

PATENT SPECIFICATION

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(54) A METHOD OF TRIMMING PHOTORESIST FILM

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America of
5 Wilmington, Delaware, 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
10 described in and by the following statement:

This invention relates to a method of trimming a photoresist film and, more particularly, to a method of trimming a photoresist film, laminated to a substrate,
15 along the edges of the substrate to facilitate further processing of the substrate-film laminate.

In the use of dry film photoresist materials, it is customary to laminate the
20 film to a substrate which may be a circuit board or other surface to be processed. When using printed circuit boards and similar, relatively strong materials, particularly those having a well defined contour, it is customary to trim the board by running
25 a razor blade or similar instrument along the edges thereof to cut away the excess film. In the case of fragile substrates, or substrates having an odd shape, such as
30 is often the case in the field of micro-electronics, when using silicon wafers and the like such manual trimming becomes not only tedious but also time consuming. In fact, such wafers are often damaged during
35 trimming due to their fragility.

This invention provides an improved method of trimming photoresist material from the edges of laminated substrates.

In accordance with the invention there is
40 provided a method of applying a photoresist film supported by a coversheet to a substrate by laminating one side of said film to said substrate and trimming said film along the edges of said substrate, which
45 method comprises:

(i) applying a film weakening agent to the substrate side of said film by either

(a) applying said film weakening agent to those portions of the substrate side of said film that are unprotected
50 by said substrate; or

(b) laminating a pliable, permeable sheet to the substrate side of said film forming a laminate with said substrate in the middle, said permeable sheet having a wetted adhesive strength to said film that is greater than the wetted adhesive strength of said coversheet to said film,
55 applying said weakening agent to 60 said permeable sheet and separating said permeable sheet from said substrate, and

(ii) separating said coversheet from said film at least in the region thereof corresponding to the portion of the film adhered to said substrate, the steps (i) and (ii) being carried out in the order (i) and then (ii) in the case of alternative (i)(a) and simultaneously or in either order in the case of
65 alternative (i) (b), the combination of steps (i) and (ii) resulting in trimming of the film along the edges of the substrate.

If desired, after the coversheet has been removed, the bare surface of the photoresist film may be protected with a suitable cover or coating. The substrate with the photoresist film adhered thereto may then be processed using conventional handling equipment for the exposure and development of the film. Removal of the coversheet may take place before or after the weakening agent has been applied when the pliable permeable sheet is used in step (i)(b).
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The method of the invention is particularly advantageous in that it permits relatively fragile, weak, irregular shaped substrates to be trimmed accurately, precisely easily and without damage to the substrate. Such a method is particularly
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useful for the processing, for example, of silicon wafers.

The method of this invention will be described in conjunction with the processing of a fragile substrate such as a silicon wafer by laminating a photoresist film to the substrate, applying a weakening agent to the film and then trimming the photoresist film from the edges of the substrate.

10 The photoresist film employed in the invention may be of the type conventionally referred to as photopolymer film resists, or "dry film resists", which are applied by lamination. Such films, which will be hereinafter referred to as photoresist films, are capable of generating resist patterns after imagewise exposure to actinic radiation, by removal of various of the layers typically with the solvent. In the case of a negative-working material, the unexposed areas are removed and the exposed areas remain as the resist image. In the case of a positive-working material, the unexposed areas form the resist image.

25 Useful materials for the practice of the invention are described in U.S. Patents 3,469,982 and 3,526,504. The photoresist resin may be an initially readily soluble, negative-working photohardenable layer (negative-working photoresist) or an initially poorly soluble photosolubilizable or photodesensitizable layer (positive-working photoresist).

30 Photohardenable materials are those which become hardened when exposed to actinic radiation and are preferably selected from photopolymerizable, photocrosslinkable and photodimerizable materials. Such materials are usually characterized by having ethylenically unsaturated or benzophenone-type groups and are described in U.S. Patents 2,760,863; 3,418,295; 3,649,268; 3,607,264; and 3,622,334, for example.

45 Photosolubilizable and photodesensitizable materials are those which are solubilized or decomposed, rather than polymerized, in areas exposed to light. When the latter are removed, the unexposed areas remain on the surface as a durable positive resist. Such materials are disclosed in U.S. Patents 3,778,270; 3,779,778; 3,782,939; and 3,837,860.

50 Photopolymer film resists, when used in the method of this invention, typically are supplied sandwiched between a layer of polyolefin and a layer of polyester film. The protective polyolefin separator sheet is peeled off the resist and the resist is laminated to the substrate. Lamination typically is achieved utilizing either pressure rolls or vacuum lamination techniques and heat. Reverse lamination techniques may also be used in which the polyester sheet is peeled off and the polyolefin protective sheet used as the "cover" sheet.

According to the method of this invention, as depicted by the block diagram of FIG. 1, a photoresist film is laminated to a substrate. The substrate may be a conventional printed circuit board or, in the preferred form or preferred use of the method, a material such as is typically used in microelectronics, i.e. a ceramic plate or silicon wafer. The invention finds particular use with ceramic plates or silicon wafers because of their typical irregular shapes and/or fragility. Such lamination may take place in a conventional laminator such as a roll laminator utilizing pressure and heat or a vacuum laminator. In the laminator, the separator sheet is peeled from the photoresist film and the substrate laminated to the now unprotected side of the film. To prevent the photoresist film from adhering to the rollers of the laminator or other surfaces in the laminator, a continuous polyolefin belt may be used to protect such surfaces.

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Either in the laminator or upon preferably leaving the laminator, a weakening agent is applied to the unprotected side of the film (the side having the substrates adhered thereto). The application of the weakening agent may be by a spray, by a roller saturated with the weakening agent, or by such other known fluid application means as desired. A spray tends to be preferred over a roller since it has less tendency to damage the substrate. After the film has left the laminator and after a sufficient time interval has elapsed for the weakening agent to reduce the tear strength or dissolve the portions of the film which it contacts, the coversheet is stripped from the film in the region of the substrate, i.e. that portion of film adhered to the substrate. The now softened and weakened film adheres to the coversheet and is removed or torn away at the edges of the substrate. Where it is protected by the substrate, the photoresist film remains strong and has a higher tensile or tear strength having not been subjected to the action of the weakening agent. If a solvent type weakening agent is used and the solvent allowed to dissolve the film it contacts, i.e. those regions not protected by the substrate, the result is substantially the same—the substrate with film adhered is accurately and precisely trimmed. The substrate may then be passed on to conventional wafer processing apparatus, as desired for exposure and development of the photoresist film. This method may also be used in double laminations. In this instance, the removal of either coversheet is sufficient to effect the trimming action leaving the other coversheet for support.

Among the weakening agents that may be used are any of those which will weaken

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the tensile or tear strength of the photoresist film. Among these are solvents for the photoresist. Any of the conventional solvents may be used as desired. Typical of such solvents are 1,1,1-trichloroethane, methylene chloride or for the semi-aqueous photoresist film, a solvent such as a mixture of water, 12% 2-butoxyethanol and 2% sodium borate. In addition various non-solvent, softening agents may be used that will tend to weaken the tensile or tear strength of the photoresist film. Among the suitable non-solvent softening agents that may be used are perchloroethylene, isopropanol, methanol, ethanol, kerosene, cyclohexane, heptane, fluorocarbons, and basic solutions (OH⁻) for aqueous films.

The various time periods during which the photoresist film must be subjected to the action of the solvent or softening agent will vary according to the film thickness, film type and particular solvent or softening agent used. Following trimming, if the coversheet has been removed, it may be desirable to apply a non-tacky coating to the film. Such coating may be a sprayed on coating of any suitable material such as polyvinyl alcohol which can detackify the film surface and yet will not affect further processing of the photoresist film. Alternatively, a photoresist film could be used having a solvent removable protective layer. Films of this type are described, for example, in U.S. Patent 3,458,311 issued July 29, 1969 to F. P. Alles. Such solvent removable protective layer can underlie the usual polyester coversheet such that the photoresist film used is a sandwich structure of the polyolefin protective sheet, the photoresist film, the solvent removable protective layer, and finally the polyester coversheet.

Reference is now made to the sequence of Figure 1 depicted by the dashed lines and to Figure 2 which is a diagrammatic representation of an apparatus for performing the method of this invention. In this particularly preferred embodiment, a feed roll 10 of conventional photoresist 12 having a polyester coversheet 22, a photoresist layer or film 24, and a polyolefin protective layer 19, is passed with the coversheet 22 side up through a conventional roll type laminator 14. The protective layer 19 is peeled away and wound on a take up roll (not shown) leaving the unprotected underneath side of the photoresist 12 free to adhere to the substrate. A substrate such as a ceramic plate or silicon wafer 16 is also fed into the laminator to be laminated onto the now unprotected, underneath side of the photoresist 12 between the film 24 and a pliable, permeable sheet 18 which may be dispensed from a feed roll 20.

Following lamination, there is seen to be a laminate comprising coversheet 22, the

photoresist film 24, wafer 16 and permeable sheet 18. Upon leaving the laminator 14, a weakening agent is applied to the permeable sheet 18 at a point depicted by the arrow 26 and labelled "fluid application". The weakening agent may be any of those previously described. Upon being applied to the permeable material, the weakening agent permeates through the material and acts upon the photoresist film 24 thereby reducing its tensile or tear strength.

The pliable, permeable material 18 may be any porous, absorbent material that the photoresist film will stick or adhere to and which will permit the various weakening agents listed hereinbefore to pass through. Application of the fluid weakening agents may be made by spray, saturated roller, or other known means of applying fluids. After the web has moved a sufficient distance to allow time for the weakening agent to act upon the film 24, the laminate is passed through a pair of nip rolls 28. At this point, the coversheet 22 is peeled off and fed to a takeup roll 30 on the upper side; on the lower side the permeable sheet 18 is peeled back and fed to a takeup roll 32. The wafer will have its edges trimmed of the photoresist film by the action of the permeable sheet 18 pulling or tearing the weakened film along the edges of the wafer as it is peeled back. The wafer 16 now may be passed to a tray or movable belt 34 for passage to conventional wafer handling equipment.

If desired, the coversheet may be peeled back and removed prior to application of the weakening agent to the pliable, permeable material 18. In this instance, the non-tacky coating described above can be applied to the photoresist film. Heating of the thus treated substrate may be used to reduce the process time.

The permeable sheet must, in its wetted condition, adhere to the film 24 more strongly than does the coversheet 22. Describing it in another way, the permeable sheet should have a wetted adhesive strength to the photoresist film 24 that is greater than the wetted adhesive strength of the coversheet 22 to the film.

Among the various permeable sheets that may be used are paper (ordinary paper towel type material may be used) or any other permeable material that has a sufficiently roughened or porous surface that will permit adherence to the photoresist film as described. Among such materials are a non-woven polyester sheet such as that sold under the Tradename REMAY or a non-woven polyolefin fiber such as sold under the Registered Trademark "TYVEK". Both are products of E. I. du Pont de Nemours and Company. In addition, cotton cloth, woolen cloth, linen

and similar materials which are soft and absorbent may be used. The materials may be woven or non-woven so long as they meet the requirements of adherence to the photoresist film as set forth above. The only restriction placed upon the type of materials that may be used in that it should not dissolve to a significant degree in the weakening agents employed or have its own tensile strength reduced to less than the strength of the resist.

In still another alternative method, the weakening agent may be applied to the permeable sheet 18 prior to lamination, instead of after, say at the point as depicted by the phantom arrow 27. The remainder of the method remains unchanged.

There is described in copending application U.S.S.N. 745680 (U.S. Patent No. 4069076) a method of applying swelling agents to the substrate prior to the laminating step to swell the film and facilitate its conforming to contours on the surface of the substrate. The method of trimming the edges of substrates described herein has particular application to such liquid laminating method. Excess swelling agent squeezed off the substrate will permeate the permeable sheet and react and soften the photoresist film along the edges of the substrate permitting the trimming action described herein when the permeable sheet is removed.

EXAMPLE 1

In one method according to this invention a semi-aqueous photoresist film and coversheet ("Riston" M-811, sold by E. I. du Pont de Nemours and Company, Wilmington, Delaware—"Riston" is a Registered Trade Mark) 1 mil thick was laminated to a silicon wafer with a paper towel backing. A softening agent of perchloroethylene was applied onto the porous material and allowed to remain for a period of one minute. Following this, the paper was peeled away from the wafer and coversheet. The result was that the softened photoresist film was torn accurately and precisely along the edges of the wafer without damage to the film remaining on the wafer and without damage to the wafer itself.

EXAMPLE 2

In another application of the method a solvent processable ("Riston" M-810, sold by E. I. du Pont de Nemours and Company,

Wilmington, Delaware) photoresist film and coversheet. 1 mil thick was used and subjected to the solvent methylene chloride for a period of one minute. Similar accurate trimming results were obtained when the paper backing was pulled away from the wafer.

The method is seen to facilitate the accurate trimming of fragile wafers, quickly and as an adjuvant to the photoresist film laminating process.

WHAT WE CLAIM IS:—

1. A method of applying a photoresist film supported by a coversheet to a substrate by laminating one side of said film to said substrate and trimming said film along the edges of said substrate, which method comprises:

(i) applying a film weakening agent to the substrate side of said film by either

(a) applying said film weakening agent to those portions of the substrate side of said film that are unprotected by said substrate; or

(b) laminating a pliable, permeable sheet to the substrate side of said film forming a laminate with said substrate in the middle, said permeable sheet having a wetted adhesive strength to said film that is greater than the wetted adhesive strength of said coversheet to said film applying said weakening agent to said permeable sheet and separating said permeable sheet from said substrate, and

(ii) separating said coversheet from said film at least in the region thereof corresponding to the portion of the film adhered to said substrate, the steps (i) and (ii) being carried out in the order (i) and then (ii) in the case of alternative (i)(a) and simultaneously or in either order in the case of alternative (i)(b). the combination of steps (i) and (ii) resulting in trimming of the film along the edges of the substrate.

2. A method according to claim 1 wherein step (i)(b) comprises separating said permeable sheet from said substrate and said coversheet.

3. A method according to claim 2 wherein said coversheet and said permeable sheet are simultaneously separated.

4. A method according to claim 1, 2 or 3 wherein said weakening agent is a solvent



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and similar materials which are soft and absorbent may be used. The materials may be woven or non-woven so long as they meet the requirements of adherence to the photoresist film as set forth above. The only restriction placed upon the type of materials that may be used in that it should not dissolve to a significant degree in the weakening agents employed or have its own tensile strength reduced to less than the strength of the resist.

15 In still another alternative method, the weakening agent may be applied to the permeable sheet 18 prior to lamination, instead of after, say at the point as depicted by the phantom arrow 27. The remainder of the method remains unchanged.

20 There is described in copending application U.S.S.N. 745680 (U.S. Patent No. 4069076) a method of applying swelling agents to the substrate prior to the laminating step to swell the film and facilitate its conforming to contours on the surface of the substrate. The method of trimming the edges of substrates described herein has particular application to such liquid laminating method. Excess swelling agent squeezed off the substrate will permeate the permeable sheet and react and soften the photoresist film along the edges of the substrate permitting the trimming action described herein when the permeable sheet is removed.

EXAMPLE 1

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EXAMPLE 2

55 In another application of the method a solvent processable ("Riston" M-810, sold by E. I. du Pont de Nemours and Company,

Wilmington, Delaware) photoresist film and coversheet. 1 mil thick was used and subjected to the solvent methylene chloride for a period of one minute. Similar accurate trimming results were obtained when the paper backing was pulled away from the wafer.

The method is seen to facilitate the accurate trimming of fragile wafers, quickly and as an adjuvant to the photoresist film laminating process.

WHAT WE CLAIM IS:—

1. A method of applying a photoresist film supported by a coversheet to a substrate by laminating one side of said film to said substrate and trimming said film along the edges of said substrate, which method comprises:

(i) applying a film weakening agent to the substrate side of said film by either

(a) applying said film weakening agent to those portions of the substrate side of said film that are unprotected by said substrate; or

(b) laminating a pliable, permeable sheet to the substrate side of said film forming a laminate with said substrate in the middle, said permeable sheet having a wetted adhesive strength to said film that is greater than the wetted adhesive strength of said coversheet to said film applying said weakening agent to said permeable sheet and separating said permeable sheet from said substrate, and

(ii) separating said coversheet from said film at least in the region thereof corresponding to the portion of the film adhered to said substrate, the steps (i) and (ii) being carried out in the order (i) and then (ii) in the case of alternative (i)(a) and simultaneously or in either order in the case of alternative (i)(b), the combination of steps (i) and (ii) resulting in trimming of the film along the edges of the substrate.

2. A method according to claim 1 wherein step (i)(b) comprises separating said permeable sheet from said substrate and said coversheet.

3. A method according to claim 2 wherein said coversheet and said permeable sheet are simultaneously separated.

4. A method according to claim 1, 2 or 3 wherein said weakening agent is a solvent



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or non-solvent softening agent for said film.

5. A method according to any one of the preceding claims wherein a cover or coating is provided to protect said film after removal of the coversheet.

6. A method according to claim 1 substantially as described in Example 1 or 2.

7. A method according to claim 1 substantially as described with reference to, and as illustrated by, the accompanying draw-

ings.

8. A substrate having a trimmed photoresist film thereon when prepared by a method as claimed in any one of the preceding claims.

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