

Now, the vinyl groups 16 of the silane surface active agent are juxtaposed on the substrate surface forming a film [FIG. 1(b)], and will undergo polymerization reaction among surrounding vinyl groups under irradiation by electron beams. Accordingly electron beams 18 are irradiated onto the surface in a pattern, as shown in FIG. 1(c). Then, as shown in FIG. 1(d), the double bonds of the vinyl groups at the parts 20 which are irradiated by electron beams are mutually combined to be selectively deactivated.

Then, as shown in FIG. 1(e), the substrate is transferred into a polymerizing monomer, for example, methyl methacrylate monomer vapor 21 at about 1 to 3 Torr (other examples of polymerizing monomer may include trimethyl vinyl silane, tributyl vinyl silane, diallyl vinyl silane, styrene, tetrafluoroethylene, acrylonitrile, methacrylic acid, divinyl benzene, vinyl toluene, and amide maleate), and the entire surface is irradiated again with far ultraviolet rays or X ray or electron beam, etc. 22 for a short time to activate the responsive group in the portion not previously deactivated, thereby additionally polymerizing 24 the monomer in a pattern. In this step, a film pattern 26 is formed [FIG. 1(f)].

This embodiment relates to a substrate producing



bonding by reacting with the $-\text{SiCl}_3$ group of a silane surface activating agent, that is, a Si substrate forming SiO_2 , but. However, Al_2O_3 , glass or the like may be usable as inorganic matter, and polyvinyl alcohol, gelatine, caseine, or the like as organic matter. Or when the substrate surface is coated with other water-repellent substance, hydrophilic groups may be arranged in line on the whole surface of the substrate by forming a Langmuir-Blodgett film, or the substrate may be made hydrophilic by O_2 plasma treatment or other process. In the Langmuir-Blodgett film, incidentally, the contact power is inferior, but if the substance on the substrate surface is water-repellent, after the accumulation is stopped when the water-repellent surface comes to the substrate side, it is possible to turn the entire surface hydrophilic.

Or when O_2 plasma processing is done, the substrate surface is oxidized to show hydrophilicity.

Embodiment 2

Instead of steps (e) and (f) in FIG. 1, as shown in FIG. 3, the substrate is put into vacuum and the entire surface is irradiated with energy beam (such as electron beam, X ray, far ultraviolet beam) to activate the responsive group in the portion not deactivated, and immediately vapor of polymerizing monomer, for example, methyl methacrylate monomer at about 1 to 3 Torr (other examples of polymerizing monomer may include trimethyl vinyl silane, tributyl vinyl silane, diallyl methyl phenyl silane, styrene, tetrafluoroethylene, acrylonitrile, methacrylic acid, divinyl benzene, vinyl toluene, and amide maleate) is introduced to additionally polymerize 24 the monomer in a pattern. By employing this method, too, a similar film pattern 26 as in Embodiment 1 may be formed.

Therefore, as shown in FIG. 2, a substrate 10 is coated with organic film, for example, a photo resist 28

of rubber compound or novolak, and O_2 plasma (for example, 0.01 Torr, 100 W, 30 sec) processing is given to form a treated layer 30, and a silane surface activating agent is adsorbed on the resist surface by the same technique as in the first embodiment [FIG. 2(a)], and a pattern 26 is formed by the same process as in the preceding embodiment [FIG. 2(b)]. Afterwards, using the pattern 26 as mask, O_2 is added by 10%, and plasma processing is done in CF_4 gas to selectively remove the responsive film 20 including the Si in the previously deactivated portion, and successively O_2 plasma or O_2 reactive sputter etching is done to selectively remove the resist 28, so that the selective polymerized film pattern 26 may be transferred on the resist 28 [FIG. 2(c)]. In this case, photo resist is used as organic film, but it is evident that any other material may be used as far as it may be etched by O_2 plasma. Or, as the polymerizing monomer, when a monomer containing Si, such as trimethyl vinyl silane, is used, Si is contained in the polymerized pattern, and SiO_2 is formed by O_2 plasma, and sufficient resistance to O_2 plasma etching may be achieved without increasing the thickness of the polymerized film so much, so that a high resolution may be obtained. On the other hand, when a pattern is transferred on the photo resist, the thickness of the photo resist may be sufficiently increased, so that it may be used as a very fine resist pattern with a sufficient etching resistance even against dry etching generally employed in the VLSI manufacturing process (for example, reactive sputter etching using CF_4 to etch SiO_2 or Si).

In the above two embodiments, a method of adsorbing and reacting a silicon surface active agent as responsive film is shown, but it is also possible to form a responsive film by Langmuir-Blodgett's method using well-balanced amphiphatic reagents, such as reagents having $-\text{Cl}-$ replaced by $-\text{OH}[\text{CH}_2=\text{CH}-(\text{CH}_2)_n-\text{Si}(\text{OH})_3, \text{etc.}]$, w-tricocene acid [$\text{CH}_2=\text{CH}-(\text{CH}_2)_{20}\text{COOH}$], w-heptadecene acid [$\text{CH}_2=\text{CH}-(\text{CH}_2)_{14}\text{COOH}$], and acetylene derivative [$\text{CH}\equiv\text{C}-(\text{CH}_2)_n\text{COOH}$].

Incidentally, although the surface reaction of $-\text{SiCl}_3$ and $-\text{OH}$ is shown in the above embodiment, the substances are not limited to them as far as similar reaction mechanism is presented.

While specific embodiments of the invention have been illustrated and described herein, it is realized that modifications and changes will occur to those skilled in the art. It is, therefore, to be understood that the appended claims are intended to cover all modifications and changes as fall within the true spirit and scope of the invention.

What I claim is:

1. A pattern forming method comprising the steps of: forming on a substrate a monomolecular film having responsive groups which undergo chemical vapor reactions under irradiation of an energy beam; irradiating an energy beam in a pattern on said monomolecular film, thereby forming bonds between said responsive groups at the irradiated portion to selectively deactivate the responsive groups in the irradiated portion; transferring said substrate into a polymerizing monomer atmosphere; and irradiating the entire surface of said monomolecular film in said monomer atmosphere to activate the responsive groups in a pattern not deactivated and