which the substrate is heated to an elevated temperature (e.g. 50 to 80 °C, preferably about 60°C, for a predetermined period (e.g. 0.1 to 10 minutes, preferably about 1 minute). Temperatures above 80°C cause unwanted film crosslinking.

Subsequent to step (iii), the developed substrate may be selectively processed on those substrate areas bared of the coating composition, for example by chemically etching or plating using procedures well known in the art. For the manufacture of microelectronic substrates, for example the manufacture of silicon dioxide wafers, suitable etchants include a plasma gas etch and a hydrofluoric acid etching solution. After such processing, the resist layer may be removed from the processed substrate using known stripping procedures. The historical background, types and processing of conventional photoresists are described by DeForest, Photoresist Materials and Processes, McGraw Hill Book Company, New York, ch. 2, 1975, and by Moreau, Semiconductor Lithography, Principles, Practices and Materials, Plenum Press, New York, ch. 2 and 4, 1988, both incorporated herein for their teaching of photoresist compositions and methods of making and using the same.

The invention further resides in a substrate treated in accordance with the process of the second aspect.

The invention still further resides in a resist composition, said composition comprising an aqueous solution of fullerol and a surfactant.

Examples of the invention will now be described by way of example only with reference to the accompanying drawing, which is a plot of normalised film thickness against dose of e-beam radiation for resists made in accordance with the second aspect of the invention.

**Example 1**

$C_{60}(OH)_n$ in which n is 22 to 26 (hereinafter simply referred to as fullerol) obtained from Mercorp, USA was dissolved in ultrapure (DI) water to a concentration of 36mg/ml. 100 µl of this solution was deposited onto an $SiO_2$ terminated silicon wafer of 4 $cm^2$ size. The wafer was spun at 600 rpm for 60 seconds, followed by 3000 rpm for 10 seconds, to produce a smooth uniform film of 90 nm thickness, as measured using a surface profiler (Detak 3st Auto, Sloan). Although no pre-exposure bake was used in this example, it will be appreciated that such a procedure may be applied in other cases. A suitable pre-bake would be 50°C for 20 minutes.

The film so-prepared was exposed to irradiation with 20 keV electrons at varying doses in a patternwise manner (FEI XL30SFEG SEM). After exposure the resist was subjected to a 60 °C post exposure bake for 60 seconds and was then developed by dipping the substrate into DI water for 60 seconds. After development, unexposed areas of the film had been removed

from the substrate to leave a positive relief of resist layer on the silicon substrate.

The response curve is shown in the drawing and is discussed below.

**Example 2**

Example 1 was repeated except that a lower concentration of 6.7 mg/ml of the fullerol was achieved by the addition of a trace amount (5% by volume)of the surfactant polydimethylsiloxane (aminopropyl terminated) obtained from Sigma Aldrich. The thickness of the film obtained was 100 nm

After development, unexposed areas of the film had been removed from the substrate to leave a positive relief of resist layer on the silicon substrate.

The response curve is shown in the drawing and is discussed below.

**Example 3**

An aqueous coating solution of fullerol (1 mg/100 µl), triphenylsulphonium sulphate (0.09 mg/100 µl) and hexamethoxymethylmelamine (sold by American Cyanamid under the tradename Cymel 350) (0.003 µl/100 µl was made up in DI water together with a trace amount of the polydimethylsiloxane (aminopropyl terminated) surfactant. Coating (to give a film of thickness 90 nm) and further processing was as for example 1

After development, unexposed areas of the film had been removed from the substrate to leave a positive relief of resist layer on the silicon substrate.

The response curve is shown in the drawing and is discussed below.

**RESULTS**

Referring to the drawing, the response curves for the three examples are expressed as normalised film thickness against exposure dose. The data points indicate the (normalised) difference in depth between the exposed and unexposed areas of the resist layer after development. The sensitivity of the resist material is the dose at which the response curve reaches 50% of the original film thickness. For example 1, the sensitivity is about 4100 $\mu C/cm^2$. This is reduced by addition of the surfactant (Example 2) to about 290 $\mu C/cm^2$ and even further to about 23 $\mu C/cm^2$ by chemical amplification. The steepness of the response curves is an indication of the contrast achievable using the resist material. It will be noted that all three examples exhibit good contrast.

## Claims

1. The use as a resist material of a fullerol having the formula $C_{2x}(OH)_n$ wherein x is at least 10 and n is at least 2.

2. The use as claimed in claim 1 wherein n is at least 18 but no more than 30

3. The use as claimed in claim 1 or 2, wherein x is at least 30.

4. The use as claimed in claim 1 or 2, wherein said fullerol is $C_{50}(OH)_n$, $C_{60}(OH)_n$, or $C_{70}(OH)_n$.

5. A method for the formation of a patterned resist layer on a substrate surface by patternwise irradiation with actinic radiation comprising the steps of:-

(i) forming a coating layer comprising a fullerol having a formula of $C_{2x}(OH)_n$ where x is at least 10 and n is at least 2 on the substrate surface,

(ii) irradiating the coating layer patternwise, and

(iii) removing unirradiated areas of the coating layer.

6. The method as claimed in claim 5 wherein step (i) is achieved by application of the fullerol in solution, followed by removal of the solvent.

7. The method of claim 6 wherein the solvent used to dissolve the fullerol is water.

8. The method of claim 7 wherein the coating solution of step (i) additionally comprises a surfactant.

9. The method of claim 8 wherein the surfactant is selected from aminopropyl terminated polydimethyldisiloxane, sodium dodecyl benzene sulfonate and sodium lauryl ether sulfate.

10. The method of claim 6 wherein the solvent used to dissolve the fullerol is an organic solvent.

11. The method of claim 10 wherein $6 \leq n \leq 10$.

12. The method of any one of claims 5 to 11 wherein step (iii) is achieved by selectively dissolving the unirradiated areas of the coating layer in a solvent.

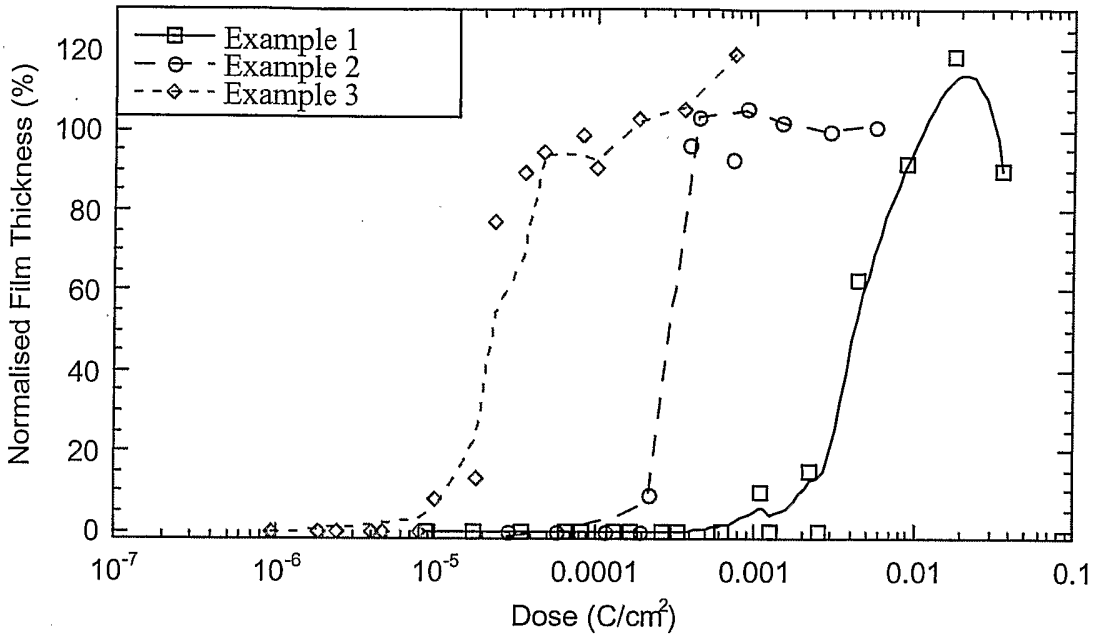
13. The method of claim 12 wherein the solvent used in step (iii) is water.

14. The method of any one of claims 5 to 13 wherein the fullerol is chemically amplified by including in the coating layer formed in step (i) at least one additional component which increases the sensitivity of the exposed layer to the actinic radiation of step (ii).

15. The method of claim 14 wherein the additional components are a photo acid generator and a cross-linker.

16. A substrate treated in accordance with the method of any one of claims 5 to 15.

17. A resist composition, comprising an aqueous solution of fullerol having a formula of $C_{2x}(OH)_n$ where x is at least 10 and n is at least 2, and a surfactant.


Example 1
Example 2
Example 3
Normalised Film Thickness (%)
120
100
80
60
40
20
0
$10^{-7}$
$10^{-6}$
$10^{-5}$
0.0001
0.001
0.01
0.1
Dose (C/cm$^2$)