semiconductor packaging require strippers that are both potent and selective in their action.

[0004] It was unexpectedly discovered that the compositions of this disclosure can remove multiple layers of different dissolution or solubility properties in an organic film on a patterned semiconductor substrate in one step without damaging the substrate or its structure.

SUMMARY OF THE DISCLOSURE

[0005] The present disclosure features a process for stripping an organic film on a patterned semiconductor substrate (e.g., a patterned metal containing semiconductor substrate). The process includes treating the organic film with an aqueous stripper composition to remove the organic film in one step. The organic film includes at least a first layer and a second layer, the first layer has a dissolution rate of at most about 0.01 μm/min in a developer at 25ºC, and the second layer has a dissolution rate of greater than about 0.01 μm/min in the developer at 25ºC.

[0006] In some embodiments, the present disclosure features a three-dimensional object formed by the processes described above. In some embodiments, the present disclosure features a semiconductor device that includes the three dimensional object. In some embodiments, the semiconductor device is an integrated circuit, a light emitting diode, a solar cell, or a transistor.

Detailed Description of the Disclosure

[0007] Some embodiments of this disclosure describe a process for stripping an organic film (e.g., a multi-layer or multi-stacked organic film) having different dissolution or solubility properties on a patterned semiconductor substrate (e.g., a patterned metal containing semiconductor substrate) in one

step by using an aqueous stripper composition. The organic film can include at least a first layer and a second layer. The first layer (e.g., a highly cross-linked layer) can be insoluble in a developer at 25ºC. The second layer (e.g., a lightly cross-linked layer or a layer that is not cross-linked) can have a higher solubility in a developer than the first layer at 25ºC. In some embodiments, the second layer can be soluble in a developer at 25ºC. In some embodiments, the organic film can include more than two (e.g., three, four, five, six, or seven) layers, some of which have dissolution/solubility properties similar to the first layer and some of which have dissolution/solubility properties similar to the second layer.

[0008] In some embodiments, the first layer is insoluble in a developer at 25ºC. For example, the first layer can have a dissolution rate of at most about 0.01 μm/min (e.g., at most about 0.005 μm/min, at most about 0.001 μm/min, at most about 0.0005 μm/min, or at most about 0.0001 μm/min) in a developer at 25ºC. The developer can include at least one organic solvent, at least one aqueous solution (e.g., a solution in the pH range of 2-14), or a mixture thereof. Examples of organic solvents that can be used as a suitable developer include, but are not limited to, *gamma*-butyrolactone (GBL), N-methyl-2-pyrrolidone (NMP), dimethylimidazolidinone, N-methylcaprolactam, N-methylpropionamide, N,N-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), N,N-diethylformamide, diethylacetamide, methyl ethyl ketone (MEK), methyl isobutyl ketone (MIBK), 2-heptanone, cyclopentanone (CP), cyclohexanone, n-butyl acetate (nBA), propylene glycol methyl ether acetate (PGMEA), propylene glycol methyl ether (PGME), ethyl lactate (EL), propyl lactate, 3-methyl-3-methoxybutanol, tetralin, isophorone, ethylene glycol monobutyl ether, diethylene glycol monoethyl ether, diethylene glycol monoethyl ether acetate, diethylene glycol dimethyl ether, diethylene glycol methylethyl ether, triethylene glycol monoethyl ether, dipropylene glycol monomethyl ether, methyl 3-methoxypropionate, ethyl 3-ethoxypropionate, diethyl malonate, ethylene glycol 1,4:3,6-dianhydrosorbitol, 2,5-dimethyl ether (2,5-dimethylisosorbide), 1,4:3,6-dianhydrosorbitol 2,5-diethyl ether (2,5-

diethylisosorbide) and mixtures thereof. In some embodiments, organic solvents that can be used as a developer include n-butyl acetate (nBA), propylene glycol methyl ether acetate (PGMEA), propylene glycol methyl ether (PGME), ethyl lactate (EL), propyl lactate, 3-methyl-3-methoxybutane and mixture thereof. Examples of aqueous solutions that can be used as a developer include, aqueous alkaline solutions (e.g., a TMAH solution) and aqueous acidic solutions. In some embodiments, the developer can be the aqueous stripper composition described herein. In some embodiments, the first layer has a weight average molecular weight of at least about 20,000 g/mol (e.g., at least about 30,000 g/mol, at least about 40,000 g/mol, at least about 50,000 g/mol, at least about 60,000 g/mol, at least about 70,000 g/mol, at least about 80,000 g/mol, at least about 90,000 g/mol, or at least about 100,000 g/mol).

[0009] In some embodiments, the first layer can have a solubility in the above-mentioned developer that is less than about 1 gram (e.g., less than about 0.5 g, less than about 0.1 g, less than about 0.05 g, or less than about 0.01 g) in 1000 grams of the developer at 25°C.

[0010] In some embodiments, the second layer has a higher solubility at 25ºC than the first layer in the same developer described above. For example, the second layer can have a dissolution rate greater than about 0.01 μm/min (e.g., greater than about 0.05 μm/min, greater than about 0.1 μm/min, greater than about 0.5 μm/min, or greater than about 1 μm/min) in a developer at 25ºC. In some embodiments, the second layer can have a solubility in the above-mentioned developer that is greater than about 1 gram (e.g., greater than about 5 g, greater than about 10 g, greater than about 50 g, or greater about 100 g) in 1000 grams of the developer at 25°C. In some embodiments, the second layer can be soluble in the developer (e.g., having a dissolution rate of greater than 1 μm/min or having a solubility of greater than 50 g in 1000 grams of the developer) at 25ºC. In some embodiments, the second layer has a weight average molecular weight of at most about 200,000 g/mol (e.g., at most about 150,000 g/mol, at most about

Composition Example 1b

Formulation to create dry film (F-2)

[0045] To a 3-neck round bottom flask equipped with a mechanical stirrer was added 300 parts of cyclopentanone, 100 parts of the polymer obtained in Synthesis Example 1 (Poly-1), 5 parts of 3-(methacryloyloxy)propyltrimethoxy-silane, 3 parts of NCI-831 (trade name, available from ADEKA corporation), 31.75 parts of tetraethylene glycol diacrylate, 11.25 parts of pentaerithritol triacrylate. The composition was mechanically stirred for 18 hours. This composition was then filtered by using a 0.2 μm filter (Ultradyne from Meissner Filtration Product, Inc.).

Preparation of dry film (DF-1)

[0046] The filtered photosensitive solution (F-2) was applied via slot-die coater from Frontier Industrial Technologies (Towanda, PA) with line speed of 5 feet/minutes (150 cm per minutes) onto a polyethylene terephthalate (PET) film TA 30 (manufactured by Toray Plastics America, Inc.) having a thickness of 36 μm used as a carrier substrate and dried at 180-200°F to obtain polymeric layer with thickness of 15 microns (DF-1). On this polymeric layer, a biaxially oriented polypropylene (BOPP) films (manufactured by IMPEX GLOBAL LLC, trade name 80ga BOPP) was laminated by a roll compression to act as a protective layer.

Preparation of Highly cross-linked Layer (HCL-1)

[0047] A four inch wafer containing copper structures is coated with formulation (F-1) followed by two stage softbake process (90°C for 3 minutes and 130°C for 3 minutes) to obtain a film of 20 μm. The film is then thermally cured at 160°C for 30 minutes to produce a highly cross-linked layer.

Lamination of Dry Film Example (L-1)

[0048] After the removal of the protective layer of DF-1 by peeling, the polymeric layer of the dry film structure (6”x 6”) is placed on the 4 inch structured wafer containing the highly cross-linked layer (HCL-1). The polymeric layer is

CLAIMS

1. A process for stripping an organic film on a patterned semiconductor substrate, comprising:

treating the organic film with an aqueous stripper composition, thereby removing the organic film in one step;

wherein the organic film comprises at least a first layer and a second layer, the first layer has a dissolution rate of at most about 0.01 μm/min in a developer at 25ºC, and the second layer has a dissolution rate of greater than about 0.01 μm/min in the developer at 25ºC.

2. The process of claim 1, wherein the first layer is cross-linked.

3. The process of claim 1, wherein the patterned semiconductor substrate comprises at least one element having a feature size of at most about 5 micron.

4. The process of claim 1, wherein the patterned semiconductor substrate comprises two patterns separated by a space of at most about 200 microns.

5. The process of claim 1, wherein the patterned semiconductor substrate comprises two groups of patterns and the two groups are separated by a space of at most about 100 millimeters.

6. The process of claim 1, wherein substantially no film residue of the organic film remains after the treatment step.

7. The process of claim 1, wherein, after the treatment step, the residue of the organic film has a thickness that is less than about 5% of the original film thickness.

8. The process of claim 1, further comprising performing a plasma treatment to the patterned semiconductor substrate after the treatment step.

9. The process of claim 1, further comprising rinsing the patterned semiconductor substrate with a rinse solvent after the treatment step.

10. The process of claim 9, further comprising drying the patterned semiconductor substrate after the rinsing step.

11. The process of claim 1, wherein the patterned semiconductor substrate comprises a metal.

12. The process of claim 1, wherein the aqueous stripper composition comprises:

an alkaline compound in the amount of about 0.5 to about 25 percent by weight of the composition;

water in the amount of about 65 to 95 percent by weight of the composition;

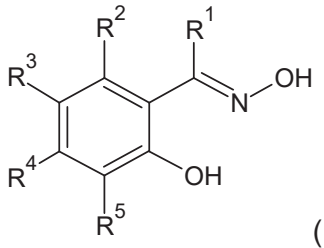
a corrosion inhibitor compound in the amount of about 0.1 to about 5 percent by weight of the composition; and

a surfactant in the amount of 0 to about 5 percent by weight of the composition.

13. The process of claim 12, wherein the alkaline compound is selected from the group consisting of tetramethyl ammonium hydroxide (TMAH), 2-hydroxyltrimethyl ammonium hydroxide, tetraethyl ammonium hydroxide (TEAH), tetrapropyl ammonium hydroxide (TPAH), tetrabutyl ammonium hydroxide (TBAH), and a mixture thereof.

14. The process of claim 12, wherein the corrosion inhibitor is a tetrazole, a triazole, a benzotriazole, a substituted triazole, or a substituted benzotriazole.

15. The process of claim 12, wherein the corrosion inhibitor is a compound of Structure (I)



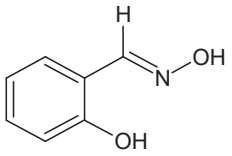
(I),

wherein

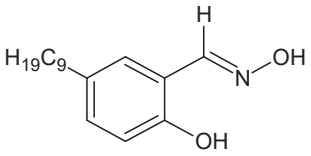
R^1 is selected from the group consisting of hydrogen, substituted or unsubstituted C_1-C_{12} linear or branched alkyl, substituted or unsubstituted C_5-C_{12} cycloalkyl or heterocycloalkyl, and substituted or unsubstituted C_5-C_{12} aryl or heteroaryl; and

R^2 to R^5 are each independently selected from the group consisting of hydrogen, halogen, substituted or unsubstituted C_1-C_{12} linear or branched alkyl, substituted or unsubstituted C_5-C_{12} cycloalkyl or heterocycloalkyl, and substituted or unsubstituted C_5-C_{12} aryl or heteroaryl; or any two adjacent groups of R^2 to R^5, together with the ring carbon atoms to which they are attached, form a six-membered ring.

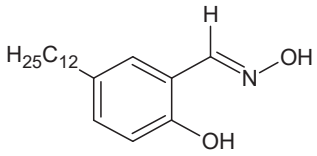
16. The process of claim 12, wherein the corrosion inhibitor is



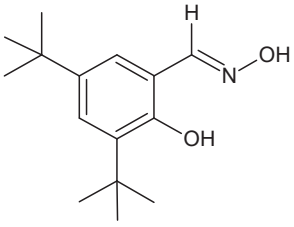
(I-a)



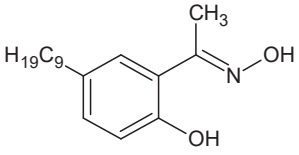
(I-b)



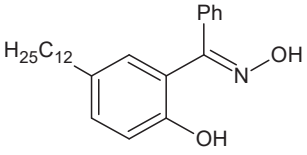
(I-c)



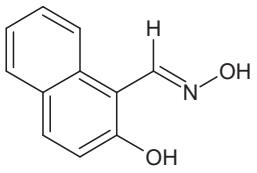
(I-d)



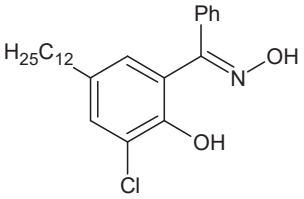
(I-e)



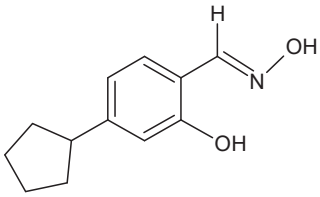
(I-f)



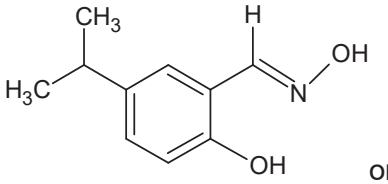
(I-g)



(I-h)

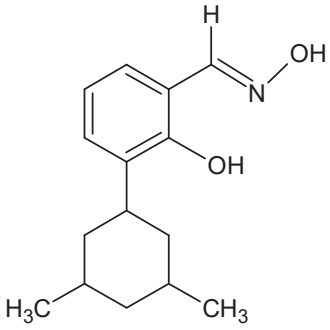


(I-i)



(I-j)

or



(I-k).

17. A three dimensional object formed by the process of claim 1.

18. A semiconductor device, comprising the three dimensional object of claim 17.

19. The semiconductor device of claim 18, wherein the semiconductor device is an integrated circuit, a light emitting diode, a solar cell, or a transistor.

20. The process of claim 1, wherein the aqueous stripper composition comprises:

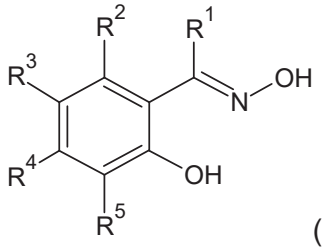
an alkaline compound in the amount of about 0.5 to about 25 percent by weight of the composition;

water in the amount of about 65 to 95 percent by weight of the composition;

a corrosion inhibitor compound in the amount of about 0.1 to about 5 percent by weight of the composition; and

a surfactant in the amount of 0.005 to about 5 percent by weight of the composition.

21. The process of claim 1, wherein the aqueous stripper composition comprises an alkaline compound, water, a corrosion inhibitor compound, and a surfactant, in which the corrosion inhibitor compound is a compound of Structure (I)



(I),

wherein

R^1 is selected from the group consisting of hydrogen, substituted or unsubstituted C_1-C_{12} linear or branched alkyl, substituted or unsubstituted C_5-C_{12} cycloalkyl or heterocycloalkyl, and substituted or unsubstituted C_5-C_{12} aryl or heteroaryl; and

R^2 to R^5 are each independently selected from the group consisting of hydrogen, halogen, substituted or unsubstituted C_1-C_{12} linear or branched alkyl, substituted or unsubstituted C_5-C_{12} cycloalkyl or heterocycloalkyl, and substituted or unsubstituted C_5-C_{12} aryl or heteroaryl; or any two adjacent groups of R^2 to R^5, together with the ring carbon atoms to which they are attached, form a six-membered ring.