

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. Photo-generated 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 hexamethyl-disilazane(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.

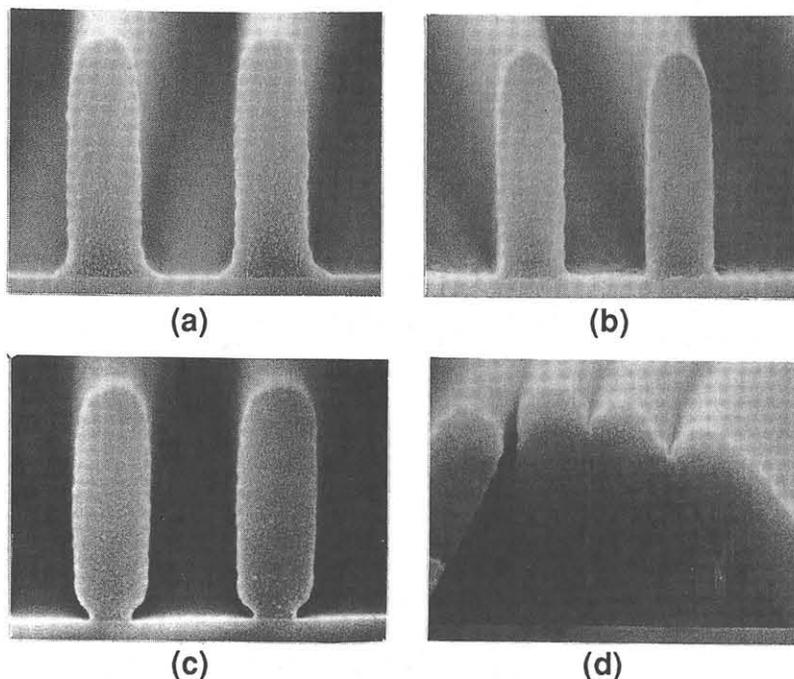


Table 1 Measured contact angles of water on the substrate surface.

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. 1 SEM photographs of $0.3\mu\text{m}$ 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.

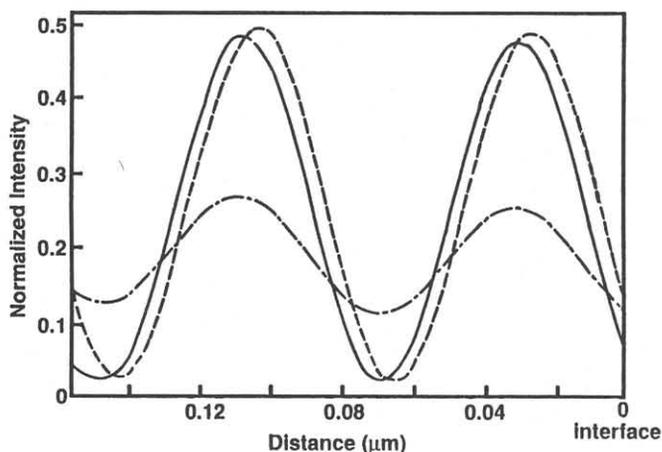


Fig. 2 Calculated light intensities in the resist at the interface between resist and bare Si (—), SiO(---) or SiN(-.-).

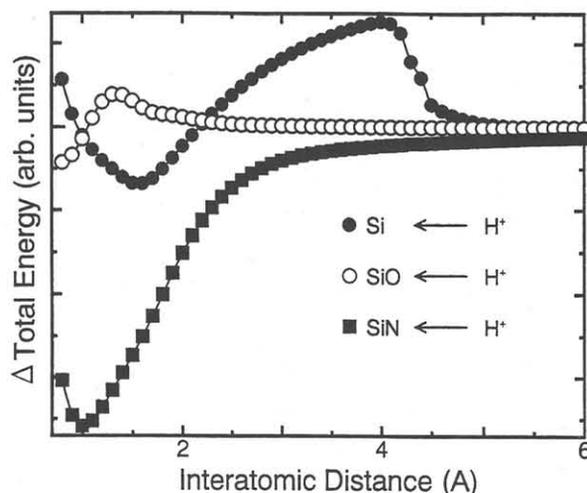


Fig. 3 Calculated total energy curves of the proton as a function of the distance for substrate surfaces.

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

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.

