Improved Pattern Profile Based on Analyzing between Substrate Surface and Chemically Amplified Resist

Shigeyasu MORI, Kouichirou ADACHI, Takashi SUGIHARA, Takashi FUKUSHIMA, and Junkou TAKAGI

Central Research Laboratories, SHARP Corporation 2613-1 Ichinomoto-cho, Tenri-shi Nara 632, Japan

It has been found that pattern profiles of a chemically amplified negative resist depend on substrate surfaces. The dependence is caused by the interaction at the interface between the protons in the resist and the substrate surface components. The protons behavior is clarified by using molecular orbital method. A novel pattern formation technique has been proposed, which form a non-activated layer for the proton on the substrate surface. By using this technique, a stable patterning process is established, and the resolution limit is improved.

INTRODUCTION

The density of LSI circuits is raising rapidly, minimum feature size decreases considerably and their structures become higher. In the production of 256M DRAM and beyond, it is necessary to resolve quarter micron patterns using KrF excimer laser lithography with the chemically amplified resists (1). On the patterning process, there are some problems caused by instability of photo-generated acids (2). The stability of chemically amplified negative resist is superior to positive one on post exposure delay effect, and is expected to be used in actual device fabrication processes (3). Currently diazonaphtoquinone-novolak resist are reported to be lifted-off depending on primed conditions (4). And chemically amplified resists have several problems on the pattern profiles at the interfaces between some substrate surfaces and resist. Photogenerated acids lose their activities on spin on grass (5) and TiN (6).

It is important to control the interaction between chemically amplified resists and the substrate surface to resolve the quarter micron patterns. In this paper, we studied the substrate surface effect of chemically amplified negative resist by analyzing several factors. We also analyze the interface effect using molecular orbital method. Based on the results, we propose a novel proton behavior mechanism and a pattern formation technique controlling the substrate surface component.

EXPERIMENTAL

Substrates were primed with hexamethyldisilazane(HMDS) and then coated with the chemically amplified negative resist C04 (Mitsubishi Kasei Co.). The wafer was then prebaked and exposed on a deepUV stepper (NA :0.45) equipped with a KrF excimer laser. The exposed wafer was post exposure baked, developed in tetramethyl ammonium hydroxide aqueous base, and rinsed with water. Developed images were observed on a Hitachi model S-900 scanning electron microscope (SEM). Contact angle was measured with a ST-1 from Shimadzu Co., Ltd.. Quantum chemistry calculation was done using a semiempirical self-consistent field molecular orbital method at the Hartree-Fock level (MOPAC version 6) on CAChe system.

RESULTS and DISCUSSION

Figure 1(a)(b)(c) show the pattern profiles which are formed on bare Si, SiO layer(40A) and SiN layer(1200A), cleaned with HF solution, and primed with HMDS(120°C 40sec.). At the interface between resist and substrate, we can recognize the difference of pattern profiles depending on substrate surface components. Figure 1(d) shows the pattern profiles which are formed on SiN without HMDS. The HMDS affects the adhesion of patterns, since the patterns lie back in other patterns. The pattern profiles at the interface are the same profiles formed with HMDS, so the HMDS can not act as quencher for protons. The calculated light intensities in the resist is shown in figure 2.



 Fig. 1 SEM photographs of 0.3μm line and space patterns on bare Si(a), SiO layer(b) and SiN layer(c), cleaned with HF solution, and primed with HMDS, SiN layer(d) without HMDS priming.



Fig. 2 Calculated light intensities in the resist at the interface between resist and bare Si (_____), SiO(_____) or SiN(____).

There is no difference of the light intensities at the interface, on bare Si and SiO layer. On SiN layer, the amplitude of the standing wave is smaller than others, but this can not cause the degradation of the reverse tapered patterns, due to the position of the node. To evaluate the adhesion of the substrates, table 1 shows the measured contact angles of water on each substrate. These contact angles are almost same, so the adhesion can not have effect on pattern profiles.

Here, we propose to consider the influence of the proton which exists on the interface

Table 1 Measured contact angles of water on the substrate surface.

Substrate	Contact angle
Bare Si	73.2 degrees
SiO	65.4 degrees
SiN	64.5 degrees

Table 2 Calculated dissociative energies of the hydrogen terminated on substrate surfaces.

Substrate	Energy
Bare Si	124.6 kcal/mol
SiO	164.0 kcal/mol
SiN	168.0 kcal/mol



Fig. 3 Calculated total energy curves of the proton as a function of the distance for substrate surfaces.

between resist and substrate. Table 2 shows the calculated dissociative energies of the hydrogen terminated on each substrate surfaces. The energy on bare Si is much lower (about 40kcal/mol) than others, so we consider that the terminated hydrogen on bare Si dissociates easily comparing with others. Therefore, the density of protons at the interface increases, and the pattern profile on bare Si has the degradation of the tapered patterns.



Fig. 4 SEM photographs of 0.26µm line and space pattern on bare Si(a) and SiN layer(b), treated with oxygen plasma, SiN layer(c) irradiated by UV.



Scheme 1 Trapping mechanism of the protons on the SiN surface.

Figure 3 shows the calculated total energy curves of the proton as a function of the distance for each substrate. The potential energies for the bare Si and SiO surface have the maximum at the distance 4.0A for bare Si and 1.4A for SiO. On the other hand, the total energy for the SiN surface has the minimum at the distance 1.0A, and increases with distance. It suggests that the proton is easily trapped on unshared electron pair of nitrogen at the SiN surface and lose its activity as catalyst according to scheme 1, because there is no energy barrier. So, the density of protons at the interface decreases, and the pattern profile has the degradation of the reverse tapered We can understand that the patterns. movement of the proton between the resist and the substrate surfaces has an effect on the pattern profile.

As above results, we can recognize that it is effective to improve the substrate surface. We propose a novel pattern formation technique which form a thin SiO layer nonactivated for the proton on the substrate surface. Figure 4(a)(b) show the pattern profiles which are formed on bare Si and SiN layer(1200A) with oxygen plasma treatment. It is clear that a vertical pattern is formed at the interface. There is no movement of proton at the interface. Figure 4(c) shows the pattern profiles on the SiN layer formed with UV irradiation. They have small degradation of the reverse tapered patterns, because it is not sufficient to prevent proton from being trapped. The resolution limit is improved using these methods.

CONCLUSION

For chemically amplified negative resist, we indicated the pattern formation technique controlling the substrate surface. Also, we clarified the protons behavior mechanism on the substrate surface.

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