

Description

This invention is concerned with microplastic structures, processes for forming such microplastic structures, and photomasks suitable for use in such processes.

As used herein, the terms "microplastic structures", "independently selected", and "aspect ratio" have the following meanings:-

"Microplastic structures":

crosslinked polymer articles which are thermally stable to temperatures in excess of 200°C and where the size, length, width and thickness of the desired structure can be independently selected before fabrication.

"Independently selected":

means, as it relates to the dimensions of a microplastic structure, not only that the thickness, width and length of the structure can be selected independently prior to fabrication, within the aspect ratio and resolution capability of the photosensitive composition used in the process, but also that each of these dimensions can be varied throughout the structure. For example, the thickness of a structure at its center may be different from its thickness at other points in the structure. Thus, "independent selection" of the microplastic structure contemplates the pre-fabrication selection of structures having an almost limitless number of different configurations and sizes.

"Aspect ratio":

refers to the maximum ratio of image or structure height or thickness to image or structure width, respectively. An aspect ratio of 1.5 therefore means that for an image or structure of a given width the maximum image or structure height is 1.5 times its width.

Microelectronics have been revolutionizing how we communicate, store and process information. Complex electrical circuits and devices can now be placed onto a single silicon chip. Rapid advances are continuing to be made in accelerating the processes used to incorporate electrical circuits onto silicon chips and in miniaturizing the circuits and devices containing them. Miniaturization of electrical circuits has resulted in a demand for smaller electrical, mechanical, chemical and optical devices such as sensors used with silicon chip circuits. A "sensor" is a device that converts a physical, chemical or optical change in a system into an electrical signal. The signal may be transmitted to a computer or microprocessor for measurement or response to the change in accordance with a set of programmed instructions. For example, a microprocessor may respond to a signal from a sensor by sending another signal to another device, such as an actuator, which regulates one or more variables in the system, thereby automatically controlling the

system. Sensors may be used to measure or compensate for changes in a number of parameters such as size, angle, position, vibration, motion, velocity, acceleration, rotation, force, torque, time, mass, density, color, luminance, radiation, flow, volume, level, sound, humidity, acidity, temperature, pressure (see, for example, Tschulene and Selders, Sensor Technology in the Microelectronic Age, Battelle Technical Inputs to Planning, Report No. 40 (1984); R. Allen, Sensors in Silicon, High Tech Sept. 1984, page 43; J. McDermott, Popular Science, June 1984, page 87; Transducers '85, 1985 International Conference on Solid-State Sensors and Actuators, IEEE; H. Wohltzen, Anal. Chem. 56 (1) 16 (A) (1984)).

Traditionally sensors have been fabricated separately from the silicon chip circuits, thereby requiring connection thereto by wires. There is a growing interest in what are commonly referred to as "smart" sensors which are constructed as integral elements of the silicon circuitry itself such as for use in robotics.

Structures in which two dimensions are independently selected prior to fabrication have been developed by the anisotropic etching of a silicon wafer, along its crystalline planes, to take advantage of the mechanical and electrical properties of the silicon itself. Anisotropic etching of two dimensional patterns has been used with photolithographic materials such as in the construction of ink jet printer nozzles where the uniformity and size of the orifice is critical (see, for example, U.S. Patents Nos. 3,921,916 and 4,007,464). A complete miniature gas chromatographic device fabricated on a silicon wafer capable of resolving six component mixtures has also been reported in U.S. Patent No. 3,538,744 and K.E. Peterson, Proc. IEEE 70(5), page 420, (1982). These subtractive techniques require the removal of portions of the silicon itself to leave a structure thereon and do not contemplate the addition of a photosensitive coating to the silicon surface and the processing of the coating to form the structure, hereinafter referred to as an "additive" technique.

At the present time there is no acceptable or simple additive technique for preparing three dimensional microplastic structures directly on the surface of a silicon wafer to function as a smart sensor. Conventional photoresist compositions cannot be used to form microplastic structures for a number of reasons. Conventional photoresist materials typically are not thermally stable to temperatures in excess of about 120°C, and are only useful to produce two-dimensional or stencil images having a fixed thickness, aspect ratios of about 1.5, and maximum commercial resolution capability of about 1.5 micrometers.

Prior attempts at fabricating microplastic structures have utilized the placement of thermally stable, photosensitive polyimide dielectric pads as permanent structures on wafer surfaces. (see for example, *Polymers in Electronics*, ACS Symposium Series No. 242 (1984) pages 239-258 and references cited therein). The photosensitive coatings used to form the polyimide pads are difficult to handle and can only be imaged in the plane parallel to the surface onto which the coating is deposited (length and width) but not in a plane perpendicular to the surface (height or thickness). Accordingly only two dimensionally variable or stencil structures, analogous to cookies cut from a baking pan using a cookie cutter, may be prepared by this technique.

The only reported attempt to prepare independently selected three dimensional structures using a photosensitive composition and an additive technique was described by William Salmre in *Three Dimensional Microfabrication on Thick Film Photoresist Mandrels*, SPIE Vol. 469 *Advances in Resist Technology* (1984). Salmre found that it was not possible, however, to produce crosslink structures from a thick film resist by exposing the top side (side farthest from the substrate surface on which the resist is deposited) of the resist to actinic radiation through a conventional photomask. Salmre found that when the resist was laminated directly onto the photomask and exposed from below the substrate surface (bottom side), instead of from the top side, it was possible to prepare conically shaped thermoplastic structures which, while limited in thickness, did not topple over as easily as the structures formed from top side imaging. Salmre also suggested aligning multiple photomasks and exposing the resist from both the top and bottom sides to produce more vertically perpendicular structures. Salmre's photomasks also functioned as the substrate itself and are disclosed as being useful as mandrels for depositing electroformed, plated or deposited parts. Salmre described the formation of hemispherical blobs or tetons by modifying the bottom side exposure dosage followed by development, and reexposure from the top side through a second mask followed by subsequent redevelopment. By using multiple resists and masks and by exposing the resists from both the top and bottom sides, Salmre suggests that structures having other shapes such as a stepped mandrel ("Ziggurat"), volcanic ("Fujiyama") or a parabolic ("Sombrero") shape are possible. Salmre acknowledges the difficulty in aligning the masks using elaborate equipment and claims that such elaborate equipment need not be used if a positive-acting photosensitive sheet fastened to the photomask were used. Salmre concluded by speculating on other shaped articles, such as "ant hills", that could possibly be

formed using other techniques such as laser holography.

As indicated by Salmre the possibilities in this field are unlimited; however, Salmre's process requires simplification and other modifications for it to be of commercial utility. For example, for commercial applications, it would be desirable to have crosslinked, thermally and dimensionally stable structures which resist attack by common solvents and temperatures of at least 200 °C.

We have now surprisingly found that three dimensional, thermally stable, microplastic structures can be prepared having a variety of configurations suitable for a wide range of use in or with electrical, chemical, mechanical or optical devices. For example, such thermally stable microplastic structures can be prepared, having individually selected micrometer size dimensions directly on the surface of a silicon wafer without requiring multiple photomasks or elaborate alignment equipment and procedures and by using a technique which is compatible with conventional integrated circuit production techniques. We have also found that layered microplastic structures can be prepared in which multiple structures are aligned and connected one on top of another.

According to the present invention there is provided a process for forming a micrometer-sized microplastic structure which is thermally stable to temperatures of at least 200 °C, wherein the dimensions of size, length, width and thickness are independently selectable before fabrication, and wherein each of such dimensions are variable throughout the structure, the process comprising utilizing one or more photomasks to selectively control the amount of exposing radiation in the thickness of a photosensitive coating comprising a polymer system which is aqueously-developable and capable of being crosslinked by the action of said exposing radiation and heat, and wherein said one or more photomasks comprise:-

- (a) one or more radiation attenuating photomasks; or
- (b) two or more different photomasks having opaque and transparent regions with the photosensitive coating being subjected to sequential and different dosages of actinic radiation.

Preferably the process of the present invention comprises:-

- (a) depositing a photosensitive coating composition comprising The present invention also provides a micrometer-sized microplastic structure obtainable by the process of the invention from about 40 to about 99.9 weight percent of a crosslinkable polymer and from about 0.1 to about 60 weight percent photoacid generator, the percentages being based on the weight of crosslinkable polymer plus photoacid generator,

as the coating on a substrate surface;

(b) exposing a portion or portions of the coating to a source of actinic radiation through the one or more photomasks;

(c) heating the exposed coating to a temperature of from about 70 °C to about 120 °C to crosslink the exposed coating portion(s);

(d) removing portion(s) of said coating using an aqueous base solution to produce a microplastic structure;

it being understood that steps (c) and (d) can be carried out in either order and that, when step (d) is carried out before step (c), an additional step is carried out between steps (d) and (c), the additional step comprising flood exposing the coating to actinic radiation.

The present invention also provides a micrometer-sized microplastic structure obtainable by the process of the invention.

The present invention provides a process which is useful for forming thermally stable, micrometer size microplastic structures having three, independently selected, dimensions. The process conveniently involves the selection of a suitable photosensitive composition, the deposition of the photosensitive composition as a coating on a substrate surface, the exposure of the coating to actinic radiation, e.g. in the near or deep ultraviolet wavelength region, through a suitable photomask, preferably a specially designed radiation attenuating photomask having a preformed pattern conforming to the dimensions of the desired microplastic structure, and the development of the microplastic structure by removing portions of the coating using an aqueous solution. The microplastic structures may be prepared in the positive or negative mode using near ultraviolet exposing radiation and in the negative mode using deep ultraviolet exposing radiation.

The crosslinked microplastic structures so formed are stable to temperature in excess of 200 °C and can be prepared with a limitless variety of shapes without the need for elaborate alignment, multiple exposure and redevelopment techniques. This process permits the fabrication of low cost structures useful as components of electrical, chemical, mechanical and optical systems such as smart sensors.

The photosensitive composition contains a crosslinkable polymer and a sufficient amount of a selected photoacid generating compound for crosslinking the polymer when the photoacid generator is activated by a sufficient quantity of the selected actinic radiation. Overall, the photosensitive composition preferably contains from about 40 to about 99.9 weight percent of acid-hardening resin system and from about 0.1 to about 60 weight percent of a suitable photoacid generator, the percentages be-

ing based on the weight of said crosslinkable polymer-containing composition.

The polymers useful in the photosensitive composition include acid-hardening resin systems as described in detail in our EP-A-0164248. The acid-hardening resin systems contain a polymer that crosslinks in the presence of an acid catalyst and heat. The acid-hardening resin system may be prepared from a variety of aminoplast or phenoplast resins in combination with compounds or low molecular weight polymers that contain a plurality of hydroxyl, carboxyl, amide or imide groups.

Suitable aminoplast resins include urea-formaldehyde, benzoguanamine-formaldehyde, melamine-formaldehyde, and glycoluril-formaldehyde resins, and combinations thereof. The aminoplasts are used in combination with reactive hydrogen-containing compounds such as novolak resins, polyvinylphenol, polyglutarimide, poly(meth)acrylic acid copolymers, alkali-soluble polyacrylamide and polymethacrylamide copolymers, copolymers containing 2-hydroxyethyl acrylate and methacrylate, polyvinyl alcohols, such as those prepared from partially hydrolyzed polyvinylacetates, alkali-soluble styrene-allyl alcohol copolymers, and mixtures thereof. Preferred reactive hydrogen-containing compounds are novolak resins containing hydroxyl groups, sites for the electrophilic substitution of aromatic rings at positions ortho or para to the hydroxyl group, and having a weight average molecular weight of from about 300 to about 100,000, preferably from about 1000 to about 20,000.

The acid-hardening resin system may be prepared by combining a phenoplast resin with a latent formaldehyde-generating compound such as s-trioxane, N(2-hydroxyethyl) oxazolidine and oxazolidinylethyl methacrylate.

The polymer in the photosensitive composition can be selected based on known specific and desirable chemical and/or physical properties so that the microplastic structures, which are formed therefrom, have the mechanical, chemical, electrical and/or optical properties needed for a specific application. For example, an acid-hardening resin system which has a specific modulus of elasticity, reactivity towards enzymes, resistance to the flow of electrons and/or refractive index can be selected for preparing microplastic structures for a specified end use application.

The photoacid-generating compounds useful in combination with the crosslinkable polymer in the photosensitive composition are conveniently neutral compounds or mixtures which are converted to acids upon exposure to actinic radiation. The photoacid generators should be soluble in or form a homogeneous solution in the photosensitive com-

position containing the crosslinkable polymer itself as well as in the solvent used to form the coating solution. The photoacid generator should not phase separate from the photosensitive composition when the coating, deposited from the coating solution on a substrate surface, is heated to remove solvent ("soft baked"). The photoacid generator should be sufficiently developable in suitable aqueous base developer solutions to permit the removal of coating portions after exposure. The photoacid generator should be non-reactive with the components of the photosensitive composition in the absence of activating radiation and be non-reactive with the substrate itself. The photoacid generator should have no adverse effect on the adhesion, uniformity or quality of the photosensitive coating deposited on the substrate surface. The photoacid generator should be capable of crosslinking the photosensitive coating containing the crosslinkable polymer upon exposure to activating radiation and heating to elevated temperatures when utilizing the negative mode without prematurely catalyzing the crosslinking reaction at ambient temperatures. The crosslinked structure formed using the photoacid generator in combination with the crosslinkable polymer should be thermally stable to temperatures in excess of 200 °C. The photoacid generator should also not substantially volatilize from the photosensitive coating upon softbaking to remove solvent from the coating.

We have found that it is possible to prepare the microplastic structures in the negative mode using deep ultraviolet radiation by employing specially selected deep UV photoacid generators in the photosensitive composition. Deep ultraviolet radiation, hereinafter referred to as "deep UV", refers to ultraviolet radiation having wavelengths of from about 210 to about 299 nanometers, e.g. about 254 nanometers. The deep UV photoacid generators suitable for use in preparing the microplastic structures of the invention are highly sensitive to deep UV radiation and insensitive to near UV radiation. Suitable deep UV photoacid generators are those which are compatible with the photosensitive coating compositions, are developable in aqueous developers, and have a high degree of sensitivity to deep UV radiation. Unlike conventional photoacid generators, such as those used in near UV photosensitive compositions which may be used in the process of the invention, the deep UV photoacid generators are typically capable of producing a crosslinked polymer structure when employed in the photosensitive composition at a concentration of as low as 0.1 weight percent, based on the total solids content of the photosensitive composition, when the coating formed using the composition, is exposed to a deep UV exposure of about 10 millijoules per square centimeter (10 mJ/cm²) of the

coating and when the photosensitive composition contains a suitable crosslinkable polymer, such as an acid-hardening resin system. These deep UV photoacid generators are preferably halogenated organic compounds which generate a water-soluble halogen acid upon exposure to deep UV radiation, such halogenated photoacid generators being described in more detail in our EP-A-0.232.972.

For example, suitable deep UV photoacid generators include halogenated organic compounds such as:

1,1-bis-(p-chlorophenyl)-2,2,2-trichloroethane (also known as DDT),
 1,1-bis[p-methoxyphenyl]-2,2,2-trichloroethane (Methoxychlor)
 1,2,5,6,9,10-hexabromocyclodecane;
 1,10-dibromodecane;
 1,1-bis[p-chlorophenyl]-2,2-dichloroethane;
 4,4'-dichloro-2-(trichloromethyl)benzhydrol also known as 1,1-bis[p-chlorophenyl]-2,2,2-trichloroethanol (Kelthane);
 hexachlorodimethyl sulfone;
 2-chloro-6-(trichloromethyl)pyridine;
 0,0-diethyl-0-(3,5,6-trichloro-2-pyridyl)-phosphothioate (Dursban)
 1,2,3,4,5,6-hexachlorocyclohexane;
 N(1,1-bis[p-chlorophenyl]-2,2,2-trichloroethyl)-acetamide;
 tris[2,3-dibromopropyl]isocyanurate;
 2,2-bis[p-chlorophenyl]-1,1-dichloroethylene;
 and their isomers and homologs. The preferred halogenated, deep UV photoacid generators are DDT, Methoxychlor, Kelthane and tris(2,3-dibromopropyl)isocyanurate.

The preferred deep UV photoacid generators are those capable of being used at concentrations as low as about 0.1 weight percent when the deep UV exposure dosage is 10 mJ/cm².

When near ultraviolet light ("near UV") having wavelengths of from about 300 to about 500 nanometers, e.g. about 365 nanometers, is desired to be used to form microplastic images and structures in the positive or negative mode, the photoacid generators may be compounds or mixtures that generate aqueous soluble, carboxylic acids upon exposure to the near UV radiation. The preferred near UV photoacid generators are o-naphthoquinone diazides, and in particular the phenolic esters of naphthoquinone diazide sulfonic acids. These preferred near UV photoacid generators, as described in our EP-A-0 164 248 and references cited therein, may be present in the photosensitive composition at a concentration ranging from about 5 to about 80 weight percent, based on the total solids content of the photosensitive composition. Naphthoquinone diazides and polymers thereof which generate indenecarboxylic acids when exposed to near UV radiation are preferred near UV

photoacid generators. Other suitable near UV photoacid generators include ortho-nitrotoluene derivatives that generate carboxylic acids when exposed to near UV radiation such as, for example, orthonitrobenzaldehyde, esters of ortho-nitrobenzyl alcohol, acetyls and hemiacetals of ortho-nitrobenzaldehyde.

The photosensitive composition containing the crosslinkable polymer and photoacid generator compound is dissolved in a non-reacting solvent. These solvents include: glycol ethers such as ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, Propasol P and Propasol B; Cellosolve esters such as methyl Cellosolve acetate, ethyl Cellosolve acetate and acetates of Propasol B and P; aromatic hydrocarbons such as toluene and xylene; ketones such as methylethyl ketone, cyclopentanone and cyclohexanone; esters such as ethyl acetate, butyl acetate, isobutyl isobutyrate and butyrolactone; amides such as dimethyl acetamide (DMAC), n-methyl-pyrrolidinone (NMP) and dimethylformamide (DMF); chlorinated hydrocarbons such as ethylene dichloride, chlorobenzene and ortho-dichlorobenzene; nitrobenzene; dimethylsulfoxide; and mixtures of such solvents.

The photosensitive coating solution may contain at least 50 percent by weight solvent and preferably contains from about 65 to about 95 percent by weight solvent.

Various additives can also be added to the photosensitive composition in minor amounts ranging from about 0.001 percent to about 10 percent by weight, based on the weight of total solids. The additives may enhance the performance of the coating solution and the resulting coating. They can, for example, act as flow and levelling agents, anti-striation agents, plasticizers, compatibilizing agents, light attenuating substances and/or anti-reflective dyes. Alkaline decomposition control can be accomplished by the addition of from about 0.001 to 2 weight percent, based on solids weight, of weak organic acids such as acetic, propionic, tartaric, malonic, succinic, glutaric or phthalic acid. Small quantities of water, for example from 0.001 to 1 percent, can be added to assist in the decomposition of the exposed photoacid generator. Low molecular weight monomeric alcohols or glycol ethers can be added, for example, at concentrations of from about 1 to about 20 weight percent to stabilize aminoplast resins in the photosensitive composition.

The preferred photosensitive compositions useful to prepare microplastic structures using near UV exposure contain from about 3 to about 50 percentage by weight of aminoplast resin, about 90 percentage to about 40 percentage by weight reactive hydrogen generating compound, and from about 2 to about 30 percentage by weight near UV

photoacid generator, or from about 50 to about 95 percentage by weight of a phenoplast resin, from about 40 to about 3 percentage by weight formaldehyde-generating compound and about 2 to about 30 percentage by weight near UV photoacid generator. A more preferred concentration of the near UV photoacid generator is from about 15 to 25 percentage by weight. When microplastic structures are desired to be prepared in the negative mode using the minimum amount of deep UV exposure, the preferred photosensitive composition will contain the same concentration of aminoplast resin and reactive hydrogen generating compound, or phenoplast resin and formaldehyde-generating compound, as described above for use in the near UV, but the preferred concentration of the deep UV photoacid generator will range from about 0.1 to about 5 percent by weight.

A photosensitive composition useful for preparing microplastic structures using near UV exposure may be prepared by adding an aminoplast resin to a conventional solution of a novolak resin and near UV photoacid generator. The resulting photosensitive coating solution may then be deposited on a substrate surface as a uniform coating having a thickness of from about 0.5 to about 50 micrometers by conventional techniques such as by spin coating. After the coating solution has been applied to the substrate, the substrate and coating solution may be heated to a temperature of about 90 °C for about 30 minutes to volatilize the solvent ("soft baking"). The touch-tack free coating that results may then be processed in either the positive or negative mode in the near UV or in the negative mode in the deep UV to form three dimensional, aqueously-developable, thermally stable microplastic structures. Suitable substrate surfaces for use with the photosensitive coating solutions with near UV or deep UV exposure through a suitable photomask, e.g. a radiation attenuating photomask, include silicon or silicon dioxide coated, aluminum-aluminum oxide or silicon nitride wafers.

The thermally stable microplastic structures of the invention may be formed in a negative or positive manner when near UV photoacid generators are employed, and in the negative mode when deep UV photoacid generators are used. We have found that when near UV exposure is employed, it is preferable to form the microplastic structures using the negative mode of action. When the negative mode of action is employed with a photosensitive coating more latitude exists for the exposure and development parameters needed to prepare highly resolved images than when the positive mode is employed. We have also found that the aspect ratio for the near UV negative image is at least twice that achievable with the corresponding near UV positive image. For accept-

able near UV negative images aspect ratios greater than 3 are easily achieved, while in the case of near UV positive images an aspect ratio of only about 1.6 can be achieved but with difficulty. This means that, for a structure of a given height or thickness, the width of the near UV negative structure can be half the width of a corresponding positive structure or, for a structure of a given width, the height or thickness of the microplastic structure formed in the negative mode can be more than twice the height of a corresponding positive structure formed from the same photosensitive composition. The preference for the negative mode of action with near and deep UV exposure is a result of the fact that the negative image structure is crosslinked before development while the positive image structure is crosslinked after development. When the image structure is crosslinked before development, the crosslinked image structure is virtually insoluble in the aqueous developer. When the positive mode is employed in the near UV, development of the image structure depends on the relative solubilities of the unexposed/uncrosslinked portion and exposed/uncrosslinked latent image portions of the photosensitive coating. Establishment of optimum exposure conditions, developer type and concentration is, therefore, more difficult and critical for highly resolved near UV positive image structures than when the negative mode of action is employed.

In the negative mode, using near UV or deep UV photoacid generators, the coating is exposed to the appropriate actinic radiation through a suitable photomask, preferably a specially designed photomask, and heated to from about 70°C to about 120°C to crosslink the exposed portion of the coating. The unexposed portions of the coating may then be flood exposed (no photomask) to the same actinic radiation. The coating is then developed and the unexposed portions of the coating are removed using an aqueous base developer. In the positive mode of action using the near UV exposure the coating is exposed to the appropriate near UV actinic radiation through the suitable photomask, preferably the specially designed photomask, and the exposed portion of the coating is developed and removed using an aqueous base solution. The previously unexposed portions of the coating are then flood exposed to the appropriate near UV actinic radiation and heated to from about 70°C to about 120°C, and preferably from about 100°C to about 125°C, to crosslink the subsequently exposed portions of the coating.

During the course of our experiments with the dual-acting, near UV, add-hardening resin-containing photoresists, we observed that when the photoresist is exposed to actinic radiation a con-

centration gradient of photogenerated acid is established in the coating. This concentration gradient is established in the thickness of the coating, the highest concentrations of photoacid being present in the portion of the coating closest to the source of the actinic radiation and the lowest concentration in the portion farthest away from the radiation source. This observation is in accord with Beer's law since the radiation is attenuated as it passes through the coating thickness. In order to process the dual-acting, near UV resist in the positive mode we found it necessary to carefully adjust the amount of exposing near UV radiation to obtain complete conversion of the photosensitive composition in the coating portion in contact with the substrate for subsequent complete removal by the aqueous base developer. Insufficient exposure was found to leave a portion of the resist, namely the resist in contact with the substrate, insoluble in aqueous base developer. Similarly, in the near UV and deep UV negative mode of action in the process of the present invention the exposure dosage must be sufficient to generate sufficient photoacid in the exposed coating portion in contact with the substrate to effectively crosslink the exposed coating. We postulated that, if the amount of radiation used to expose the coating was intentionally controlled such that different amounts of radiation are permitted to reach different levels in the coating thickness, it would be possible to selectively manipulate the final thickness of the microplastic structure at any point in the coating as well as pre-selecting its length and width. Once the desired thickness of the microplastic structure is correlated with the minimum dose of exposing actinic radiation needed to generate a sufficient quantity of photoacid in the exposed coating portion in contact with the substrate to crosslink the image upon heating, it would be possible to design a photomask which permits a controlled transmission of a sufficient amount of actinic radiation to reach different levels in the photosensitive coating deposited on the substrate.

Accordingly a photomask was prepared having areas that permit the transmission of different amounts of exposing radiation. The mask was prepared with partially vacuum metallized "grey" areas that permit the transmission of from about 1 to about 32 percent of the actinic radiation, as well as areas that transmit 100% and 0% of the exposing radiation, to the coating. This attenuation was done in eight steps for each of nine different size patterns on the mask ranging from 1 to 100 times magnification. This resulted in a grid or matrix of patterns or "image clusters" on the mask having various sizes, configurations, and transmission patterns. Using such a mask the amount of actinic radiation used to expose the photosensitive coating

can be selectively attenuated to form structures of different, "independently selected" sizes and shapes. The radiation attenuation feature of the photomask is especially useful for manipulating the thickness of a structure. A structure having different thicknesses along its width and length, varying from the full thickness of the deposited photosensitive coating down to a very thin layer on the substrate, can be prepared using the process and a single attenuating mask pattern. By controlling the exposure dosage of actinic radiation it is also possible to form structures with negative or positive sloping side wall profiles as well as with side walls which are vertically perpendicular to the substrate surface. By so designing the side wall profile, it is also possible to form microplastic structures which can be easily lifted off from the substrate.

In the case of the negative mode and top imaging, as described in more detail hereinafter, we found it possible to form tunneled structures since the areas of the coatings completely exposed to actinic radiation became crosslinked from the top of the coating down to the coating/substrate interface, while in partially exposed areas only those coating areas receiving a sufficient dosage were capable of being crosslinked at all. As long as there are adequately exposed and crosslinkable coating areas adjacent to partially (insufficiently) or unexposed coating areas it is possible to form hollow, undercut or tunneled structures. In the case of the near UV positive mode, with top imaging, it was possible to form intaglio, relief, or recessed images below the top surface of the coating.

If the substrate itself is capable of transmitting actinic radiation and the radiation attenuating photomask is placed beneath the substrate or the photosensitive coating is deposited on the bottom substrate surface, instead of on the top side or side closest to the exposing radiation, exposure of the coating through the mask and substrate can be used to form an inverted image since the concentration gradient of photoacid in the coating is inverted.

The present invention will now be further illustrated by way of the following Examples in conjunction with the accompanying drawings.

In the accompanying drawings:-

Figure 1 is a pictorial representation of a radiation attenuating photomask map;

Figure 2 illustrates the image clusters of a light margin design photomask;

Figure 3 illustrates the image clusters of a dark margin design photomask;

Figure 4 illustrates top and bottom imaging of a photoresist;

Figure 5 illustrates a checkerboard mask pattern (light margin Pattern hereinafter referred to as "Pattern 5(a)") and the microplastic structures

formed therefrom in the negative and positive (near UV) modes using top and bottom imaging; Figure 6 illustrates a checkerboard mask pattern (dark margin Pattern hereinafter referred to as "Pattern 6(a)") and the microplastic structures formed therefrom in the negative and positive (near UV) mode using top and bottom imaging; Figure 7 illustrates how the checkerboard structures of Figures 5 and 6 fit together to form a solid cube;

Figure 8 illustrates a bullseye mask (dark margin) and the four microplastic structures resulting therefrom;

Figure 9 illustrates a bullseye mask (light margin) and the four microplastic structures resulting therefrom;

Figures 10(a) and 10(b) illustrate other bullseye mask patterns and microplastic structures prepared therefrom;

Figure 11 illustrates the microplastic structures formed from the image cluster light margin photomask of Figure 2;

Figure 12 illustrates the microplastic structures formed from the image cluster dark margin photomask of Figure 3;

Figure 13 illustrates conventional photomask patterns for a five level microplastic structure; and

Figure 14 illustrates the five level microplastic structure formed using the photomask patterns of Figure 13.

The radiation attenuating photomasks used in our experiments are illustrated in Figures 1-3. The photomasks were prepared one with a light margin design (Figure 2) and one with a dark margin design (Figure 3). When the near UV positive mode of action is desired, the margin areas in the photomask are made transparent to the exposing radiation (light margin design) so as to cause the resulting microplastic structures to be isolated from one another. When a negative mode of action is desired, such as with the near or deep UV photoacid-containing photosensitive compositions, the margin areas in the photomask are made opaque to the exposing radiation (dark margin design) to isolate the microplastic structures produced. The selection of the proper margin design permits the resulting microplastic structure to be easily isolated from the surrounding portions of the photosensitive coating. In the light margin design, the spaces between each image pattern permits the transmission of 100% of the exposing radiation, while in the dark margin design the spaces between each image pattern is opaque to the exposing radiation (0% transmission). With these two photomask designs (light and dark margin area) it is possible to prepare structures and their inverse structures in the near UV using one photosensitive composition

and a single mode (positive or negative) of operation.

Figures 2 and 3 illustrate the image matrix or "cluster" on the radiation attenuating photomask used in our experiments. In these figures the unshaded areas represent transparent areas of the masks, the cross-hatched areas represent semi-transparent areas of the mask, and the dotted areas represent opaque areas of the mask. Patterns in the first row, first and third columns are referred to as "checkerboards"; the pattern in the first row, second column is referred to as a "cantilever beam"; the patterns in the second row, first column and third row, second column are referred to as "tunnels"; the pattern in the second row, second column is referred to as "penta"; the pattern in the second row, third column is referred to as an "overhung projection"; and the patterns in the third row, first and third columns are referred to as "bullseyes".

Figure 1 provides a map of the 8 x 8 quartz 3 photomask with vacuum deposited images. The column indicates the differing degrees of actinic radiation transmission ("B" referring to the light attenuation, i.e. % transmission) while the rows identify image clusters of different sizes ("A" referring to image size). In the examples that follow reference is made to this map and to the position of the smallest highly resolved image cluster. In such references, the prefix sign identifies whether the structure was prepared in the positive (+) or negative (-) mode. For example the nomenclature "-6,5" refers to a negative mode structure produced at 25 times magnification and 16% transmission. Each row and column in the matrix contains a full 3 x 3 image cluster.

Figure 4 illustrates both top and bottom imaging. A photoresist is generally applied as a coating to the surface of a silicon wafer and exposed to actinic radiation through a photomask. The photomask is typically positioned between the source of the actinic radiation and the photosensitive coating at the coating/air interface (topside) rather than the substrate/air interface (bottomside). This first type of exposure is referred to herein as "top" imaging since the portion of the coating furthest from the substrate surface is the first portion contacted by the exposing radiation.

If an actinic radiation transparent substrate, such as for example an ultraviolet light transparent quartz disk, is used as a substrate it is possible to project an image through the substrate such that the portion of the coating on the substrate closest to the substrate and farthest from the coating/air interface is exposed first. This type of exposure is referred to herein as "bottom" imaging.

If the identical photomask is used to prepare structures by top imaging and by bottom imaging,

the structure formed by top imaging will be the inverse of the structure formed by bottom imaging; only the side wall profile of the structures being different.

In Figure 4, 1 represents a light source, 3 represents a transparent photomask and 7 represents a photoresist. Figure 4(a) illustrates "top imaging" and, in this Figure, 9 represents a resist support. Figure 4(b) illustrates "bottom imaging" and, in this Figure, 5 represents a transparent resist support.

Figures 5 and 6 illustrate the two checkerboard patterns (Pattern (a)) for the light attenuating photomask. If Pattern 5(a) or Pattern 6(a) of Figure 5 or Figure 6, respectively, were projected on the surface of a silicon wafer in the negative mode (light margin and top imaging) the structure produced would be as shown in Figure 5(b) or Figure 6(b), respectively; while if Pattern 5(a) or Pattern 6(a) of Figure 5 or Figure 6, respectively, were projected in the near UV positive mode (top imaging), the structure produced would be as shown in Figure 5(d) or Figure 6(d), respectively. If the structures of Figures 5(b) and 5(d) or Figures 6(b) or 6(d) were separated from their substrates and placed together, they would fit together to form a completely filled solid cube as shown in Figure 7.

Figures 5(c) and 6(c) illustrate the images that would be produced using Pattern 5(a) or Pattern 6(a) of Figures 5 or 6, respectively, in the negative mode and with bottom imaging, whereas Figures 5(e) and 6(e), illustrate the images that would be produced using Pattern 5(a) or Pattern 6(a) of Figures 5 or 6, respectively, in the positive mode and with bottom imaging.

Figures 8 and 9 illustrate the four image structures formed using the bullseye pattern represented by Figure 8(a) (dark margin) and the four image structures which can be formed from the bullseye pattern represented by Figure 9(a) (light margin). In Figures 8 and 9, (b) represents top imaging negative; (c) represents bottom imaging negative; (d) represents top imaging positive, and (e) represents bottom imaging positive. Other three ring bullseye image structures which could be formed using a light attenuating photomask pattern and the dual-imageable, near UV photosensitive composition are illustrated in Figures 10(a) and 10(b).

In Figures 10(a) and 10(b): Figure 10(a)(i) represents the top negative image structures formed using the bullseye photomasks illustrated in Figure 10(a)(iii); Figure 10(a)(ii) represents the top positive image structures formed using the bullseye photomasks illustrated in Figure 10(a)(iii); Figure 10(b)(iv) represents the bottom positive image structures formed using the bullseye photomasks illustrated in Figure 10(a)(iii); and Figure 10(b)(v) represents the bottom negative image structures

formed using the bullseye photomasks illustrated in Figure 10(a)(iii).

Figure 11 illustrates all the image clusters formed by top imaging a dual imageable photosensitive coating of 12 micrometers in thickness using a light margin attenuated photomask, Figure 11(a) being the negative images and Figure 11(b) being the positive images. Figure 12 illustrates the image clusters formed by top imaging the dual-imageable photosensitive coating of 12 micrometers in thickness using a dark margin attenuated photomask, Figure 12(a) being the negative images and Figure 12(b) being the positive images.

The dual image, near UV, photosensitive coating composition is preferably used in conjunction with the light attenuating photomasks to produce microplastic structures. These structures were capable of being prepared in both the negative and positive modes at all sizes and percent transmittance of the 8 x 8 matrix. For each size image cluster, type of photosensitive composition, coating thickness, radiation source and processing parameters, there is one optimum exposure condition. Other image clusters, receiving more or less of the exposing radiation, will be over or under exposed, respectively. Identical structures could be made from more than one traditional (opaque/transparent only) photomask by the use of sequential exposures of similar and different intensity actinic radiation to create the same latent image as that created by one exposure through the attenuating mask. The attenuating mask is also particularly useful in defining the useful exposure dose needed for defining the desired vertical dimension in the image.

The negative image structures formed using the radiation attenuating mask were found to be more easily prepared than the positive image structures because of difficulties in establishing the proper exposure for the positive image structures as well as the inherent limitations on solubility resulting from processing uncrosslinked exposed and unexposed coating portions. Since the negative image microplastic structures are crosslinked prior to development the resulting structures are virtually insoluble in the aqueous developer and are more easily processed. In preparing the microplastic structures using the near UV photosensitive compositions, we found that the negative mode of action produced images of higher aspect ratios than when the positive mode is employed. We also found that the positive mode resulted in structures having peaks and valleys in the structure's surface. We believe that these peaks and valleys are the result of standing waves produced by internal reflections of the exposing radiation within the structure. These reflections are believed to result in reinforcement and nullification of the radiation pat-

tern resulting in the peak and valleys. The extent of these surface irregularities are very slight but become more noticeable in the positive mode as the aspect ratio is increased. When the negative mode of action is employed these standing wave irregularities are not as pronounced as in the corresponding positive mode of action using near UV exposure.

We have also found that when thick structures, of about 15 to about 50 micrometers in thickness, are desired to be produced using the photosensitive compositions in the positive mode it is preferable to use a photoacid generator which does not generate nitrogen gas upon exposure. When photoacid generators which generate nitrogen gas upon exposure are employed with the positive acting, near UV photosensitive coatings of the invention to form thick microplastic structures, the nitrogen gas formed upon exposure forms bubbles which become trapped in the structure. It appears that the dissolved nitrogen gas diffuses slowly from the structures into the air at ambient temperatures. If the structure is heated too rapidly during the final baking step, the nitrogen bubbles form and interfere with the dimensional integrity of the resulting structure.

It is possible to construct microplastic structures by placing structures on top of previously formed structures using the same or different photosensitive composition and conventional photomasks having different patterns. Figure 14 illustrates a five level microplastic structure which can be formed from the photomask patterns illustrated in Figure 13 using the negative acting near UV photosensitive composition.

The microplastic structures of the invention may be used as mandrels or forms onto which metals can be electrolessly plated or vacuum deposited. Once the structures are so plated, the microplastic structure, used as the mold or form, can be removed, such as by chemical action or by heating in air at elevated temperatures, leaving only the metallic form on the surface. The structures could be used as molds for casting metals, glasses or polymerizable resins or as forms or mandrels which can be electroplated or electroformed. The microplastic structures, therefore, can be used to prepare lenses and prisms for optical or solar devices; for attaching optical fibers over light sensitive electronics; as orifices to control the flow of gases or liquids to a chemical sensor; for a chromatographic column over a thermally conductive detector; as a structure to retain materials such as ionic gels over a chemical sensor; or as a reactive structure, which for example could contain excess amino resin such as for subsequent reaction with biomaterials such as enzymes, antibodies, or containing other chemicals as part of a chemical

sensor. Vacuum metallizing the surface of the microplastic structure containing reactive sites could leave the reactive sites in the structure for subsequent reactions. If the structure is deposited on a surface containing a soluble polymer coating, such as a coating of a polyvinyl alcohol, free standing crosslinked microplastic structures can be prepared. These free-standing structures could be used as a size and/or shape selective filtration device or as a filtration media for trapping chemicals or microorganisms of a specific size or configuration. By selecting the crosslinkable polymer, such as an acid-hardening resin system, based on its known physical, electrical or optical properties, for example, modulus of elasticity, electron flow resistance, refractive index or reactivity towards a specific chemical, the microplastic structures of the invention can be tailor-made for specific end use applications.

The present invention will now be further illustrated by way of the following Examples which are intended to illustrate the capability of the photosensitive compositions of the invention to form three dimensional, thermally stable, microplastic structures using near and deep UV exposing radiation with a radiation attenuating photomask. The structures so formed are illustrative only and should not be interpreted as constituting any limitation on the configurations which could be prepared using the photosensitive compositions and techniques described herein.

Example 1 - Positive and Negative Image Structures on a Silicon wafer using a dual Near UV image photoresist

To 30 grams of a 27 percent by weight (solids) photosensitive mixture, (Shipley Company Microposit 1470 photoresist), consisting of a novolak resin and a diazonaphthoquinone photoacid generator dissolved in a suitable organic solvent system (Shipley Microposit thinner), was added 1.62 grams of a melamine-formaldehyde resin (Cymel 303). The photosensitive coating solution was stirred at 25°C until a homogeneous solution was formed. The surface of a 7.62 cm (3 in) diameter silicon oxide coated wafer was vapor primed (minimum of 5 minutes) with hexamethyldisilazane (HMDS) to remove surface moisture. The coating solution was then either spin coated or dip-coated onto the wafer surface. To spin coat, 1.0 ml of coating solution was spun onto the wafer at 500 rpm for 5 - 7 seconds to form a 5 micrometers thick coating. A second 1.0 ml of the coating solution was then placed onto the surface of the first layer by spinning at 500 rpm for an additional 5-7 seconds. This second coating step was to form a final coating of about 10 micrometers in thickness.

After the coating was deposited, it was soft baked at 90°C for 30 minutes to remove the solvent from the coating. To dip coat, about 20 ml coating solution was placed in the bottom of a Petri dish and the primed wafer was immersed, polished side up, in the coating solution. The wafer was then drained and allowed to air dry at 25°C for 1 hour and then heated ("soft baked") at 90°C for 0.5 hours.

1) Formation of Positive Image

The wafer in contact with the metallic images of the 3D Image Cluster Mask, (light margin) was exposed to broadband actinic radiation of 365 nanometers (nm) from a high pressure mercury vapor lamp at a dose of 2300 millijoules per square centimeter (mJ/cm²). A Hybrid Technology Group Model No. L84-5X contact printer with a 500 watt mercury vapor lamp was used. The wafer was developed with Shipley Company Microposit 351 Developer, a proprietary mixture of strong aqueous bases, diluted one part by volume with five parts by volume of deionized water, for 9.0 minutes at 20°C with agitation. The resulting images were approximately 11.0 micrometers thick.

The smallest highly resolved image cluster was found at position +5.2. A small amount of unexposed film loss occurred, as evidenced by "ridges" along the image sidewalls, due to the fact that the unexposed film has a finite solubility in the developer (about less than two Angstroms/sec.). To form microplastic structures, the images were then flood exposed at 365 nm, using the lamp described above, at a dose of 2000 mJ/cm². The wafer was then heated in a forced air oven for 92 hours at 75°C and then the temperature was raised to 175°C in 5 equal time increments of over 30 minutes. The wafer was finally placed in a 190°C forced air oven for 120 minutes before finally heating at 300°C in a high temperature furnace for 15 minutes. No significant loss in image quality was observed in scanning electron micrographs of images before and after heating to 300°C.

2) Formation of Negative Image Structure

The coated wafer was placed in contact with the light margin 3D Image Cluster Mask and exposed to 3000 mJ/cm² of 365nm radiation using the lamp and printer described above. The imaged wafer was soft baked in a forced air oven for 30 minutes at 90°C. It was then flood exposed with 1500 mJ/cm² of 365 nm radiation. The image was developed at 20°C in a 3:1 diluted solution of Shipley Microposit 351 Developer and deionized water for 10.0 minutes with mild agitation. The resulting images were about 8.0 micrometers (μm)

thick.

The smallest highly resolved image cluster was found at position -5,1. The image was then heated 44 hrs at 90 °C in an oven and then for 15 minutes at 300 °C. No loss in image quality occurred during this heat treatment.

Example 2 - Deep UV Negative Image Structures

a) 1% 1,1-bis (p-chlorophenyl)-2,2,2-trichloroethane Deep UV Photoacid Generator

To 15.0 grams of a proprietary novolak resin, Shipley Company XP-0103 at 30% solids in Shipley Microposit thinner, was added 0.92 grams Cymel 303 and 0.055 grams 1,1-bis (p-chlorophenyl)-2,2,2-trichloroethane (Aldrich Chemical). The photosensitive coating solution, containing 1% of the deep UV photoacid generator on weight of total solids, was stirred for 15 minutes until a homogeneous solution was formed. The solution was then spin coated onto an HMDS vapor-primed 7.62 cm (3 in) diameter silicon oxide wafer at 3000 rpm for 60 seconds. The coated wafer was then soft baked for 30 minutes in a forced-air oven at 90 °C to remove solvent. It was then placed in contact with the 3D Image Cluster Mask. A 5.08 cm (2 in) square bandpass filter, from Action Research Corporation, was placed between the mercury vapor lamp and the mask. The filter had a peak wavelength of 248.5 nm, a center wavelength of 255.8 nm, and a bandwidth of 42.5 nm. The wafer was exposed to the filtered actinic radiation of about 256 nm at a dose of 60 mJ/cm² using the lamp and printer described in Example 1. The wafer was then heated in a forced air oven for 30 minutes at 90 °C. After cooling to ambient temperature the negative image structure was developed in Shipley Microposit 351 Developer 2:1 diluted with deionized water for 4.5 minutes to give a 1.6 μm thick structure. The smallest resolved image cluster was found at position -6,1.

b) 10% 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane

To 40.0 grams of the previously described novolak resin, was added 2.4 grams of Cymel 303 and 1.4 grams 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane. Example 2(a) was repeated for the 10% 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane solution, by exposing to 30 mJ/cm² at 256 nm and developing in a 1:1 diluted Shipley 351/deionized water developer for 7.5 min.

The smallest resolved image cluster was at position -4,1 (2.8 μm).

Example 3 - Deep UV Resist-Thick Negative Image Structures Produced from Halogen Acid Generators

1) 5% 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane

To 12.0 grams of the previously described novolak resin solution (Example 1) was added 0.77 grams Cymel 303 and 0.22 grams 1,1-bis(p-chlorophenyl)-2,2,2-trichloroethane. The mixture was stirred for 30 minutes until a homogeneous solution was formed. The coating solution containing 5% by weight deep UV photoacid generator was spin coated onto an HMDS vapor-primed (5 minutes) 7.62 cm (3 in) silicon oxide wafer at 1000 rpm for 90 seconds. The coated wafer was soft baked at 90 °C in a forced air oven for 15 minutes before application of a second layer of resin. The wafer was cooled to ambient temperature before the second layer was spin-coated on top of the first layer at 1000 rpm for 60 seconds. The wafer was then dried (soft baked) in a forced air oven at 90 °C for 40 minutes to remove solvent. The coating was exposed to 150 mJ/cm² at 256 nm deep UV from the high pressure mercury vapor lamp, using the bandpass filter, printer, and 3D Image Mask described in Example 2(a). The wafer was then heated at 90 °C for 30 minutes. The image was developed in neat Shipley 351 Microposit Developer (no dilution with deionized water) for 3.0 minutes.

The smallest resolved image cluster (8.9 μm) was found at position -4,2.

2) 3% tris(2,3-dibromopropyl)isocyanurate

To a mixture of 12.0g of the previously described novolak resin solution was added 0.77 g of Cymel 303 and 0.20 grams tris(2,3-dibromopropyl)-isocyanurate (Aldrich Chemical, 97%) and the mixture was stirred over night at room temperature at which time a homogeneous solution was found. The coating, containing 5% by weight deep UV photoacid generator, was applied to a wafer and baked as described in Example 3(1). The 8.7 μm thick coating was exposed to 200 mJ/cm² actinic radiation of 256 nm using the same procedure as Example 3(1), and developed for 7.0 min. in a 1:1 Shipley 351/deionized water developer solution.

The smallest highly resolved image cluster was position -6,2.

3) Thermally Stabilized Images

Thermally stable negative images were prepared by placing the developed wafers of Experiment 2 in a forced air oven at 90 °C for 24 hours to remove products of the acid-hardening crosslinking reaction such as alcohol and water. After heating at 110 °C for 20 min. the wafers were then heated to

140°C for 45 minutes and then to 190°C for 20 minutes. They were then placed in a 300°C furnace for 15 minutes to demonstrate thermal stability.

No significant loss in image quality was observed in the SEM's of the images before the after heating to 300°C. The hollow and undercut structures remained intact.

Example 4 - Resists with Onium Salt Sensitizers Thin Negative Images Produced with Onium Salt Sensitizers in the Deep UV

1) UVE-1014 Sensitizer

To 8.33 grams of the novolak resin solution described in Experiment 2 was added 0.49 grams Cymel 303 and 0.27 grams of a proprietary onium salt photosensitizer, (General Electric UVE 1014). The coating containing 4% sensitizer (based on 50% sensitizer solids) was spin coated onto a primed wafer at 2500 rpm for 60 seconds, then baked at 90°C for 30 minutes. The coated wafer was placed in contact with the 3D Image Cluster Mask and exposed to 40 mJ/cm² at 256 nm, using the filter and printer described in Example 1. The wafer was baked at 90°C for 30 minutes, and then developed in a 1:1 Shipley 351 developer/deionized water for 4.25 minutes to produce a 3.0 µm image. The smallest resolved image cluster was position -8,1. Structures heated to 300°C for 15 minutes remain dimensionally stable.

2) FC-508 Sensitizer

A resist containing a proprietary onium salt sensitizer (3M Company FC-508), was prepared in the same manner as above, and the coated wafer was processed in the same way. The image was developed for 4.5 minutes in 1:1 diluted Shipley 351/deionized water developer to produce 2.8 µm images. The smallest resolved image cluster was position -8,1.

3) Thermal Stability

Thermally stable structures resulted after heating the structures formed in Example 4 (1) and 4 (2) according to the procedure used in Example 3. No loss in image quality was seen by SEM analysis.

Example 5 - Thick Negative Image Structures Produced from UVE-1014 in the Deep UV

A thick (about 10 micrometers) coating containing the UVE-1014 photosensitizer was coated onto a silicon wafer using the coating solution from

Example 4 (1) and the coating method described in Example 3. The dried film was exposed to 150 mJ/cm² at 256 µm using the same mask, lamp, filter and printer as in Example 1. After a 90°C, 30 minute postbake, the wafer was developed in a 0.5:1 diluted Shipley 351/deionized water developer for 7.2 minutes to give 9.6 µm thick images. The smallest resolved image cluster was position -3,2.

Example 6 - Thick Positive Image Structures from Shipley 1470 Photoresist (Comparative Example)

A thick film of Shipley Microposit 1470 photoresist was double spin coated onto an HMDS vapor primed wafer (as described in example 1) and air dried for 1.5 hours at ambient temperature. The film was then soft baked at 90°C for 30 minutes, and then exposed through the Image Mask to 2000 mJ/cm² at 365 nanometers (near UV). The exposed areas of the film were developed in a 5:1 diluted Shipley 351/deionized water developer for 3.75 minutes to produce 12.0 µm thick images. The smallest resolved image cluster was position +4,2. The resulting images showed a loss of resolution, such as by loss of sharp edges, when heated at 90°C for 30 minutes and then slowly to 120°C over 30 minutes. The images were not thermally stable.

The terms "Methoxychlor", "Dursban", "Kelthane", "Propasol", "Cellosolve" are trade marks, which may or may not be registered in some or all of the designated states.

Claims

1. A process for forming a micrometer-sized microplastic structure which is thermally stable to temperatures of at least 200°C, wherein the dimensions of size, length, width and thickness are independently selectable before fabrication, and wherein each of such dimensions are variable throughout the structure, the process comprising utilizing one or more photomasks to selectively control the amount of exposing radiation in the thickness of a photosensitive coating comprising a polymer system which is aqueously-developable and capable of being crosslinked by the action of said exposing radiation and heat, and wherein said one or more photomasks comprise:
 - (a) one or more radiation attenuating photomasks; or
 - (b) two or more different photomasks having opaque and transparent regions with the photosensitive coating being subjected to sequential and different dosages of actinic radiation.

140°C for 45 minutes and then to 190°C for 20 minutes. They were then placed in a 300°C furnace for 15 minutes to demonstrate thermal stability.

No significant loss in image quality was observed in the SEM's of the images before the after heating to 300°C. The hollow and undercut structures remained intact.

Example 4 - Resists with Onium Salt Sensitizers Thin Negative Images Produced with Onium Salt Sensitizers in the Deep UV

1) UVE-1014 Sensitizer

To 8.33 grams of the novolak resin solution described in Experiment 2 was added 0.49 grams Cymel 303 and 0.27 grams of a proprietary onium salt photosensitizer, (General Electric UVE 1014). The coating containing 4% sensitizer (based on 50% sensitizer solids) was spin coated onto a primed wafer at 2500 rpm for 60 seconds, then baked at 90°C for 30 minutes. The coated wafer was placed in contact with the 3D Image Cluster Mask and exposed to 40 mJ/cm² at 256 nm, using the filter and printer described in Example 1. The wafer was baked at 90°C for 30 minutes, and then developed in a 1:1 Shipley 351 developer/deionized water for 4.25 minutes to produce a 3.0 µm image. The smallest resolved image cluster was position -8,1. Structures heated to 300°C for 15 minutes remain dimensionally stable.

2) FC-508 Sensitizer

A resist containing a proprietary onium salt sensitizer (3M Company FC-508), was prepared in the same manner as above, and the coated wafer was processed in the same way. The image was developed for 4.5 minutes in 1:1 diluted Shipley 351/deionized water developer to produce 2.8 µm images. The smallest resolved image cluster was position -8,1.

3) Thermal Stability

Thermally stable structures resulted after heating the structures formed in Example 4 (1) and 4 (2) according to the procedure used in Example 3. No loss in image quality was seen by SEM analysis.

Example 5 - Thick Negative Image Structures Produced from UVE-1014 in the Deep UV

A thick (about 10 micrometers) coating containing the UVE-1014 photosensitizer was coated onto a silicon wafer using the coating solution from

Example 4 (1) and the coating method described in Example 3. The dried film was exposed to 150 mJ/cm² at 256 µm using the same mask, lamp, filter and printer as in Example 1. After a 90°C, 30 minute postbake, the wafer was developed in a 0.5:1 diluted Shipley 351/deionized water developer for 7.2 minutes to give 9.6 µm thick images. The smallest resolved image cluster was position -3,2.

Example 6 - Thick Positive Image Structures from Shipley 1470 Photoresist (Comparative Example)

A thick film of Shipley Microposit 1470 photoresist was double spin coated onto an HMDS vapor primed wafer (as described in example 1) and air dried for 1.5 hours at ambient temperature. The film was then soft baked at 90°C for 30 minutes, and then exposed through the Image Mask to 2000 mJ/cm² at 365 nanometers (near UV). The exposed areas of the film were developed in a 5:1 diluted Shipley 351/deionized water developer for 3.75 minutes to produce 12.0 µm thick images. The smallest resolved image cluster was position +4,2. The resulting images showed a loss of resolution, such as by loss of sharp edges, when heated at 90°C for 30 minutes and then slowly to 120°C over 30 minutes. The images were not thermally stable.

The terms "Methoxychlor", "Dursban", "Kelthane", "Propasol", "Cellosolve" are trade marks, which may or may not be registered in some or all of the designated states.

Claims

1. A process for forming a micrometer-sized microplastic structure which is thermally stable to temperatures of at least 200°C, wherein the dimensions of size, length, width and thickness are independently selectable before fabrication, and wherein each of such dimensions are variable throughout the structure, the process comprising utilizing one or more photomasks to selectively control the amount of exposing radiation in the thickness of a photosensitive coating comprising a polymer system which is aqueously-developable and capable of being crosslinked by the action of said exposing radiation and heat, and wherein said one or more photomasks comprise:-

- (a) one or more radiation attenuating photomasks; or
- (b) two or more different photomasks having opaque and transparent regions with the photosensitive coating being subjected to sequential and different dosages of actinic radiation.



2. A process as claimed in claim 1, which comprises:-

(a) depositing a photosensitive coating composition comprising from about 40 to about 99.9 weight percent of a crosslinkable polymer and from about 0.1 to about 60 weight percent photoacid generator, the percentages being based on the weight of crosslinkable polymer plus photoacid generator, as the coating on a substrate surface;

(b) exposing a portion or portions of the coating to a source of actinic radiation through the one or more photomasks;

(c) heating the exposed coating to a temperature of from about 70°C to about 120°C to crosslink the exposed coating portion(s);

(d) removing portion(s) of said coating using an aqueous base solution to produce a microplastic structure;

it being understood that steps (c) and (d) can be carried out in either order and that, when step (d) is carried out before step (c), an additional step is carried out between steps (d) and (c), the additional step comprising exposing the coating to actinic radiation.

3. A process as claimed in claim 2, wherein the microplastic structure is formed in the negative or positive mode.

4. A process as claimed in claim 2 or claim 3, wherein said actinic radiation used to expose said coating is near UV radiation.

5. A process as claimed in claim 4, wherein the photosensitive coating composition comprises from about 3 to about 50 weight percent of aminoplast resin, from about 90 to about 40 weight percent of reactive hydrogen-containing compound, and from about 2 to about 30 weight percent of photoacid generator sensitive to actinic radiation in the near UV.

6. A process as claimed in claim 3, wherein the photosensitive coating composition comprises from about 50 to about 95 weight percent of phenoplast resin, from about 40 to about 3 weight percent of formaldehyde-generating compound, and from about 2 to about 30 weight percent of photoacid generator sensitive to actinic radiation in the near UV.

7. A process as claimed in claim 2, wherein the photosensitive coating composition comprises from about 95 to about 99.9 weight percent acid-hardening resin system and from about 0.1 to about 5 weight percent photoacid gener-

ator sensitive to actinic radiation in the deep UV, and wherein said actinic radiation used to expose said coating is deep UV radiation, preferably having an exposure dosage of about 10 millijoules per square centimetre of coating.

8. A process as claimed in claim 7, wherein the deep UV photoacid generator comprises halogenated organic compound which:

(a) is compatible with the photosensitive coating dissolved in a suitable solvent and with the acid-hardening resin system contained in the photosensitive coating;

(b) does not phase separate from the acid-hardening resin system when the coating is heated;

(c) is developable in aqueous base developer;

(d) is non-reactive with the substrate and acid-hardening resin system before exposure to deep UV and after exposure to deep UV but before heating to a temperature sufficient to crosslink the coating;

(e) is capable of crosslinking the acid-hardening resin system in the portion(s) exposed to a sufficient dosage of deep UV radiation; and

(f) is substantially less volatile than the solvent used with the acid-hardening resin system.

9. A process as claimed in claim 8, wherein the deep UV photoacid generator is selected from: 1,1-bis[p-methoxyphenyl]-2,2,2-trichloroethane, 1,2,5,6,9,10-hexabromocyclodecane; 1,10-dibromodecane; 1,1-bis[p-chlorophenyl]-2,2-dichloroethane; 4,4'-dichloro-2-(trichloromethyl)benzhydrol (1,1-bis[p-chlorophenyl]-2,2,2-trichloroethanol); hexachlorodimethyl sulfone; 2-chloro-6-(trichloromethyl)pyridine; 0,0-diethyl-0-(3,5,6-trichloro-2-pyridyl)-phosphothioate; 1,2,3,4,5,6-hexachlorocyclohexane; N(1,1-bis[p-chlorophenyl]-2,2,2-trichloroethyl)-acetamide; tris[2,3-dibromopropyl]isocyanurate; 2,2-bis[p-chlorophenyl]-1,1-dichloroethylene; 1,1-bis-(p-chlorophenyl)-2,2,2-trichloroethane; and their isomers and homologs.

10. A process as claimed in any of claims 7 to 9, wherein the microplastic structure is formed in the negative mode.

11. A process as claimed in any of claims 1 to 10, wherein the photomask(s) comprises a radiation attenuating photomask.



12. A micrometer-sized microplastic structure obtainable by a process as claimed in any of claims 1 to 11.

13. A radiation attenuating photomask for use in the process according to any of claims 1 to 11, or for use in the formation of thermally stable microplastic structures according to claim 12, the photomask having areas that permit the transmission of different amounts of exposing radiation.

Patentansprüche

1. Verfahren zur Ausbildung einer mikroplastischen Struktur in Mikrometergröße, die bis zu Temperaturen von mindestens 200 °C thermisch stabil ist, worin die Dimensionen von Größe, Länge, Breite und Dicke unabhängig von Herstellung auswählbar sind und worin jede dieser Dimensionen innerhalb der Struktur variierbar ist, wobei das Verfahren die Verwendung von ein oder mehr Photomasken zur selektiven Kontrolle der Menge der Bestrahlung in der Dicke einer photosensitiven ein Polymersystem enthaltenden Schicht umfaßt, die wäßrig entwickelbar und in der Lage ist, durch die Wirkung der Bestrahlung und Wärme quervernetzt zu werden, und worin ein oder mehr Photomasken umfassen:

(a) ein oder mehr Bestrahlungs-abschwächende Photomasken, oder

(b) zwei oder mehr verschiedene Photomasken, die undurchsichtige und durchsichtige Bereiche mit der photosensitiven Schicht aufweisen, welche sequentiellen und unterschiedlichen Dosierungen einer actinischen Bestrahlung unterworfen wird.

2. Verfahren nach Anspruch 1, bei dem

(a) eine photosensitive Schichtzusammensetzung, umfassend etwa 40 bis etwa 99,9 Gew.-% eines quervernetzbaaren Polymers und etwa 0,1 bis etwa 60 Gew.-% eines Photosäure-Erzeugers, als Schicht auf einer Substratoberfläche angebracht wird, wobei die Prozentsätze auf dem Gewicht des quervernetzbaaren Polymers plus Photosäure-Erzeugers basieren,

(b) ein Teil oder Teile der Schicht einer Quelle actinischer Bestrahlung durch ein oder mehrere Photomasken ausgesetzt werden,

(c) die Schicht auf eine Temperatur von etwa 70 °C bis etwa 120 °C erhitzt wird, wodurch der (die) Teil(e) quervernetzt wird (werden),

(d) der (die) Teil(e) der Schicht unter Verwendung einer wäßrigen Basenlösung entfernt wird (werden), wodurch eine mikroplastische Struktur hergestellt wird,

wobei die Schritte (c) und (d) in jeder Reihenfolge ausgeführt werden können und, wenn Schritt (d) vor Schritt (c) durchgeführt wird, ein zusätzlicher Schritt zwischen den Schritten (d) und (c) durchgeführt wird, wobei der zusätzliche Schritt einen Schritt umfaßt, bei dem die Schicht einer actinischen Bestrahlung ausgesetzt wird.

3. Verfahren nach Anspruch 2, worin die mikroplastische Struktur in der negativen oder positiven Weise ausgebildet wird.

4. Verfahren nach Anspruch 2 oder 3, worin die zur Bestrahlung der Schicht verwendete actinische Bestrahlung nahe einer UV-Bestrahlung ist.

5. Verfahren nach Anspruch 4, worin die photosensitive Schichtzusammensetzung etwa 3 bis etwa 50 Gew.-% eines Aminoplastharzes, etwa 90 bis 40 Gew.-% einer reaktiven, Wasserstoff-enthaltenden Verbindung und etwa 2 bis etwa 30 Gew.-% eines Photosäure-Erzeugers umfaßt, der für eine actinische Bestrahlung nahe UV sensitiv ist.

6. Verfahren nach Anspruch 3, worin die photosensitive Schichtzusammensetzung etwa 50 bis etwa 95 Gew.-% eines Phenoplastharzes, etwa 40 bis etwa 3 Gew.-% einer Formaldehyd-erzeugenden Verbindung und etwa 2 bis etwa 30 Gew.-% eines Photosäure-Erzeugers umfaßt, der für eine actinische Bestrahlung nahe UV sensitiv ist.

7. Verfahren nach Anspruch 2, worin die photosensitive Schichtzusammensetzung etwa 95 bis etwa 99,9 Gew.-% eines Säure-härtenden Harzsystems und etwa 0,1 bis etwa 5 Gew.-% eines Photosäure-Erzeugers umfaßt, der für eine actinische Bestrahlung in dunklem UV sensitiv ist, und worin die zur Bestrahlung der Schicht verwendete actinische Bestrahlung eine dunkle UV-Bestrahlung ist, vorzugsweise mit einer Bestrahlungsdosierung von etwa 10 Millijoules pro cm² Schicht.

8. Verfahren nach Anspruch 7, worin der Dunkel-UV-Photosäure-Erzeuger eine halogenierte organische Verbindung umfaßt, die:

(a) mit der in einem geeigneten Lösungsmittel gelösten photosensitiven Schicht und mit dem Säure-härtenden Harzsystem ver-



träglich ist, das in der photosensitiven Schicht enthalten ist,

(b) sich von dem Säure-härtenden Harzsystem nicht phasentrennt, wenn die Schicht erwärmt wird,

(c) in einem wäßrigen Basenentwickler entwickelbar ist,

(d) mit dem Substrat und dem Säure-härtenden Harzsystem vor der Bestrahlung durch dunkles UV und nach Bestrahlung durch dunkles UV, jedoch vor Erwärmung auf eine zur Quervernetzung der Schicht ausreichende Temperatur nicht-reaktiv ist,

(e) zur Quervernetzung des Säure-härtenden Harzsystems in dem (den) Teil(en) fähig ist, die einer ausreichenden Dosierung von dunkler UV-Bestrahlung ausgesetzt werden, und

(f) im wesentlichen weniger flüchtig ist, als das mit dem Säure-härtenden Harzsystem verwendete Lösungsmittel.

9. Verfahren nach Anspruch 8, worin der Photosäure-Erzeuger von tiefem UV ausgewählt ist von:

1,1-bis/p-Methoxyphenyl/-2,2,2-trichlorethan;

1,2,5,6,9,10-Hexabromcyclodecan;

1,10-Dibromdecan;

1,1-bis/p-Chlorphenyl/-2,2-dichlorethan;

4,4'-Dichlor-2-(trichlormethyl)benzhydrol(1,1-bis/p-chlorphenyl/2,2,2-trichlorethanol);

Hexachlordimethylsulfon;

2-Chlor-6-(trichlormethyl)pyridin;

0,0-Diethyl-0-(3,5,6-trichlor-2-pyridyl)-phosphothioat;

1,2,3,4,5,6-Hexachlorcyclohexan;

N(1,1-bis/p-Chlorphenyl/-2,2,2-trichlorethyl)-acetamid;

tris/2,3-Dibrompropyl/isocyanurat;

2,2-bis/p-Chlorphenyl/-1,1-dichlorethylen;

1,1-bis-(p-Chlorphenyl)-2,2,2-trichlorethan

und ihren Isomeren und Homologen.

10. Verfahren nach einem der Ansprüche 7 bis 9, worin die mikroplastische Struktur in der negativen Weise ausgebildet wird.

11. Verfahren nach einem der Ansprüche 1 bis 10, worin die Photomaske(n) eine Bestrahlungsabschwächende Photomaske umfaßt (umfassen).

12. Mikroplastische Struktur in Mikrometergröße, erhältlich durch ein Verfahren nach einem der Ansprüche 1 bis 11.

13. Bestrahlungsabschwächende Photomaske zur Verwendung in dem Verfahren nach einem der

Ansprüche 1 bis 11 oder zur Verwendung in der Ausbildung von thermisch stabilen mikroplastischen Strukturen nach Anspruch 12, wobei die Photomaske Bereiche hat, die die Transmission von verschiedenen Mengen der Bestrahlung hindurchlassen.

Revendications

1. Procédé pour la formation d'une structure microplastique de taille de l'ordre du micromètre, qui est thermiquement stable à des températures d'au moins 200 °C, dans laquelle les dimensions de taille, longueur, largeur et épaisseur peuvent être indépendamment choisies avant la fabrication, et dans laquelle chacune de ces dimensions est variable dans l'ensemble de la structure, le procédé comprenant l'utilisation d'un ou plusieurs masques de photogravure pour régler sélectivement la quantité de rayonnement d'exposition dans l'épaisseur d'un revêtement photosensible comprenant un système polymère qui est apte au développement dans une solution aqueuse et capable d'être réticulé par l'action dudit rayonnement d'exposition et de chaleur, et dans lequel ledit (lesdits) un ou plusieurs masques de photogravure comprend (comprennent):

a) un ou plusieurs masques de photogravure atténuateurs de rayonnement; ou

b) deux masques de photogravure différents ou plus, comportant des régions opaques et des régions transparentes, le revêtement photosensible étant soumis à des doses successives et différentes de rayonnement actinique.

2. Procédé selon la revendication 1, comprenant :

a) le dépôt d'une composition photosensible de revêtement, comprenant d'environ 40 à environ 99,9 % en poids d'un polymère réticulable et d'environ 0,1 à environ 60 % en poids d'un générateur d'acide photoactivable, les pourcentages étant basés sur le poids du polymère réticulable plus le générateur d'acide photoactivable, en tant que revêtement sur une surface du support ;

b) l'exposition d'une partie ou de parties du revêtement à une source de rayonnement actinique, à travers le ou les masques de photogravure ;

c) le chauffage du revêtement exposé à une température d'environ 70 à environ 120 °C, pour réticuler la (les) partie(s) exposée(s) du revêtement ;

d) l'élimination d'une (de) partie(s) dudit revêtement à l'aide d'une solution aqueuse d'une base, pour l'obtention d'une structure



- microplastique;
 étant entendu que les étapes (c) et (d)
 peuvent être effectuées dans un ordre ou
 dans l'autre, et que, lorsque l'étape (d) est
 effectuée avant l'étape (c), on effectue une
 étape supplémentaire entre les étapes (d) et
 (c), l'étape supplémentaire comprenant
 l'étape d'exposition du revêtement à un
 rayonnement actinique.
3. Procédé selon la revendication 2, dans lequel
 la structure microplastique est formée en
 mode négatif ou positif.
4. Procédé selon la revendication 2 ou 3, dans
 lequel ledit rayonnement actinique utilisé pour
 l'exposition dudit revêtement est un rayonne-
 ment UV proche.
5. Procédé selon la revendication 4, dans lequel
 la composition photosensible de revêtement
 comprend d'environ 3 à environ 50 % en poids
 de résine aminoplaste, d'environ 90 à environ
 40 % en poids d'un composé contenant de
 l'hydrogène actif, et d'environ 2 à environ 30
 % en poids d'un générateur d'acide photoacti-
 vable, sensible à un rayonnement actinique
 dans l'UV proche.
6. Procédé selon la revendication 3, dans lequel
 la composition photosensible de revêtement
 comprend d'environ 50 à environ 95 % en
 poids de résine phénoplaste, d'environ 40 à
 environ 3% en poids de composé générateur
 de formaldéhyde et d'environ 2 à environ 30%
 en poids de générateur d'acide photoactivable
 , sensible à un rayonnement actinique dans
 l'UV proche.
7. Procédé selon la revendication 2, dans lequel
 la composition photosensible de revêtement
 comprend d'environ 95 à environ 99,9 % en
 poids d'un système de résine durcissant sous
 l'effet d'un acide et d'environ 0,1 à environ 5
 % en poids d'un générateur d'acide photoacti-
 vable, sensible à un rayonnement actinique
 dans l'UV lointain, et dans lequel ledit rayonne-
 ment actinique utilisé pour l'exposition dudit
 revêtement est un rayonnement UV lointain,
 ayant de préférence une dose d'exposition
 d'environ 10 mJ par cm² de revêtement.
8. Procédé selon la revendication 7, dans lequel
 le générateur d'acide photoactivable par un
 rayonnement dans l'UV lointain comprend un
 composé organique halogène qui:
 a) est compatible avec le revêtement photo-
 sensible dissous dans un solvant approprié
- et avec le système de résine durcissant
 sous l'effet d'un acide, contenu dans le re-
 vêtement photosensible ;
 b) ne se sépare pas en phases du système
 de résine durcissant sous l'effet d'un acide,
 lorsque le revêtement est chauffé ;
 c) peut être développé dans un révélateur à
 base aqueuse ;
 d) est non réactif avec le support et le
 système de résine durcissant sous l'effet
 d'un acide, avant l'exposition à un rayonne-
 ment UV lointain et après l'exposition à un
 rayonnement UV lointain, mais avant le
 chauffage à une température suffisante pour
 réticuler le revêtement;
 e) est capable de réticuler le système de
 résine durcissant sous l'effet d'un acide,
 dans la (les) partie(s) exposée(s) à une
 dose suffisante de rayonnement UV lointain
 ; et
 f) est nettement moins volatil que le solvant
 utilisé avec le système de résine durcissant
 sous l'effet d'un acide.
9. Procédé selon la revendication 8, dans lequel
 le générateur d'acide photoactivable par un
 rayonnement UV lointain est choisi parmi :
 le 1,1-bis[p-méthoxyphényl]-2,2,2-trichlorétha-
 ne,
 le 1,2,5,6,9,10-hexabromocyclodécane,
 le 1,10-dibromodécane,
 le 1,1-bis[p-chlorophényl]-2,2-dichloréthane,
 le 4,4-dichloro-2-(trichlorométhyl)benzhydrol,
 le (1,1-bis[p-chlorophényl]-2,2,2-trichlorétha-
 nol),
 l'hexachlorodiméthylsulfone,
 la 2-chloro-6-(trichlorométhyl)pyridine,
 l'O,O-diéthyl-O-(3,5,6-trichloro-2-pyridyl) phos-
 phothioate,
 le 1,2,3,4,5,6-hexachlorocyclohexane,
 le N-1,1-bis[p-chlorophényl]-2,2,2-trichloréthyl)-
 acétamide
 le tris(2,3-dibromopropyl)isocyanurate,
 le 2,2-bis(p-chlorophényl)-1,1-dichloréthylène,
 le 1,1-bis(p-chlorophényl)-2,2,2-trichloréthane,
 et leurs isomères et homologues.
10. Procédé selon l'une quelconque des revendi-
 cations 7 à 9, dans lequel la structure micro-
 plastique est formée dans le mode négatif.
11. Procédé selon l'une quelconque des revendi-
 cations 1 à 10, dans lequel le(s) masque(s) de
 photogravure comprend (prennent) un masque
 de photogravure atténuateur de rayonnement.
12. Structure microplastique de taille de l'ordre du
 micromètre, pouvant être obtenue par un pro-



cédé selon l'une quelconque des revendications 1 à 11.

13. Masque de photogravure atténuateur de rayonnement, pour utilisation dans le procédé selon l'une quelconque des revendications 1 à 11, ou pour utilisation dans la formation de structures microplastiques thermiquement stables selon la revendication 12, le masque de photogravure comportant des zones permettant la transmission de qualités différentes de rayonnement d'exposition.

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