

Description

This invention is concerned with positive photoresist systems. It is particularly concerned with processes for making photoresist systems, photoresists useful therein, the film or films formed from the photoresists (that is to say the photoresist systems themselves), processes for forming an image involving said systems and solvents useful in said photoresists.

Positive-acting photoresists, commonly referred to as positive photoresists, or positive resists, are useful for forming images on surfaces in lithographic and semiconductor processes. Typically, positive photoresists contain a mixture of a photoactive sensitizing compound or sensitizer, a coupler resin, and optionally minor amounts of additives, dissolved in a single solvent or mixed solvent system. The photoresist must be capable of being applied as a thin adherent layer or film, having a thickness of about 0.5 to about 3 micrometers, on the surface of a base material such as a silicon wafer or printed circuit board. After the film or resist layer is dried to remove the solvent, a photomask with opaque image areas, delineating the desired pattern or circuitry to be imaged onto the surface, is brought into close contact with the photoresist film. When the photomask is in position, the positive photoresist layer, not covered or blocked by the photomask, is exposed to a source of energy, such as ultraviolet, visible light, x-ray, electron beam or other electromagnetic radiation. The portion of the positive photoresist layer exposed to the radiation undergoes a chemical change which renders the exposed portion of the layer more soluble in a developing solution, such as an aqueous base, than the unexposed portion of the photoresist layer.

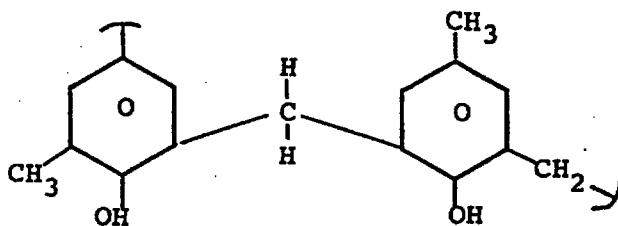
The coupler resin to be used in a positive resist should be soluble in a solvent used in the photoresist, as well as in the developing solution used, and should be able to form an adherent film on a substrate. The solubility of the coupler resin in a developing solution is inhibited by the presence of the photoactive sensitizer compound. The sensitizer, in the areas not exposed to the radiation, is not soluble in the developing solution. The sensitizer compound, however, undergoes a chemical reaction upon absorption of the exposing radiation. The exposed sensitizer is at least partially converted to a compound which is soluble in the developing solution. Based on the difference in the dissolution rate of the unexposed film and the exposed film, the developing solution preferentially dissolves the exposed areas of the photoresist film. Following this developing step, the substrate has been imaged and is ready for circuitry to be placed on the surface in the imaged or developed areas. Subsequently, the unexposed photoresist is stripped from the surface by a stripping solution.

Therefore, the coupler resin, sensitizer, solvent, developing solution and stripping solution are selected based on their compatibility and effectiveness as components in an efficient and accurate imaging process.

The coupler resin serves to provide adhesion of the coating to the surface, to fortify the coating for better chemical resistance, to reduce the tendency for the sensitizer to precipitate from the coating, to increase the viscosity and coating characteristics of the photoresist film, and to reduce the cost of the photoresist. Generally, for aqueous base developed photoresist systems, the resins are not photosensitive and are not extremely hydrophobic, but dissolve slowly in aqueous base and are resistant to acids. If the resin dissolves too rapidly in aqueous alkaline solutions, however, the unexposed areas of the film can be leached away during developing and no useful image can be formed. The resin therefore must be as hydrophobic as possible and yet remain capable of being dissolved in aqueous alkaline developing solutions. Resins containing phenols, ethers formed from phenols, and aromatic amines have been used in positive photoresists containing photoactive sensitizing compounds.

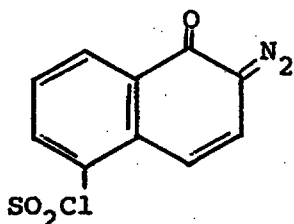
A typical conventional coupler resin is a low molecular weight, e.g. of about 3000 to about 5000 weight average molecular weight, condensation polymer of a phenol, such as cresol, and formaldehyde. Typical sensitizers used with such coupler resins are derivatives of compounds variously called diazo oxides or orthoquinone diazides prepared in either naphthalene or benzene forms. The selection of a suitable non-reacting solvent for the resin and sensitizer is critical in the formation of a uniform coating or film and in the prevention of the sensitizer from crystallizing and precipitating from the photoresist.

The background, types and operation of conventional photoresists are described in W.S. DeForest, Photoresist Materials and Processes, McGraw-Hill, 1975. In order to understand the factors which are important in formulating and evaluating a positive photoresist, the advantages and disadvantages of a typical positive photoresist, containing a commercial coupler resin, will be described. Novolak is a generic term used to identify low molecular weight condensation polymers of phenols, such as cresol, and formaldehyde having repeating units of the following chemical structure:



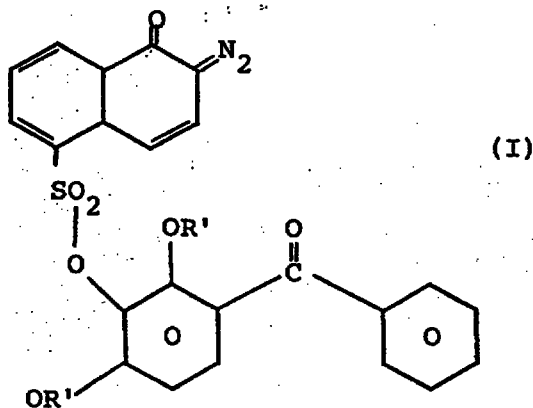
On a solids basis, a conventional photoresist contains about 75 percent by weight of the solids of a novolak coupler resin and about 25 percent of the solids of a sensitizer dissolved in a solvent system.

A typical positive acting sensitizer, useful with coupler resins such as novolak, is a naphthalene diazoketone or naphthoquinone diazide formed by reacting naphthoquinone-1,2-diazide-5-sulfochloride, having the following chemical structure:



(formula R),

with trihydroxy benzophenone to form a mixture of primary, secondary and tertiary substituted sulfonate esters having the structural formula:



(I)

where R' is a hydrogen or the naphthoquinone-1,2-diazide-5-sulfonate ester. This mixture primarily containing the triester is referred to herein as "SOX". Sensitizer compounds are often referred to as inhibitors because they act to inhibit the rate of dissolution of the unexposed resin in the developer. Sensitizers can also be referred to as accelerators because upon exposure they increase the dissolution rate of the exposed film in the developer.

A suitable solvent for this novolak resin/sensitizer mixture is a mixture of cellosolve acetate (ethylene glycol monoethylether acetate), xylene and butyl acetate in a weight ratio of about 80/10/10 (hereinafter referred to as "Conventional Solvent" or "CS").

The conventional positive photoresist is typically deposited as a film from the solvent onto a substrate, such as a silicon wafer, by spin casting the photoresist. The solvent in the photoresist which does not evaporate at the ambient spinning conditions is subsequently removed by a "soft-bake" of the film at about 90° C for about one half an hour. The photoresist film is then exposed, through the photomask at ambient temperatures, to a source of radiation such as "near" UV. The terms "near", "mid" and "deep" UV, as used herein, refer to ultraviolet light having the following range of wavelengths: near UV being greater than about 330 nanometers and less than about 450 nanometers, mid UV being from about 280 nanometers to 330 nanometers, and deep UV being from about 200 nanometers to 280 nanometers.

The positive photoresist film exposed to the radiation undergoes a chemical change that increases the

rate of dissolution of the exposed areas in an aqueous developing solution, preferably an aqueous base. This chemical change is caused by the conversion of the sensitizer to an aqueous base soluble form. Upon absorption of the radiation, the sensitizer breaks down forming a ketene with nitrogen gas being evolved. The ketene is then converted to an aqueous base soluble compound having a carboxylic acid group either by reaction with ambient water or by the formation of a lactone with unexposed sensitizer molecules, the lactone ring being further broken down in the presence of the aqueous base developing solution to the carboxylic acid form. By either mechanism, the exposed areas of the film become soluble in an aqueous base developing solution. The difference in the dissolution rate between the exposed film and the unexposed film in the developing solution determines the effectiveness of the photoresist system without reducing the thickness of the unexposed film to an unacceptable level.

Such conventional positive photoresists based on phenolic (novolak) coupler resins suffer from a number of drawbacks. The low thermal stability of such coupler resins is a major disadvantage because the photoresist layer on a silicon wafer is subjected to high temperatures during processing. If the processing temperature exceeds the glass transition temperature of the coupler resin, the unexposed photoresist layer will begin to melt or flow. Flow of the resist layer reduces the area between the exposed film areas and leads to reduced image resolution. In order to attempt to minimize flow problems, hardening of the exposed photoresist layer before the application of high temperatures has been employed. Novolak type resists are hardened by crosslinking the unexposed resist either by a gradual post baking, known as ramped post bake, or by exposing the unexposed resist to deep UV (See Hiraoka, et al. J. Vc. Sci. Tech., 19(4), page 1132 (1981) and W. Ma. SPIE Conference Proceedings, V. 333, Submicron Lithography, page 19, Santa Clara, California, 1982). Ramped post bake involves oxidizing the resin by gradual heating in the presence of air to crosslink the resist. This post baking is disadvantageous as it consumes time and introduces another step into the processing operation. Crosslinking the unexposed photoresist layer by either mechanism is also disadvantageous since once the resist is crosslinked it cannot be as easily stripped from the surface.

Additionally, crosslinking the unexposed novolak photoresist layers is also required when dry, plasma, or reactive ion etching (RIE) is employed. In certain semiconductor manufacturing operations, an insulating layer, such as silicon dioxide, is formed on the surface of a silicon wafer. The photoresist film is then applied to the insulating layer, exposed and developed. Following this step, the insulating layer is etched away down to the surface of the silicon substrate. Typical wet etchants, such as buffered aqueous hydrofluoric acid solutions containing hydrogen fluoride and ammonium fluoride, result in isotropic etching. Isotropic etching means that the etchant dissolves the insulating layer in all directions including the area under the unexposed photoresist layer. Isotropic etching results, therefore, in an undercutting of the photoresist. As the feature size defined by the imaged photoresist approaches the thickness of the insulating layer to be etched, an isotropic etch can lead to inadequate photoresist protection for the substrate. Reactive ion etching (RIE), however, results in an anisotropic etch, namely preferential etching in a single direction only. Anisotropic etching maintains intact the insulating layer directly under the unexposed photoresist. RIE typically involves the application of a high potential, such as that achieved with the application of a high voltage radio frequency field (R_F) to a low pressure chamber creating a glow discharge. A reactive gas such as carbon tetrafluoride, for etching the insulating layer, and optionally an inert gas, such as argon, are introduced into the chamber. The high applied potential results in a glow discharge or plasma containing fluorine radicals and positively charged ions in the chamber. The fluorine radicals react with the silicon dioxide insulating layer yielding the volatile reactant silicon tetrafluoride. The evolution of these gases provides a method for removing the insulating layer. The positive carbon tetrafluoride and argon ions become attracted to the negatively charged wafer surface. This ion bombardment assists in activating the surface. The fluorine radicals react much more rapidly with the unprotected surface than those surface areas protected from the ion bombardment by the photoresist. This produces a directional etch and enables the definition of geometries smaller than those attainable with isotropic etching.

Plasma and RIE conditions cross link novolak-containing photoresists. This crosslinking is caused by the exposure of the resist to deep UV radiation generated by the glow discharge and by the high surface temperatures which can be created with high etch rates. The crosslinked polymer becomes difficult to strip in subsequent processing steps.

Novolak resins can withstand reactive ion etching to a much better degree than most other photoresist resins. The rate of silicon dioxide erosion divided by the rate of photoresist layer erosion for novolak type resins is about 4 to 6 : 1 while other resist resins, such as those based on polymethyl methacrylate, have ratios approaching 1 to 1; meaning that the resist becomes etched away at the same rate as the insulating layer.

Reactive ion etching, even with resistant novolak, may lead, however, to a photoresist layer having a

reticulated surface, namely one having peaks and valleys caused by either the ion bombardment or the high surface temperature ("fried"). The depth of the valleys can extend through the resist layer to the silicon dioxide insulating surface and can therefore lead to decreased protection of the silicon wafer.

Another problem with novolak type coupler photoresists is limited transparency. "Transparency" in the context of photoresists, and as used herein, refers to the ability of a resist layer to allow the passage of exposing radiation to the sensitizer for initiation of its chemical conversion. If a photoresist is opaque, and not transparent, to a certain radiation wavelength, the coupler resin and not the sensitizer absorbs the radiation. This absorption by the resist does not result in a useful chemical reaction. Novolak type resins are transparent to near UV radiation. However, the transparency of these novolak type resins is significantly decreased over the mid UV wavelength range and only a very small, partially transparent window exists at about 250 nanometers in deep UV. Therefore, phenolic resins are transparent only over the near UV, and generally opaque over the mid and deep UV.

The strong absorption of novolak type resins over most of the deep UV makes them more suitable as photomasks rather than as transparent photoresists when such exposing radiation is employed (See Lin, et al, AZ1350J As Deep-UV Mask Material, IBM Research Center, Yorktown Heights, NY, SPIE, Vol. 174, Developments in Semiconductor Microlithography, IV, page 114 (1979)).

In order to obtain improved image resolution, depth of field focusing and silicon wafer throughput, the state of the art is moving in the direction of shorter wavelength radiation such as deep UV. Since conventional photoresists are not transparent over such wavelengths, those in the art are seeking improved positive photoresists which are useful with such wavelengths (See M.L. Long, Practical Deep Ultraviolet - The Multilayer Approach, SPIE Proceedings, Vol. 333, page 54, Santa Clara, California, March 1982).

Other disadvantages of phenolic positive photoresists include the cost of the resin, the difficulty in reproducibly synthesizing the photoresists and the waste of the resin and sensitizer upon spin casting due to the high solids content (about 30 percent by weight) needed for adequate film thicknesses.

US-A-4,121,936 (Matsuda et al) describes resist materials which are capable of forming positive images by the action of radiation, the resist materials being derived from poly(methacrylamide), crosslinked, and only sparingly soluble in water. Therefore, in order to develop these resists using water, they must be subjected to a solvent post-development step using an organic solvent having compatibility with water and which doesn't dissolve the poly(methacrylamide)-derived resist material.

Attempts have been made to improve the thermal stability of conventional positive photoresists. US-A-3,964,908 (Bargon et al) describes a process for forming an image using a dimethylglutarimide polymer having high thermal stability. The photoresist film is formed directly on the substrate surface by reacting a film of a dimethylacrylic acid-containing polymer with gaseous ammonia, methyl or ethyl amine at low pressure in a heated oil bath. It is contended that this in situ formation of a positive photoresist film on the surface is advantageous over spin casting a preformed resist formulation of the same coupler resin dissolved in a solvent onto the substrate because of the negligible solubility of such polymers in commonly used non-reacting solvents. This photoresist does not contain a sensitizer because known photo-sensitizers thermally decompose at temperatures below that used in the in situ polymerization reaction used to form the resist.

The absence of a photosensitizer hampers the photospeed of such a photoresist and requires higher doses of exposing radiation and/or longer exposure times to the radiation in order to cause the polymer chain itself to degrade. This in situ approach also suffers because the synthesis route for the preparation of the polymer is complex and difficult to control and use in conventional semiconductor processing. Also, certain dopants, such as phosphorus, which are incorporated into silicon wafers to increase electrical properties, are known to be amine sensitive. Therefore, the introduction of ammonia or alkylamines to form such photoresists in situ can interfere with the dopants and lead to the alteration of the electrical properties of the device sought to be improved with the dopants. Furthermore, when dimethylglutarimides are prepared from alkylamines, the resulting polymers are not soluble in aqueous developing or stripping solutions.

In situ formation of polyglutarimides is also disclosed by Bargon in J. Appl. Polym. Sci, 1978, 22(12), pages 3397-403 (C.A. Vol 90, No. 14, April 1979, page 607, Abstract No. 112 976n).

Workers in the art are also attempting to develop photoresists capable of obtaining micrometer to submicrometer images on non-uniform substrate surfaces having varied topographies and reflectivities. Variations in the substrate's thickness limit the ability to obtain good resolution with single layer photoresist systems. Multilevel or multilayer photoresist systems have been proposed to solve this problem. However, at the present time, no multilayer photoresist systems capable of micrometer to submicrometer image resolution are commercially available. Multilevel photoresist systems involve segregating the imaging and protection function of a photoresist system into two or more discrete film layers. Typically a bottom

planarizing layer of sufficient thickness is applied to the surface to cover all the surface features creating a flat or planar surface. A thin layer of a different photoresist is then deposited on the planarizing sublayer. Sometimes an intermediate layer, between the planarizing layer and thin top layer, is also employed. The object of a multilayer resist system is to expose and develop the thin top layer, achieving enhanced resolution, without exposing the underlying intermediate layer (if present) and planarizing layer. This can be accomplished if the layers are not sensitive to the same exposing radiation. After the thin top layer is exposed and developed forming a high resolution image, this image is used sequentially as a photomask for the adjacent intermediate or planarizing layer. The transfer of the image pattern from the top layer and intermediate layer down through the thicker planarizing layer may be accomplished by dry plasma etching or by deep UV exposure and development.

When plasma etching is used for developing the planarizing layer, an intermediate layer is typically present. The planarizing layer is coated with an intermediate layer of an inorganic material, such as silicon dioxide, silicon nitride or silicon, which is resistant to oxygen plasma etchant. After the images are formed in the thin top layer, the wafer is subjected to a carbon tetrafluoride etch. The intermediate layer is etched by the carbon tetrafluoride plasma using the top layer images as a mask. The wafer is then subjected to an anisotropic oxygen plasma etch. The previously etched intermediate layer then becomes the mask for the anisotropic oxygen plasma etching of the planarizing layer. The thin top layer and the intermediate layer are, therefore, utilized as sequential masks by altering the etching conditions.

Another multilayer approach known as the portable conformable mask technique (PCM), utilizes a high molecular weight polymethyl methacrylate as the planarizing layer. The polymer undergoes degradation upon exposure to deep UV radiation but is transparent to near UV radiation. A conventional novolak diazoketone positive resist is deposited as a coating on the planarizing layer and subjected to near UV exposure and developed to form the mask for the planarizing layer. The polymethyl methacrylate planarizing layer is then exposed to keep UV radiation and developed as by the use of an organic solvent developer such as methylethyl ketone or chlorobenzene.

This PCM approach results in a problem not encountered with trilayer photoresist systems utilizing an intermediate layer. The polymethyl methacrylate planarizing layer and the novolak based thin top layer mix and lead to the formation of an insoluble interfacial product referred to herein as an interfacial scum. This interfacial scum must be removed before the development of the planarizing layer can occur. Removal of the interfacial scum can be accomplished by either a dry plasma etching step or by a vigorous separate development step. This adds undesirable processing steps and time to the PCM technique. Furthermore, the separate development step can threaten the integrity of the existing images.

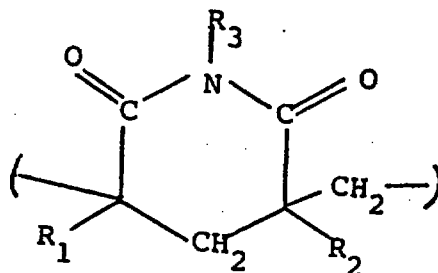
The use of organic solvents to develop the planarizing bottom layer also presents a problem in that these solvents pose potential health, flammability, and environmental problems. In addition, the solvents can cause the polymer film to swell thereby reducing the resolution of the formed images. The use of polymethyl methacrylate as a planarizing layer also suffers from a thermal stability (low glass transition temperature) and plasma etch resistance standpoint. Polymethyl methacrylate is not a satisfactory masking material for use in ion implantation and dry plasma etching procedures. The high temperatures generated during dry etching may exceed the glass transition temperature of polymethyl methacrylate resulting in loss of image resolution due to image flow. Wet etching can circumvent the problems encountered with dry etching polymethyl methacrylate. However, dry etching may lead to other problems such as the loss of adhesion of the images from the substrate.

By practice of the present invention there may be provided one or more of the following:-

- (i) a positive photoresist which solves the problems encountered by those skilled in the art with conventional positive photoresists;
- (ii) a positive photoresist system having high thermal stability and good image resolution without the need for subsequent film hardening;
- (iii) a positive photoresist system possessing a high degree of thermal stability, resolution over a wide range of exposing radiation wavelengths, and other properties useful for forming an image on a substrate;
- (iv) a positive photoresist system having excellent transparency over a wide range of exposing radiation and particularly over the entire ultraviolet wavelength spectrum;
- (v) a positive photoresist system having resistance to reticulation upon reactive ion etching;
- (vi) a positive photoresist that is simple to prepare and apply, as by spin casting, to deposit an adherent, uniform film, resistant to changes in physical properties over time, developable in aqueous base, easily stripped from the surface, and which does not increase processing times or costs; and
- (vii) a positive photoresist useful as a planarizing layer in a multilayer resist system which obviates the need for additional processing steps by eliminating interfacial mixing of the layers as in conventional

multilayer resist systems.

According to the present invention there is provided a positive photoresist, comprising preformed, non-crosslinked polyglutarimide polymer formed from an ester of (meth)acrylic acid and having at least five percent by weight glutarimide units of the structure



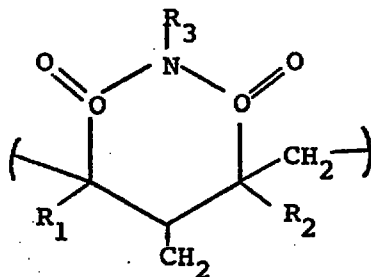
where R_1 , R_2 and R_3 independently represent hydrogen or unsubstituted or substituted alkyl, aryl, aralkyl, or alkaryl hydrocarbons having from one to twenty carbon atoms and where at least 20 mole percent of the R_3 substituents are hydrogen, dissolved in non-aqueous, spinning solvent which is one or more non-aqueous, non-reactive solvent for the polyglutarimide, said solvent being selected from: amide, polar, aprotic solvents; hydroxylic, polar, protic solvents; polar, aprotic, ketonic solvents; small chain, polar, carboxylic acids; and polar, basic ethers; said solvent for the polyglutarimide, optionally, being used in combination with one or more of acetyl acetone, 1-methoxy-2-propanol, cyclohexanone, chlorobenzene, xylene, toluene, butyl acetate, 1,2-dimethoxy ethane, ethylene glycol monomethyl ether, 2,4-pentanedione, and a mixture of ethylene glycol monoethyl ether acetate, xylene and butyl acetate, and where the photoresist, after exposure to energy, is developable with an aqueous solution.

According to the present invention there is also provided a process for the formation of a single or multilayer photoresist system developable with an aqueous solution wherein preformed polyglutarimide polymer of the invention is used in the formation of at least one layer.

We have found that preformed, partially water-soluble, imidized acrylic polymers, referred to herein as "polyglutarimides", can be dissolved in non-reactive, non-aqueous spinning solvents to form a positive photoresist that can be deposited, e.g. by spin casting as an adherent film on a substrate capable of high image resolution. We have also found that a preformed, partially water-soluble, imidized acrylic polymer having a high degree of thermal stability can be dissolved in non-reactive, non-aqueous spinning solvent systems to form effective positive photoresists, and that such photoresists unexpectedly possess improved properties as compared with conventional positive photoresists.

When the positive photoresist is utilized as a single layer resist, sensitizers may be added to the photoresist to provide transparency and increased photospeed over a wide wavelength range of exposing radiation. When the photoresist is utilized as a planarizing layer in a multi layer resist system, the photoresist can be formulated with or without photosensitive compounds, depending on the means utilized to expose and develop the images on the planarizing layer.

The polyglutarimides which are the coupler resin of the positive photoresist of the present invention include partially water-soluble, non-crosslinked, imidized acrylic polymers as described in U.S. Patent-A-4,246,374 to Kopchik, the disclosure of which is incorporated in pertinent part by reference herein. The polyglutarimide polymers have at least about 5 percent by weight glutarimide units of the following structural formula:



where R_1 , R_2 and R_3 independently represent hydrogen or unsubstituted or substituted alkyl, aryl, aralkyl,

or alkaryl hydrocarbons having from one to twenty carbon atoms, or mixtures thereof.

Polyglutarimides may be formed by reacting an acrylic polymer containing units derived from esters of acrylic or methacrylic acid, such as polymethyl methacrylate homopolymer or copolymers of polymethyl methacrylate, with ammonia, primary amines or mixtures thereof. In order for the polyglutarimide to be useful as the coupler resin in an aqueous base developable and strippable, positive photoresist system, the polyglutarimide must be at least partially soluble in aqueous base. The polyglutarimide will be soluble in aqueous base developing solutions when at least about 20 mole percent of the R_3 substituents, and preferably from about 50 mole percent to about 100 mole percent of the R_3 substituents, are hydrogen. The R_3 substituents of the polyglutarimide will contain at least about 50 mole percent hydrogen when ammonia is used as a single reactant with the acrylic polymer. When mixtures of ammonia and alkyl amines are used to react with the acrylic polymer to form the polyglutarimide, the R_3 substituents of the polyglutarimide will be both hydrogen and alkyl groups. Other beneficial physical properties of the polyglutarimides may be obtained by adjusting the ratio of ammonia to alkyl amine reactant in the reactant mixture. In the practice of the invention, it is preferable to prepare the polyglutarimides by imidizing polymethyl methacrylate with ammonia to obtain the desired degree of aqueous base solubility and other physical properties.

The polyglutarimides may be prepared by a continuous extrusion process, as described in U.S.-A-4,246,374. The degree of imidization of the polyglutarimide can be adjusted by varying the process conditions such as residence time, pressures and temperatures. Polyglutarimides having up to about 95 mole percent imidization can be readily achieved by converting the ester moieties of the acrylic polymer to glutarimide moieties.

The physical properties of the resulting photoresist film can also be adjusted by varying the molecular weight of the polyglutarimide coupler resin. The molecular weight of the resulting polyglutarimide is typically close to the molecular weight of the precursor acrylic polymer. Therefore, by selecting an acrylic polymer of known molecular weight and forming a polyglutarimide, the film properties of the positive photoresist system of the present invention can be optimized for each admixture of polyglutarimide and solvent with or without the addition of a photoactive sensitizer. Typically the molecular weight of the polyglutarimide coupler resin used in the present invention ranges from about 4,500 weight average molecular weight to about 200,000 weight average molecular weight. In order to achieve optimum development of the positive resist films of the invention in an aqueous base developing solution, the molecular weight of the polyglutarimide resin should preferably be at least about 50,000 weight average molecular weight.

One of the distinguishing characteristics of polyglutarimides which makes them especially useful as coupler resins in a positive photoresist is their high degree of thermal stability. The thermal stability of polyglutarimides increases with increasing percent imidization. A 95% imidized polyglutarimide derived from ammonia has a glass transition temperature (T_g) of about 250°C and a T_g midpoint of 231°C as determined by Differential Scanning Calorimetry (DSC). A nearly completely imidized polyglutarimide (95% imidization) derived from N-methylamine has a T_g of about 180°C. Depending on the process conditions, the ratio of ammonia to alkyl amine reactant, the acrylic polymer precursor, and the extent of imidization of the acrylic polymer precursor, the thermal stability of the polyglutarimide, as determined by its glass transition temperature (T_g) or VICAT softening point (ASTM D1 525-70), can range from about 130°C up to about 250°C.

It is preferred that the polyglutarimides used as coupler resins in photoresists of the present invention be at least about 80 percent imidized with a T_g of at least 140°C, preferably up to about 180°C, and in certain cases, as for example when reactive ion etching is to be utilized, even more preferably up to about 240°C.

The thermal stability of the photoresist film is especially important when image resolution on the order of from less than about one micrometer to about 1.5 micrometers is desired. As described above, flow of photoresist films is a problem with conventional systems when such a high degree of image resolution is desired, and when ion implantation of the silicon wafer surface or reactive ion etching is utilized. For example, ion doping or implantation of the silicon surface is used in certain cases to improve the electrical conductivity of the silicon wafer. Doping of the silicon is achieved by implanting conductive ions, such as phosphorus or boron ions, into the exposed silicon wafer surface. The amount of such ions that can be implanted into the silicon surface is a function of the thermal stability of the photoresist layer. Ion implantation leads to high film surface temperatures which can lead to the deformation of images formed using conventional positive photoresists. If a photoresist begins to flow during ion implantation, the level of doping and electrical properties of the wafer, as well as image resolution, will suffer.

The thermally stable polyglutarimides used in the present invention can resist flow under ion implanta-

tion conditions. No additional hardening of the photoresist, as by crosslinking, is necessary to improve the thermal stability of the photoresist layer. Accordingly, the extra processing steps and additional processing time needed with conventional phenolic type photoresists may be avoided. Furthermore, since the polyglutarimide does not require hardening, stripping the resist is not made more difficult.

In addition, reactive ion etching also requires a highly thermally stable photoresist film. The rate of substrate erosion to resist erosion with the polyglutarimide based positive photoresist of the invention is comparable to novolak type resins, about 4 to about 6 : 1 when silicon dioxide is being etched. This ratio is much higher than with other types of conventional organic polymers. The resistance of the photoresist to reactive ion etching leads to fast etch times, increases wafer throughput and lowers processing cost. The polyglutarimide positive resists of the invention are superior to novolak resins for reactive etching because no reticulation of the resist layer has been found to occur by scanning electron microscopic examination. The improved resistance to reticulation means that the positive photoresist film of the invention is a more effective shield to anisotropic etching than novolak type resins.

It is surprising that the polyglutarimides are capable of being dissolved in non-aqueous, non-reactive spinning solvents and that the system may be used to deposit an adherent, high quality, aqueous base developable, positive resist film on a substrate for lithographic applications. When the positive photoresist is used as a single layer resist, and optionally when it is used as the planarizing layer in a multilayer resist, conventional positive acting photosensitizers have been found to be compatible with the polyglutarimide resin and soluble in the same solvents in which the polyglutarimide is soluble. These photosensitizers include diazo oxides such as the 4',2',3'-trihydroxy benzophenone ester of 1-oxo-diazo naphthalene-5-sulfonic acid (SOX) having the structural formula (I) shown hereinbefore

Other useful sensitizers can be formed from quinone diazides, for example, benzoquinone diazides such as benzoquinone 1,2-diazide-4-sulfonylchloride; and naphthoquinone diazides such as naphthoquinone-1,2-diazide-5-sulfochloride, naphthoquinone-1,2-diazide-4-sulfochloride, naphthoquinone-2,1-diazide-4-sulfochloride, and naphthoquinone-2,1-diazide-5-sulfochloride. Diazo compounds, other than the diazo oxides or quinone diazide compounds, may also be suitable reagents for forming positive sensitizers which can be used in this invention.

Further, certain additives may be added to the positive photoresist of the invention to increase the sensitivity of quinone diazide sensitizers, as described in US Patent-A-3,661,582, as well as the dibasic carboxylic acids, monobasic unsaturated aromatic acids, hydroxyphthalic acids alone or in combination in amounts of from 0.1% to about 15% on a weight basis based on the weight of the polyglutarimide coupler resin as disclosed in US Patent-A-4,009,033.

We have found that mixtures of the polyglutarimides and these positive sensitizers in weight ratios of from about 99:1 to about 1:1 may be spun cast from a suitable solvent to give high quality clear films with no hazing or other indications of component separation due to incompatibility. Typically the level of the sensitizer compound ranges from about 5 to about 30 weight percent based on the weight of the polyglutarimide coupler resin.

The preferred sensitizer compound for use in the positive photoresist of the invention may be determined by matching its absorption spectrum to the particular wavelength range of the desired exposing radiation.

A solvent which is capable of dissolving the polyglutarimide and sensitizer and aid in spin casting a photoresist film is referred to herein as a spinning solvent.

Suitable non-aqueous, non-reactive solvents useful for dissolving polyglutarimides and sensitizers include: amide, polar, aprotic solvents such as dimethylformamide (DMF), dimethylacetamide (DMAC), N-methylpyrrolidinone (NMP), and dimethylpropyleneurea (DMPU); hydroxylic, polar, protic solvents such as cellosolve acetate (CA), tetrahydrofurfuryl alcohol (THFA), acetol, methyl carbitol (MeCarb) and 2-methoxy ethanol; polar, aprotic, ketonic solvents such as cyclopentanone (CP); small chain, polar, carboxylic acids such as acetic acid and formic acid; polar, basic, ethers, for example, n-alkyl morpholines such as n-methyl morpholine and n-ethyl morpholine, and tetrahydrofuran; and mixtures of the above.

Other compounds which are not by themselves solvents for polyglutarimides can be combined with one or more of the above-mentioned solvents to form spinning solvents. Some examples of these other compounds include acetyl acetone, 1-methoxy-2-propanol, cyclohexanone, chlorobenzene (CB), conventional solvent, xylene, toluene, butyl acetate, 1,2-dimethoxyethane, ethylene glycol mono methyl ether, 2,4-pentanedione, and the like.

Preferred spinning solvent systems for use in the positive photoresist of the invention include mixtures of DMF/CS/chlorobenzene (CB), THFA/CS, cyclopentanone, THFA/methyl acetoacetate, and chlorobenzene/2-methoxy ethanol.

The polyglutarimide coupler resin is typically dissolved in the solvent system to a concentration of from

about 5 to about 30 weight percent.

The positive photoresist may be spun cast from the solution to deposit an adherent film on a substrate, eg, an oxide coated, nitride coated or uncoated silicon wafer or aluminium coated substrate. The thickness of the photoresist film can be controlled by adjusting the level of coupler resin and/or sensitizer solids in the mixture, the level and type of solvent, and by varying the spin speed.

Any conventional spin casting method, such as those described in Integrated Circuit Fabrication Technology, DJ Elliott, McGraw-Hill Book Company, 1982, chapter 6, pages 125-144, can be utilized with the photoresist system of the invention.

Typically the substrate, e.g. a wafer, is placed on a rotating disc such as a Headway wafer spinner and rotated at speeds of from about 3000 to 7000 revolutions per minute. The photoresist system is deposited onto the substrate over a period of several seconds by either a continuous or dropwise addition while the substrate is stationary, or while it is spinning.

It is also possible to pretreat the substrate with a primer immediately before spin casting the photoresist to increase the adhesion of the polyglutarimide photoresist film onto the surface. We have found that primers such as hexamethyldisilazane (HMDS) and beta-3,4-epoxy cyclohexylethyl trimethoxysilane ("CHOES") can be used compatibly with the polyglutarimide photoresists of the invention. This primer may optionally be included as an additive, at levels of from about 1 to 15 weight percent based on the amount of coupler resin, in the photoresist to improve adhesion and reduce cracking of the film (crazing) during development. We have found that when the preferred solvent systems are used, primers may not be necessary to improve the adhesion of the film onto the substrate and that if a primer is used conventional primers such as HMDS are preferred. However, when less preferred solvent systems are utilized, we have found that other primers, such as beta-3,4 epoxy cyclohexylethyl trimethoxysilane increases the adhesion of the film onto the substrate.

Using these photoresists and procedures, uniform, striation-free films with thicknesses from less than about 0.1 micrometers to greater than 3 micrometers may be deposited on a substrate. These films are free from pinholes and voids which could lead to reduced quality and yields during processing. For most imaging applications, the film thickness will range from about 1 micrometer to about 1.5 micrometers.

The positive resist film containing the polyglutarimide and non-aqueous solvent can be imaged by exposure to a source of energy, such as ultraviolet light, e-beam, ion beam, x-ray and the like, that increases the dissolution rate of the polyglutarimide in a developer followed by developing the exposed film in the developer. A requirement for the positive photoresist utilizing photosensitizers is that the film deposited on the substrate is transparent to a wide wavelength range of exposing radiation. This means the film does not significantly absorb the exposing radiation at the expense of the sensitizer. The solvents used in the photoresist of the invention are also selected so that they do not interfere with the ability of the sensitizer to absorb the exposing radiation wavelengths applied.

We have found that the positive photoresists of the present invention form films that are transparent over a broad ultraviolet light range. The ability of the photoresist to be transparent over near, mid and deep UV allows for its use with conventional near UV exposure devices as well as state of the art, deep UV devices. Using deep UV allows achieving improved image resolution, depth of field focusing to alleviate image distortion problems upon thermal processing, and high semiconductor throughput. The excellent transparency of the positive photoresist films of the photoresist system of the invention is superior to conventional phenolic or novolak type resin photoresist films which are only completely transparent to near UV exposure.

Exposed polyglutarimide based positive photoresists can be developed in commercially available aqueous alkaline developers such as tetramethyl ammonium hydroxide, sodium hydroxide and the like. The developer type used and its strength is a function of the type of polyglutarimide resin used to formulate the positive photoresist and for complete development of images in a given period of time. With the photoresists of the invention complete development at 20-24 °C in about 1 minute has been achieved.

Analysis of imaged silicon wafers by means of a scanning electron microscope indicates that excellent resolution and adhesion of the resist to the substrate with retention of high image resolution is achievable with the positive photoresist of the present invention.

Once the positive photoresist is exposed to radiation and developed or imaged, the excellent thermal stability of the polyglutarimide allows for the use of high temperature post baking, ion implantation and reactive ion etching, also commonly referred to as dry or plasma etching, operations. Post baking refers to a procedure for increasing resist adhesion to the substrate before wet etching by placing imaged wafers directly in a forced air oven at 150 °C to 180 °C for 15 minutes to 1 hour, and typically for about one half an hour. Post baking also increases wafer throughput compared to normal resist hardening operations. Depending on the glass transition temperature of the polyglutarimide coupler used, the imaged wafers can

be directly hard baked at temperatures of from about 150° C to about 220° C without image distortion. This hard baking may improve the resistance of the imaged film to RIE and its adhesion to the substrate.

We have also found that the photoresist of the invention is stable upon storage and can easily be stored for extended periods of time of at least 2 weeks at elevated temperatures, on the order of about 50° C, and at least a few months at ambient temperature, without any noticeable change in performance.

The positive photoresists have also been found to be suitable as a planarizing layer in a multilayer resist system, for example, to produce a multilayer resist system which is thermally resistant to temperatures of from 140° C to 240° C. In one embodiment of the multilayer system, the top layer can be any positive or negative photoresist that is photoactive to radiation sufficient to expose the top layer and sufficiently opaque to the radiation used to expose the planarizing polyglutarimide layer. In another embodiment, we have found that it is also possible to utilize photosensitizers sensitive to the same exposing radiation wavelengths in both the top resist layer and the planarizing layer and to utilize different developers or developers of different strengths to preferentially and sequentially develop each layer independently. It is also possible to utilize a polyglutarimide resist without a photosensitizer as the planarizing layer and to etch the planarizing resist through the mask created by the imaged top layer.

The top layer resist may be applied directly by spin coating onto the bottom planarizing layer either before or after the planarizing layer is soft baked. In order to achieve optimum image resolution, the top layer should be as thin as possible while also being operable as a good mask for the bottom planarizing layer. After the top layer is exposed and developed, the planarizing layer may be exposed through the mask, formed by the imaged top layer, as in a portable conformable mask technique. When the planarizing layer is imaged using plasma etching, no photosensitizer need be present in the planarizing layer film. When the planarizing layer is exposed to deep UV radiation, the planarizing layer resist can also be formulated with deep UV sensitizers such as ortho-nitrobenzyl esters or alternatively without any photosensitizer being present. The exposed planarizing layer can then be developed using an aqueous base developing solution. The top resist film may be retained or removed as desired during the development of the planarizing layer depending on the strengths of the developer solution employed to develop the exposed planarizing layer. The polyglutarimide planarizing layer can also be used with RIE.

We have found that the polyglutarimide planarizing layer film is resistant against mixing with the thin top resist film layer. As a result, interfacial scumming is not a problem and no extra processing steps are required.

The present invention will now be further illustrated by way of the following examples which are presented solely to illustrate the invention and should not be considered to constitute limitations on the invention.

EXAMPLE 1: Preparation of Polyglutarimide

A polyglutarimide was prepared in a continuous extrusion device according to the process described in U.S. Patent-A-4,246,374. A high molecular weight polymethyl methacrylate homopolymer was introduced via the feed port of a twin-screw counter-rotating extruder at a rate of $1.36 \times 10^{-2} \text{ kg.s}^{-1}$ (108 pounds per hour). Ammonia was introduced into the extruder barrel at a rate of $5.13 \times 10^{-3} \text{ kg.s}^{-1}$ (40.7 pounds per hour) at a pressure of 9.653 MPa gauge (1400 psig). The ammonia contacted and mixed with the polymethyl methacrylate as it moved forward through the reaction zone at an extruder rpm of 225. The average barrel temperature was 293.3° C (560° F). The unreacted reagents and volatile products and by-products of the reaction were removed under vacuum at the vent. The imidized polymer product left the extruder through the die in melt form, non-foamed and essentially free of volatile materials. The polyglutarimide had a weight average molecular weight of 71,000 as determined by gel permeation chromatography and contained 58 mole percent ammonia-derived (N-H) glutarimide units and 42 mole percent methylamine-derived (N-CH₃) glutarimide units. The Vicat temperature of the polyglutarimide was measured (ASTM DI 525-70) to be 199° C and the glass transition temperature, measured by Differential Scanning Calorimetry, had a mid point between 192 and 193° C.

EXAMPLE 2: Preparation and Application of Positive Resists

The following presents the general procedure used to prepare and use the positive resists of the invention. Table 1 presents the formulations and processing conditions used to formulate and use the positive resists. Four solutions (Samples A-D) of the polyglutarimide, prepared according to Example 1, in various solvent systems were prepared by adding the polyglutarimide to the solvent with stirring and heating until no solid polyglutarimide was visible. Each solution was then cooled to room temperature and a

conventional photosensitizer, referred to herein as SOX, was added to each of the solutions to form the positive resists. Each photoresist was then filtered through a 1 micrometer Fluoropore filter to remove solid particulates.

Four 7.62 cm (3 inch) diameter silicon dioxide coated (5,000-10,000 Angstrom thick) silicon wafers were prebaked at 200° C and primed as follows. One to two milliliters of HMDS was applied via an automatic pipette to the prebaked wafers and each of the wafers were then spun at 3000 rpm on a Headway spinner for 30 seconds. One milliliter of each of the resists (samples A-D) was applied to each of the four primed wafers using a syringe. Each wafer was then spun at 3,000 rpm for 60 seconds on the Headway wafer spinner, at a relative humidity of at least 50%, to cast the resist films. Each wafer was then softbaked at 90° C in a Blue M forced air convection oven for the times listed in Table 1 to form films of approximately one micrometer thickness. Each wafer was removed from the oven, cooled to room temperature, and exposed through a quartz photomask having image patterns ranging from 0.75 micrometers to 5 micrometers in width on a HTG contact printer. Each wafer was exposed to UV radiation as shown in Table 1. Each wafer was then developed by immersion in an aqueous base developer solution at 20-24° C as set forth in Table 1 such that the exposed portions of the film were completely removed as determined by optical and scanning electron microscopy. Each wafer was then removed from the developer, rinsed for 10 to 15 seconds under a continuous stream of deionized water and dried using forced air. The adhesion of the unexposed film and the resolution of the developed images were ascertained by optical and scanning electron microscopy. Complete adhesion of the unexposed film was found in all cases. Complete adhesion, as used herein means that the images developed on the wafer remained on the wafer after development. The resolution achieved is shown in Table 1.

EXAMPLE 3: Multilayer Resist System

The planarizing positive resists containing the polyglutarimide used in the multi layer resist were formulated using the polyglutarimide described in Example 1. The formulations of the planarizing positive resists (samples E-I) are illustrated in Table 2. Five silicon wafers, 7.62 cm (3 inches) in diameter coated with silicon dioxide, were primed with HMDS as explained in Example 2. Each of the polyglutarimide planarization resist formulations (samples E-I) were then spun cast onto the primed wafers using the procedure described in Example 2 and softbaked as indicated in Table 2 to form the planarizing films. Onto each film, a one milliliter solution of a conventional, Shipley Company 1450B positive resist formulation (novolak plus diazoketone sensitizer) was spun at 3,000 rpm for 60 seconds to form a thin top film of about 0.5 micrometer thickness. Each wafer was softbaked at 90° C for 30 minutes in the Blue M forced air convection oven. Each wafer was then exposed as indicated in Table 2 using a HTG contact printer and a quartz photomask having image patterns ranging from 0.75 micrometers to 5 micrometers in width. Each wafer was then developed at 20-24° C by immersion in a developing solution as set forth in Table 2. Each wafer was removed from the developer, washed and dried as set forth in Example 2 to form the photomask for the planarizing layer. Each wafer was then exposed through the top layer photomask as set forth in Table 2. Each wafer was then developed, washed and dried as in Example 2 and according to the developing conditions set forth in Table 2. The adhesion and resolution of the developed images were determined as in Example 2. Complete adhesion of the planarizing layer to the substrate was observed in all cases and no interfacial scum was observed. The resolutions are set forth in Table 2.

EXAMPLE 4: Thermal Stability

The bilevel resist system, sample E of Example 3, was baked at 180° C for one hour and examined under the scanning electron microscope. While some rounding of the image sidewall profile was observed, the image resolution did not change.

EXAMPLE 5: Comparative Etching Resistance

This example compares the reactive ion etching resistance of the positive resist of the invention with a conventional novolak-type positive resist. The substrates used were 7.62 cm (3 inch) diameter silicon wafers having 5,000 Angstrom thick silicon nitride coatings onto which was deposited a 10,000 Angstrom thick aluminum coating. The wafers were primed as described in Example 2 with the HMDS primer without a solvent which was spun onto the aluminum coating at 3000 rpm for 30 seconds. The polyglutarimide positive resist used was that of sample D, 10 wt. % solution of polyglutarimide dissolved in a 66 wt. % chlorobenzene (CB) 33 wt. % 2-methoxyethanol solvent containing 12.5% of the SOX triester photosen-

sitizer, based on the weight of polyglutarimide, and containing 5 wt. % of the CHOES additive. This resist was spun cast onto the primed wafers at 3,000 rpm for 60 seconds at 52% relative humidity. The wafers with the deposited resist films were softbaked in a forced air oven for one half an hour at 90 to 95°C. The resulting film had a thickness of 1.3 micrometers. A conventional novolak-diazoketone positive resist was also spun cast onto identical primed wafers and softbaked.

The wafers were then exposed to near UV radiation through a contact photomask using the HTG printer. The polyglutarimide resist of the invention was exposed to 69 mJ/cm² of near UV radiation and developed in a 2.5/1 Vol/Vol solution of water and the Shipley MF312 developer. The polyglutarimide imaged wafers were then postbaked at 180°C for one hour. The novolak imaged wafers were postbaked at 130 to 135°C for 45 minutes.

Reactive ion etching was then conducted on each imaged wafer using a Plasmatherm batch etcher under the etching conditions listed in Table 3. Boron trichloride (BCl₃) was used to scavenge water and to aid in the removal of the aluminum oxide layer. Chlorine (Cl₂) gas was used as the active etching agent. The flow rate of the chlorine gas determined the severity of the etching conditions. The wafers were etched until no aluminum was visibly present. After etching, the wafers were removed from the batch etcher and quenched in water to prevent post-etching corrosion of the aluminum layer under the resist. The film thickness of the photoresist and the aluminum layers was measured before and after etching using a Ten-Cor Alpha Step profilometer to determine the relative etch rates of the samples. Each sample was repeated at least twice and the relative etch rates shown in Table 3 are average relative etch rates. The film quality was determined and reticulation was determined by visual and scanning electron microscopy.

Following reactive ion etching, the polyglutarimide resist was stripped from the wafer using an aqueous base. The novolak resists were not capable of being stripped from the wafer using conventional wet stripping agents.

TABLE 1

Sample	RESIST		Solvent		Sensitizer		Additive	
	Polyglutarimide Wt. %	Type	Composition Wt. %	Type	Wt. % (1) in Resist	Type	Wt. % in Resist	
A	12.0	DMF/CB/CS	30/55/35	SOX	12.5	None	None	
B	12.0	THFA/CS	50/50	SOX	12.5	CHOES	5	
C	10.7	CP	100	SOX	12.5	CHOES	5	
D	10.0	CB/2- methoxy ethanol	66/33	SOX	12.5	None	None	

(1) Wt. % based on weight of polyglutarimide.

TABLE 1 (continued)

Sample	Soft Bake Time (Minutes)	Exposing Radiation		Developing Conditions		
		Type	Dose mJ/cm ²	Developer Type (Vol/Vol)	Time (seconds)	Imaging Resolution (micrometer)
A	30	near UV	69	H ₂ O/Shipley (2) MF312 2.75/1	50-60	Approx. 1
B	45	near UV	69	H ₂ O/Shipley MF312 2.75/1	50-60	Approx. 1
C	30	deep UV	90	H ₂ O/Shipley MF312 2.75/1	50-60	Less than 1
		near UV	69	H ₂ O/Shipley MF312 2.75/1	90	Approx. 1
D	30	near UV	69	H ₂ O/Shipley 351 (3) 2.5/1	60	Less than 1
				H ₂ O/Shipley MF312 2.5/1	60	Approx. 1

2) Shipley MF312 is an aqueous base containing tetramethyl ammonium hydroxide

3) Shipley 351 is an aqueous sodium hydroxide solution

TABLE 2

Sample	PLAUVIZING RESIST		Solvent		Sensitizer		Additive		Softbake °C	Minutes	Film Thickness Micrometers
	Polyglutarimide Wt. %	Type	Composition Wt. %	Type	Wt. % (1)	Type	Wt. %	°C			
E	10.0	CB/2- methyl ethanol	66/33	BONP(2)	15	None	None	90	30		1.20
F	10.7	CP	100	None		None	None	150	30		2.0
G	10.7	CP	100	None		1b(3)	5	140	60		2.3(4)
H	10.7	CP	100	SOX	12.5	None	None	None			1.6
I	10.0	CP	100	SOX	12.5	None	None	None			1.8

(1) Wt. % based on polyglutarimide

(2) BONP = bis (o-nitrobenzyl) pimelate or bis (o-nitrobenzyl)-1,7 heptane dioate

(3) 1b = 1-borneol

(4) Obtained by spinning resist two times.

TABLE 2 (continued)

Sample	Exposure of --Top Layer--			Development of Top Layer--			Exposure of Planarizing layer--			Development of Planarizing layer--			Image Resolution (Micrometers)
	Type	Dose MJ/CM ²		Type	(Vol/Vol)	Time (Second)	Type	Dose mJ/cm ²		Type	(Vol/Vol)	Time (Second)	
E	near UV	76		H ₂ O/Shipley	351 5/1	30	deep UV	1500		H ₂ O/Shipley	312 2/1	70-90	Approx. 1
F	near UV	63		H ₂ O/Shipley	351 5.5/1	60	deep UV	3000		H ₂ O/Shipley	312 3.25/1	60	Approx. 1
G	near UV	63		H ₂ O/Shipley	351 6.0/1	60	deep UV	2000		H ₂ O/Shipley	312 2.25/1	60	Approx. 1
H	near UV	63		H ₂ O/Shipley	351 5.5/1	60	deep UV	100		H ₂ O/Shipley	312 3/1	60	Approx. 1
I	near UV	70		H ₂ O/Shipley	351 5.5/1	60	none			H ₂ O/Shipley	312 3/1	60	Approx. 5

TABLE 3

Sample	Resist Type	Etch Conditions					Etch Time (minutes)	Average Relative Etch Rate ³	Film Quality After Etching
		Total Pressure (millitorrs)	R _p Power (Watts)	DC bias (Volts)	Gas Flow BCl ₃ (cc/min)	Cl ₂ (cc/min)			
J	P ⁽¹⁾	27-28	425	-180	55	6	11.75	1.9	No reticulation
K	N ⁽²⁾	27-28	425	-180	55	6	11.75	1.5	No reticulation
L	P	27-28	600	-231	50	10	5.5	2.5	No reticulation
M	N	27-28	600	-231	50	10	5.5	— ⁽⁴⁾	Reticulation (fried)

(1) P = polyglutarimide resist

(2) N = novolak resist

(3) Average relative etch rate is equal to ratio of the etch rate of aluminum layer divided by the etch rate of the resist layer.

(4) Etch rate not determined because of severe reticulation of resist.

The terms "Headway", "Fluoropore" and "Ten-Cor Alpha Step" are trade marks.

Claims

1. A positive photoresist comprising preformed, non-crosslinked polyglutarimide polymer formed from an ester of (meth)acrylic acid and having at least five percent by weight glutarimide units of the structure

TABLE 3

Sample	Resist Type	Etch Conditions				Etch Time (minutes)	Average Relative Etch Rate ³	Film Quality After Etching
		Total Pressure (millitorrs)	R _F Power (Watts)	DC bias (Volts)	Gas Flow BCl ₃ (cc/min)			
J	P ⁽¹⁾	27-28	425	-180	55	6	1.9	No reticulation
K	N ⁽²⁾	27-28	425	-180	55	6	1.5	No reticulation
L	P	27-28	600	-231	50	10	2.5	No reticulation
M	N	27-28	600	-231	50	10	— ⁽⁴⁾	Reticulation (fried)

(1) P = polyglutarimide resist

(2) N = novolak resist

(3) Average relative etch rate is equal to ratio of the etch rate of aluminum layer divided by the etch rate of the resist layer.

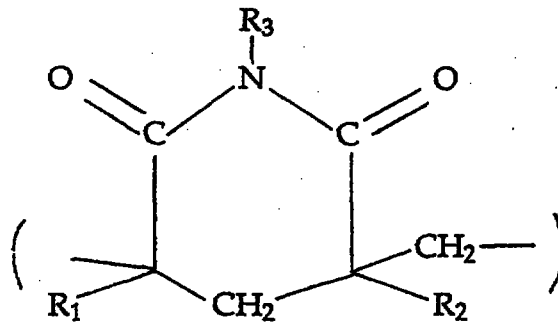
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Claims

1. A positive photoresist comprising preformed, non-crosslinked polyglutarimide polymer formed from an ester of (meth)acrylic acid and having at least five percent by weight glutarimide units of the structure





where R_1 , R_2 and R_3 independently represent hydrogen or unsubstituted or substituted alkyl, aryl, aralkyl, or alkaryl hydrocarbons having from one to twenty carbon atoms and where at least 20 mole percent of the R_3 substituents are hydrogen, dissolved in non-aqueous, spinning solvent which is one or more non-aqueous, non-reactive solvent for the polyglutarimide, said solvent being selected from: amide, polar, aprotic solvents; hydroxylic, polar, protic solvents; polar, aprotic, ketonic solvents; small chain, polar, carboxylic acids; and polar, basic ethers; said solvent for the polyglutarimide, optionally, being used in combination with one or more of acetyl acetone, 1-methoxy-2-propanol, cyclohexanone, chlorobenzene, xylene, toluene, butyl acetate, 1,2-dimethoxy ethane, ethylene glycol monomethyl ether, 2,4-pentanedione, and a mixture of ethylene glycol monoethyl ether acetate, xylene and butyl acetate, and where the photoresist, after exposure to energy, is developable with an aqueous solution.

2. A photoresist as claimed in claim 1 comprising from 5 to 30 weight percent non-crosslinked polyglutarimide and from 95 to 70 weight percent non-aqueous, spinning solvent.
3. A photoresist as claimed in claim 2 comprising from 10 to 20 weight percent non-crosslinked polyglutarimide and from 90 to 60 weight percent non-aqueous, spinning solvent.
4. A photoresist as claimed in any of claims 1 to 3 further comprising positive acting photosensitizer dissolved in said non-aqueous spinning solvent.
5. A photoresist as claimed in claim 4 wherein the concentration of said photosensitizer is from 5 to 30 weight percent, based on the weight of said preformed, non-crosslinked polyglutarimide.
6. A photoresist as claimed in claim 4 or 5 wherein said photosensitizer comprises one or more diazoxide and/or bis(o-nitrobenzyl)-1,7 heptane dioate.
7. A photoresist as claimed in any of claims 4 to 6 wherein the photosensitizer can absorb near, mid or deep UV radiation.
8. A photoresist as claimed in any of claims 1 to 7 wherein the polyglutarimide has an atomic ratio of carbon to nitrogen of at least 8 and a glass transition temperature of at least 140° C.
9. A photoresist as claimed in any of claims 1 to 8 wherein said preformed polyglutarimide is formed by imidizing a polymethyl methacrylate polymer with ammonia, or is formed by imidizing a polymethyl methacrylate polymer with a mixed reactant system comprising at least 20 weight percent ammonia and at least one alkylamine.
10. An adherent, uniform, aqueous base developable, film formed from a photoresist as claimed in any of claims 1 to 9.
11. A film as claimed in claim 10 having a thickness of about 0.5 micrometer to about 3.0 micrometers, preferably about one micrometer.
12. A multilayer photoresist system comprising a planarizing layer formed from a photoresist as claimed in any of claims 1 to 9 and at least one other layer capable of being imaged on said planarizing layer.

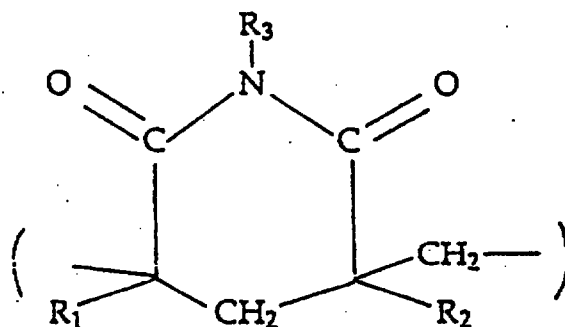


13. A multilayer photoresist system as claimed in claim 12 in which the planarizing layer and the adjacent layer deposited on said planarizing layer do not form an interfacial scum.
14. A process for the formation of a single or multilayer photoresist system developable with an aqueous solution wherein a positive photoresist system as claimed in any one of claims 1 to 9 is used in the formation of at least one layer.
15. A process for forming an image on a surface comprising depositing an adherent positive acting film on said surface from a photoresist as claimed in any of claims 1 to 9, exposing a portion of said film to a source of energy that increases the dissolution rate of the polyglutarimide in a developer, and developing the exposed portion of said film with said developer to form said image.
16. A process as claimed in claim 15 wherein said source of energy is ultraviolet, e-beam, ion beam or x-ray.
17. A process as claimed in claim 15 or 16 further comprising softbaking said film before exposing said film to said source of energy.
18. A process for forming an image on a surface comprising depositing an adherent, planarizing film on said surface forming a second surface, said planarizing film comprising a preformed non-crosslinked polyglutarimide polymer as claimed in any of claims 1 to 9,
depositing a second film capable of being imaged on said second surface,
exposing a portion of said second film to a source of radiation,
developing the exposed portion of said second film to create a mask on the planarizing film, and
transferring said image from said second film through said mask and the planarizing film and onto said surface.
19. A process as claimed in claim 18 wherein said second film comprises a positive acting photoresist.
20. A process as claimed in claim 18 or 19 wherein said image formed on said second film is transferred through said planarizing film onto said surface using reactive ion etching.
21. A process as claimed in claim 18 wherein said second film comprises a negative acting photoresist.
22. A process as claimed in claim 19 wherein said planarizing film is exposed to deep UV and developed using an aqueous base developer to transfer said image formed on said second film onto said surface.
23. A process as claimed in claim 18 or 19 further comprising adding at least one layer, intermediate to said planarizing film and said second film onto said planarizing film, said intermediate layer being resistant to said developing means used to create an image on said second film, and wherein said intermediate layer is developed through said mask formed on said second film to form a second image using plasma or wet etching to form a mask for transferring said second image onto said surface through said planarizing layer.
24. A process as claimed in claim 23 wherein said second image on said intermediate layer is transferred onto said surface by dry etching said planarizing layer through said mask formed on said intermediate layer.

Revendications

1. Photoresist positif comprenant un polymère polyglutarimide préformé, non réticulé, formé à partir d'un ester d'acide (méth)acrylique et comportant au moins 5 % en poids de motifs glutarimide de formule





dans laquelle R_1 , R_2 et R_3 représentent indépendamment des atomes d'hydrogène ou des radicaux hydrocarbonés alkyle, aryle, aralkyle ou alkaryle non substitués ou substitués, ayant de 1 à 20 atomes de carbone, et dans laquelle au moins 20 % en moles des substituants R_3 sont des atomes d'hydrogène, dissous dans un solvant de filage non aqueux, consistant en un ou plusieurs solvant(s) pour le polyglutarimide, non aqueux, non réactif(s), ledit solvant étant choisi parmi des solvants polaires aprotiques de type amide, des solvants polaires protiques hydroxylés, des solvants polaires aprotiques cétoniques, des acides carboxyliques polaires à courtes chaînes et des éthers basiques polaires, ledit solvant pour le polyglutarimide étant éventuellement utilisé en association avec un ou plusieurs composés parmi l'acétylacétone, le 1-méthoxy-2-propanol, la cyclohexanone, le chlorobenzène, le xylène, le toluène, l'acétate de butyle, le 1,2-diméthoxyéthane, l'éther monométhylique d'éthylèneglycol, la 2,4-pentanedione et un mélange d'acétate d'éther monoéthylique d'éthylèneglycol, de xylène et d'acétate de butyle, et dans lequel le photoresist, après exposition à de l'énergie, est développable avec une solution aqueuse.

2. Photoresist selon la revendication 1, comprenant de 5 à 30 % en poids de polyglutarimide non réticulé et de 95 à 70 % en poids de solvant de filage non aqueux.
3. Photoresist selon la revendication 2, comprenant de 10 à 20 % en poids de polyglutarimide non réticulé et de 90 à 80 % en poids de solvant de filage non aqueux.
4. Photoresist selon l'une quelconque des revendications 1 à 3, comprenant en outre un photosensibilisateur travaillant en positif, dissous dans ledit solvant de filage non aqueux.
5. Photoresist selon la revendication 4, dans lequel la concentration dudit photosensibilisateur va de 5 à 30 % en poids, par rapport au poids dudit polyglutarimide préformé, non réticulé.
6. Photoresist selon la revendication 4 ou 5, dans lequel ledit photosensibilisateur comprend un ou plusieurs composés de type diazo-oxyde et/ou bis(o-nitrobenzyl)-1,7-heptane-dioate.
7. Photoresist selon l'une quelconque des revendications 4 à 6, dans lequel le photosensibilisateur peut absorber un rayonnement UV proche, moyen ou lointain.
8. Photoresist selon l'une quelconque des revendications 1 à 7, dans lequel le polyglutarimide a un rapport atomique du carbone à l'azote d'au moins 8 et une température de transition vitreuse d'au moins 140 °C.
9. Photoresist selon l'une quelconque des revendications 1 à 8, dans lequel ledit polyglutarimide préformé est formé par imidation d'un polymère poly(méthacrylate de méthyle) par l'ammoniac, ou est formé par imidation d'un polymère poly(méthacrylate de méthyle) par un système réactif mixte comprenant au moins 20 % en poids d'ammoniac et au moins une alkylamine.
10. Pellicule uniforme, adhérente, à base aqueuse, développable, formée à partir d'un photoresist selon l'une quelconque des revendications 1 à 9.
11. Pellicule selon la revendication 10, ayant une épaisseur d'environ 0,5 à environ 3,0 μm , de préférence



d'environ 1 μm .

12. Système de photoresist multicouche comprenant une couche rendant plane formée à partir d'un photoresist selon l'une quelconque des revendications 1 à 9, et au moins une autre couche capable de recevoir une image, sur ladite couche rendant plane.

13. Système de photoresist multicouche selon la revendication 12, dans lequel la couche rendant plane et la couche adjacente déposée sur ladite couche rendant plane ne forment pas de voile interfacial.

14. Procédé pour la formation d'un système de photoresist mono- ou multicouche développable avec une solution aqueuse, dans lequel on utilise, dans la formation d'au moins une couche, un photoresist positif selon l'une quelconque des revendications 1 à 9.

15. Procédé pour la formation d'une image sur une surface, comprenant le dépôt sur ladite surface d'une pellicule adhérente, travaillant en positif, formée à partir d'un photoresist selon l'une quelconque des revendications 1 à 9, l'exposition d'une partie de ladite pellicule à une source d'énergie qui augmente la vitesse de dissolution du polyglutarimide dans un révélateur, et le développement de la partie exposée de ladite pellicule à l'aide dudit révélateur, pour former ladite image.

16. Procédé selon la revendication 15, dans lequel ladite source d'énergie est un rayonnement ultraviolet, un faisceau d'électrons, un faisceau ionique ou un rayonnement X.

17. Procédé selon la revendication 15 ou 16, comprenant en outre la cuisson douce de ladite pellicule avant l'exposition de ladite pellicule à ladite source d'énergie.

18. Procédé pour la formation d'une image sur une surface, comprenant le dépôt sur ladite surface d'une pellicule adhérente rendant plane, formant une seconde surface, ladite pellicule rendant plane comprenant un polymère polyglutarimide préformé non réticulé, selon l'une quelconque des revendications 1 à 9,

le dépôt d'une seconde pellicule capable de recevoir une image sur ladite seconde surface, l'exposition d'une partie de ladite seconde pellicule à une source de rayonnement, le développement de la partie exposée de ladite seconde pellicule pour la création d'un masque sur la pellicule rendant plane, et le transfert de ladite image, de ladite seconde pellicule, à travers ledit masque et ladite pellicule rendant plane, et sur ladite surface.

19. Procédé selon la revendication 18, dans lequel ladite seconde pellicule comprend un photoresist travaillant en positif.

20. Procédé selon la revendication 18 ou 19, dans lequel ladite image formée sur ladite seconde pellicule est transférée, à travers ladite pellicule rendant plane, sur ladite surface, au moyen d'attaque par ions réactifs.

21. Procédé selon la revendication 18, dans lequel ladite seconde pellicule comprend un photoresist travaillant en négatif.

22. Procédé selon la revendication 19, dans lequel ladite pellicule rendant plane est exposée à un rayonnement UV lointain et développée au moyen d'un révélateur à base aqueuse, pour le transfert sur ladite surface de ladite image formée sur ladite seconde pellicule.

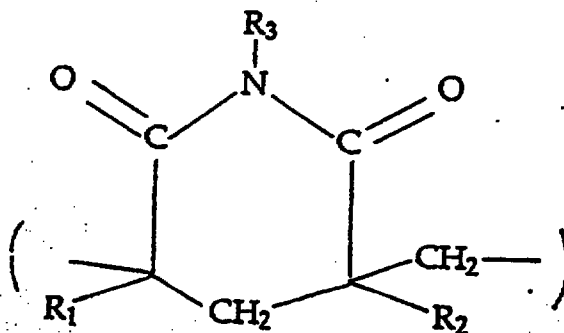
23. Procédé selon la revendication 18 ou 19, comprenant en outre l'addition sur ladite pellicule rendant plane d'au moins une couche, intermédiaire entre ladite pellicule rendant plane et ladite seconde pellicule, ladite couche intermédiaire étant résistante audit moyen de développement utilisé pour créer une image sur ladite seconde pellicule, et dans lequel ladite couche intermédiaire est développée, à travers ledit masque formé sur ladite seconde pellicule, pour la formation d'une seconde image au moyen d'attaque par plasma ou par une solution, pour la formation d'un masque pour le transfert de ladite seconde image sur ladite surface, à travers ladite couche rendant plane.



24. Procédé selon la revendication 23, dans lequel ladite seconde image sur ladite couche intermédiaire est transférée sur ladite surface par attaque à sec de ladite couche rendant plane, à travers ledit masque formé sur ladite couche intermédiaire.

5 Patentansprüche

1. Positiver Photoresist, umfassend ein vorgeformtes, nicht-vernetztes, aus einem Ester von (Meth)-acrylsäure gebildetes Polyglutarimid-Polymer, das mindestens 5 Gew.-% Glutarimideinheiten der Struktur



aufweist, in der R_1 , R_2 und R_3 unabhängig Wasserstoff oder unsubstituierte oder substituierte Alkyl-, Aryl-, Aralkyl- oder Alkarylkohlenwasserstoffe mit ein bis zwanzig Kohlenstoffatomen darstellen und wobei mindestens 20 Mol-% der substituenten R_3 Wasserstoff sind, gelöst in einem nicht-wässrigen Schleuderguß-Lösungsmittel, welches wenigstens ein nicht-wässriges, nichtreaktives Lösungsmittel ist, das ausgewählt ist aus: polaren, aprotischen Amidlösungsmitteln; polaren, protischen Hydroxyl-Lösungsmitteln; polaren, aprotischen Ketonlösungsmitteln; kurzkettigen, polaren Carbonsäuren; und polaren, basischen Ethern; wobei das Lösungsmittel für das Polyglutarimid gegebenenfalls in Kombination mit einem oder mehreren von Acetylaceton, 1-Methoxy-2-propanol, Cyclohexanon, Chlorbenzol, Xylol, Toluol, Butylacetat, 1,2-Dimethoxyethan, Ethylenglycolmonomethylether, 2,4-pentandion, und einem Gemisch aus Ethylenglycolmonoethyletheracetat, Xylol und Butylacetat verwendet wird und wobei der Photoresist, nach Belichten mit Energie, mit einer wässrigen Lösung entwickelt werden kann.

2. Photoresist nach Anspruch 1, umfassend 5 bis 30 Gew.-% nicht-vernetztes Polyglutarimid und 95 bis 70 Gew.-% nicht-wässriges Schleuderguß-Lösungsmittel.
3. Photoresist nach Anspruch 2, umfassend 10 bis 20 Gew.-% nicht-vernetztes Polyglutarimid und 90 bis 80 Gew.-% nicht-wässriges Schleuderguß-Lösungsmittel.
4. Photoresist nach einem der Ansprüche 1 bis 3, ferner umfassend einen in dem nicht-wässrigen Schleuderguß-Lösungsmittel gelösten, positiv arbeitenden Photosensibilisator.
5. Photoresist nach Anspruch 4, wobei die Konzentration des Photosensibilisators 5 bis 30 Gew.-%, bezogen auf das Gewicht des vorgeformten, nicht-vernetzten Polyglutarimids, beträgt.
6. Photoresist nach Anspruch 4 oder 5, wobei der Photosensibilisator ein oder mehrere von Diazoxid und/oder bis-(o-Nitrobenzyl)-1,7-Heptandioat umfaßt.
7. Photoresist nach einem der Ansprüche 4 bis 6, wobei der Photosensibilisator Strahlung im nahen, mittleren oder fernen UV absorbieren kann.
8. Photoresist nach einem der Ansprüche 1 bis 7, wobei das Polyglutarimid ein Atomverhältnis von Kohlenstoff zu Stickstoff von mindestens 8 und eine Glasübergangstemperatur von mindestens 140 °C aufweist.
9. Photoresist nach einem der Ansprüche 1 bis 8, wobei das vorgeformte Polyglutarimid durch Imidisieren



eines Polymethylmethacrylpolymer mit Ammoniak oder durch Imidisieren eines Polymethylmethacrylatpolymer mit einem reaktanten Gemisch, umfassend mindestens 20 Gew.-% Ammoniak und mindestens ein Alkylamin, gebildet wird.

- 5 10. Haftfähiger, gleichmäßiger, mit wäßriger Base entwickelbarer Film, gebildet aus einem Photoresist nach einem der Ansprüche 1 bis 9.
11. Film nach Anspruch 10 mit einer Dicke von etwa 0,5 μm bis etwa 3,0 μm , vorzugsweise etwa 1 μm .
- 10 12. Mehrschicht-Photoresistsystem umfassend eine aus einem Photoresist nach einem der Ansprüche 1 bis 9 gebildete ebene Schicht und mindestens eine weitere Schicht, die auf der ebenen Schicht mit einem Bild versehen werden kann.
13. Mehrschicht-Photoresistsystem nach Anspruch 12, in dem die ebene Schicht und die benachbarte, auf der ebenen Schicht aufgebraute Schicht keinen Grenzflächenschlamm ausbilden.
- 15 14. Verfahren zur Ausbildung eines ein- oder mehrschichtigen, mit einer wäßrigen Lösung entwickelbaren Photoresistsystems, wobei ein positives Photoresistsystem nach einem der Ansprüche 1 bis 9 zur Ausbildung mindestens einer Schicht verwendet wird.
- 20 15. Verfahren zur Darstellung eines Bildes auf einer Oberfläche, umfassend das Aufbringen eines haftfähigen, positiv arbeitenden Films aus einem Photoresist nach einem der Ansprüche 1 bis 9 auf der Oberfläche, Belichten eines Teils des Films mit einer Energiequelle, wobei die Lösungsgeschwindigkeit des Polyglutarimids in einem Entwickler erhöht wird, und Entwickeln des belichteten Teils des Films mit dem Entwickler, um das Bild zu erzeugen.
- 25 16. Verfahren nach Anspruch 15, wobei die Energiequelle Ultraviolett-, Elektronen-, Ionen- oder Röntgenstrahlung ist.
- 30 17. Verfahren nach Anspruch 15 oder 16, ferner umfassend eine milde Wärmebehandlung (softbaking) des Films, bevor der Film mit der Energiequelle belichtet wird.
- 35 18. Verfahren zur Darstellung eines Bildes auf einer Oberfläche, umfassend das Aufbringen eines haftfähigen, ebenen Films auf der Oberfläche, wodurch eine zweite Oberfläche gebildet wird und wobei der ebene Film ein vorgeformtes, nicht-vernetztes Polyglutarimid-Polymer nach einem der Ansprüche 1 bis 9 umfaßt;
Aufbringen eines zweiten Films, der der zweiten Oberfläche mit einem Bild versehen werden kann;
Belichten eines Teils des zweiten Films mit einer Strahlenquelle;
Entwickeln des belichteten Teils des zweiten Films, um eine Maske auf dem ebenen Film zu erzeugen und
40 Übertragen des Bildes von dem zweiten Film durch die Maske und den ebenen Film auf die Oberfläche.
- 45 19. Verfahren nach Anspruch 18, wobei der zweite Film einen positiv arbeitenden Photoresist umfaßt.
20. Verfahren nach Anspruch 18 oder 19, wobei das auf dem zweiten Film dargestellte Bild durch reaktives Ionenätzen durch den ebenen Film auf die Oberfläche übertragen wird.
21. Verfahren nach Anspruch 18, wobei der zweite Film einen negativ arbeitenden Photoresist umfaßt.
- 50 22. Verfahren nach Anspruch 19, wobei der ebene Film mit fernem UV belichtet und zur Übertragung des auf dem zweiten Film dargestellten Bildes auf die Oberfläche mit einer wäßrigen Base entwickelt wird.
- 55 23. Verfahren nach Anspruch 18 oder 19, ferner umfassend das Hinzufügen von mindestens einer Schicht zwischen den ebenen Film und den zweiten Film und auf den ebenen Film, wobei die Zwischenschicht widerstandsfähig ist gegen die zur Erzeugung des Bildes auf dem zweiten Film verwendeten Entwicklungsmittel, und wobei die Zwischenschicht durch die auf dem zweiten Film ausgebildete



Maske zur Ausbildung eines zweiten Bildes durch Plasma- oder Naßätzen entwickelt wird, um eine Maske für die Übertragung des zweiten Bildes durch die ebene Schicht auf die Oberfläche zu bilden.

24. Verfahren nach Anspruch 23, wobei das zweite Bild auf der Zwischenschicht durch Trockenätzen der ebene Schicht durch die auf der Zwischenschicht ausgebildeten Maske auf die Oberfläche übertragen wird.

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