

The present invention relates to an organic solvent. for a radiation-sensitive positive-working or negative-working photoresist mixture. The invention also relates to a process for treating a film base, provided with a photoresist, with the aid of organic solvents.

The preparation of photoresist mixtures is known and is described, for example, in US-A 3,666,473, US-A 4,115,128 and US-A 4,173,470. In these publications, alkali-soluble phenol formaldehyde/novolak resins used in conjunction with photosensitive substances, usually substituted naphthoquinonediazide compounds are involved. The resins and photosensitive substances are dissolved in an organic solvent or solvent mixture and are applied as thin film or coating to a film base suitable for the planned application.

The novolak resin component of these photoresist mixtures is soluble in aqueous alkaline solutions, but under these circumstances the photosensitive naphthoquinone compound acts on the resin as an inhibitor. However, if certain regions of the coated base are exposed to actinic radiation, the photosensitive compound undergoes a structural transformation induced by the radiation and the exposed regions of the coating become more soluble than the unexposed regions.

The photoresist relief produced on the film base by means of the process described can be used for numerous purposes such as, for example, as an exposure mask or artwork such as are used in the production of semiconductor components in microelectronics.

For many technical applications, in particular for the production of semiconductor components in microelectronics, a photoresist must have a high degree of image resolution if it is to reproduce very small line widths and gap widths (in the order of magnitude of $1\text{ }\mu\text{m}$).

The ability of a photoresist to reproduce very small dimensions in the order of magnitude of $1\text{ }\mu\text{m}$ and below is of the greatest importance in the production of VLSI circuits on silicon chips and similar components.

Assuming photolithographic processes are employed, the circuit density on such a chip can be increased only by increasing the image resolving power of the photoresist. Although negative-working photoresists, in the case of which the exposed regions of the resist film are insoluble in the developer and the unexposed regions are stripped by the developer, are used in the semiconductor industry on a large scale for this purpose, the positive-working photoresists inherently have a higher image resolution and are used as a substitute for the negative-working resists.

The present invention relates to an organic solvent for stripping and cleaning film bases provided with cured or uncured resin-like photoresist mixtures and for diluting such photoresist mixtures, and also to a process for stripping and cleaning a film base provided with a positive-working or negative-working photoresist and for diluting a photoresist.

Numerous processes with whose aid the resin-like photoresist coatings mentioned can be removed from the film base concerned by mechanical or chemical means are known, but all these processes leave something to be desired. In mechanical stripping processes, for example by squeezing off, the film base surface is damaged in almost every case. The use of certain chemical reagents or solvents also leads to unsatisfactory results since the cured resins are stripped off too slowly and/or incompletely or the electrical properties of the material are impaired by residues which remain behind on the film base and which are not completely removed even during the further processing. There is therefore a need to provide an organic solvent with whose aid the cured resins mentioned can be removed rapidly and completely from the film base surface without damage to, or contamination of, the base material occurring.

Solvent mixtures with whose aid photoresist mixtures can be diluted, undesirable cured photoresist coatings can be stripped from the bases, undesirable peripheral bulges can be removed from spun-coated photo-

resist wafers and with which equipment used in the further processing of photoresists can be cleaned are known. But such mixtures are, in general, very toxic and environmentally pollutant and/or have an unpleasant smell.

The object of the invention is to provide an organic solvent which does not have the disadvantages described.

The object set is achieved by an organic solvent for stripping and cleaning film bases provided with cured or uncured resin-like positive-working or negative-working photoresist mixtures and for diluting said photoresist mixtures, which is characterized in that the organic solvent is composed of a mixture of about 1 to 10 parts by weight of propylene glycol alkyl ether acetate and about 1 to 10 parts by weight of propylene glycol alkyl ether.

Both the acetate and the ether preferably contain (C_1 to C_4)alkyl groups. Particularly preferably the mixture is composed of propylene glycol methyl ether acetate and propylene glycol methyl ether.

US-A 4,550,069 reveals a positive-working photoresist mixture which contains propylene glycol alkyl ether acetate. DE-A 3,421,160 reveals a positive-working photoresist mixture which contains a mono(C_1 to C_4)alkyl glycol ether of 1,2-propanediol.

EP-A 0,220,645 filed simultaneously with this patent application reveals a positive-working photosensitive mixture which contains a component composed of propylene glycol alkyl ether acetate and propylene glycol alkyl ether.

Organic solvents which contain only one of the two components propylene glycol alkyl ether and propylene glycol alkyl ether acetate have a disadvantage: the use of propylene glycol monomethyl ether acetate (PGMEA) involves an extremely unpleasant olfactory irritation for about half the group of people who come into contact with this substance, and it is mainly women who complain of discomfort. The use of propylene glycol monomethyl ether

(PGME) also means an extreme olfactory irritation for about half the group of people handling this substance, and in this case it is mainly men who complain. At the same time, however, the situation is that those who find the smell of PGMEA extremely irritating, find PGME to be pleasant or at least not to have an irritating smell, and vice versa. If mixtures of these solvents, that is to say, of PGMEA and PGME, are now used, none of the groups of people affected complain about appreciable discomfort. Organic solvents for whose preparation mixtures of PGMEA and PGME are used can therefore be designated as a class of mixtures with reduced olfactory irritation.

The preparation of photoresists, in particular of positive-working photoresists, using photosensitive mixtures of a novolak resin or polyvinylphenol resin, a photosensitive compound based on a quinonediazide, and a solvent mixture is known.

The production of novolak resins as binders which can be used for preparing photosensitive mixtures is also known. A process for preparing said novolaks is described in "Chemistry and Application of Phenolic Resins" by A. Knopp and W. Scheib, Springer Verlag, New York, 1979, Chapter 4. Polyvinylphenols are described, for example, in US-A 3,869,292 and US-A 4,439,516. The person skilled in the art is also familiar with the use of o-quinonediazides as described in "Light Sensitive Systems" by J. Kosar, John Wiley & Sons, New York, 1965, Chapter 7.4. These photosensitive compounds belong to the group of substituted photosensitive naphthoquinonediazides such as are conventionally used in positive-working photoresist mixtures. Such compounds imparting photosensitivity are revealed, for example, by US-A 2,797,213, US-A 3,106,465, US-A 3,148,983, US-A 3,130,047, US-A 3,201,329, US-A 3,785,825 and US-A 3,802,885. Suitable photosensitive compounds are, for example, 1,2-naphthoquinone-2-diazide-5-sulphonyl chloride and 1,2-naphthoquinone-2-diazide-4-sulphonyl chloride condensed with phenolic compounds such as hydroxybenzophenones.

In a preferred embodiment, the content of solid

constituents in the photoresist mixture, i.e. of binder and quinonediazide, is about 15 to 99 per cent by weight of binder and about 1 to 85 per cent by weight of quinonediazide. To prepare the photoresist mixture, the binder and the diazide are mixed with a solvent mixture, for example of xylene, butylacetate and cellosolve acetate in a manner such that the solvent mixture is present in a proportion of about 40 to 90 per cent by weight, based on the weight of the total resist mixture.

The ratio of the PGMEA contained in the organic solvent according to the invention to PGME may be varied within wide limits as a function of the particular requirements of the user. The mixing ratio in the organic solvent is between 1:10 and 10:1 parts by weight. Preferably, the mixing ratio of PGMEA to PGME is between 7:3 and 3:7, in particular between 6:4 and 4:6, and very particularly preferably about 1:1.

Before application to a film base, further additives such as, for example, colorants, dyestuffs, levelling agents, plasticizers, adhesion promoters, development accelerators, further solvents and surfactants, for example nonionic surfactants, may be added to the solution composed of binder, photosensitive compound and solvent mixture.

The finished photoresist solution may be applied to a film base by one of the processes such as immersion, spraying and spinning-on which are standard in photoresist technology. For spinning-on, for example, the percentage of solids in the resist solution can be adjusted in a manner such that a coating having the desired thickness is produced as a function of the spinning-on speed used in the individual case and of the time interval scheduled for the spinning-on operation. Examples of suitable film bases are: silicon, aluminium or polymeric resins, silicon dioxide, doped silicon dioxide, silicon nitride, tantalum, copper, polycrystalline silicon (polysilicon) ceramic and aluminium/copper alloys.

If the photoresist mixture is applied to the

wafer by spinning-on, there is a danger that a photoresist bulge forms at the edge of the wafer. Spraying the organic solvent according to the invention onto the edge of the rotating wafer effects a levelling of the bulge and thus achieves a uniform thickness of the photoresist film over the entire wafer area. The organic solvent according to the invention is also well suited as a diluent for the photoresist mixture. For this purpose, the solution according to the invention is added to the liquid photoresist mixture until the latter has reached the desired degree of consistency.

After the photoresist mixture has been applied to the film base, the whole is subjected to a preliminary drying at about 20 to 110°C. This heat treatment is carried out in order to reduce and to control the residual solvent concentration in the photoresist by evaporation without a perceptible thermal decomposition of the photosensitive compound occurring at the same time. In general, an attempt is made to reduce the content of solvents to a minimum, and this first heat treatment is therefore continued until the solvents have essentially evaporated and a thin film of photoresist mixture whose thickness is about 1 μm remains behind on the film base.

The film bases coated with the photoresist mixture and exposed are usually immersed for development in an aqueous alkaline developer solution. The solution is preferably vigorously agitated, which can be done, for example, by blowing through nitrogen. Suitable developers are, for example, aqueous alkali hydroxide, ammonium hydroxide or tetramethylammonium hydroxide solutions.

The present invention also relates to a process for stripping and cleaning film bases, provided with photoresist, with the aid of an organic solvent, which is characterized in that, as organic solvent, a solvent is used which is composed of about 1 to 10 parts by weight of propylene glycol alkyl ether acetate and about 1 to 10 parts by weight of propylene glycol alkyl ether.

The organic solvent according to the invention is eminently suitable as an agent for removing, stripping,

cleaning and diluting photoresist mixtures. It may be applied to exposed or unexposed, i.e. cured or uncured, photoresist films which have been deposited on suitable film bases.

5 In the following example the invention is explained in detail. This example is not, however, intended to restrict the scope of the invention in any way and it is not intended to be interpreted as specifying conditions, parameters or other values which have
10 to be used exclusively to carry out the invention in practice.

Example

A positive-working photoresist mixture is prepared from the following constituents:

15 23.8% resin-like binder (cresol/formaldehyde novolak);
 7.0% photosensitive compound (condensation product of
 1,2-diazonaphthoquinone-(2)-5-sulphonyl (sic)
 chloride and 2,3,4-trihydroxybenzophenone; and
20 69.2% solvent mixture (cellosolve acetate, n-butyl
 acetate and xylene in the ratio of 8:1:1).

25 A silicon wafer is coated with the photoresist mixture obtained, exposed through an image and developed. It is found that the artwork used for exposure contains an error. The entire resist layer is therefore removed
 from the wafer film by immersing the wafer in a mixture of propylene glycol methyl ether and propylene glycol methyl ether acetate (mixing ratio 1:1). The film base can be used for a repeat coating after this treatment.

PATENT CLAIMS

1. Organic solvent for stripping and cleaning film bases provided with cured or uncured resin-like positive-working or negative-working photoresist mixtures and for diluting said photoresist mixtures, characterized in that it is composed of a mixture of about 1 to 10 parts by weight of propylene glycol alkyl ether acetate and about 1 to 10 parts by weight of propylene glycol alkyl ether.
2. Organic solvent according to Claim 1, characterized in that the mixture is composed of propylene glycol (C₁ - C₄)alkyl ether acetate and propylene glycol alkyl (C₁ - C₄)alkyl ether (sic).
3. Organic solvent according to Claim 1 or 2, characterized in that the mixture is composed of propylene glycol methyl ether acetate and propylene glycol methyl ether.
4. Organic solvent according to Claim 1, characterized in that the mixing ratio of propylene glycol alkyl ether acetate and propylene glycol alkyl ether is about 1:1.
5. Process for stripping and cleaning a film base, provided with a photoresist, with the aid of an organic solvent, characterized in that a solvent according to Claims 1 to 4 is used as organic solvent.
6. Process for diluting a positive-working or negative-working photoresist mixture such that an organic solvent according to Claims 1 to 4 is used.

