PHOTOCHEMICAL REACTIONS OF SILSESQUIOXANE-BASED RESISTS FOR ArF EXCIMER-LASER LITHOGRAPHY

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Two silsesquioxane polymers were investigated as ArF excimer-laser resist materials. Polyphenylmethyl silsesquioxane (PMSQ) showed positive tone characteristics when an aqueous base developer was used, while polyhydroxybenzyl silsesquioxane (HSQ) showed negative tone characteristics. Infrared (IR) spectra and X-ray photo-electron spectrometry (XPS) indicate that a major imaging mechanism is the polarity change in PMSQ. Both materials showed sub-0.2- μm resolution capability for ArF excimer laser exposure with aqueous base development.

1. Introduction

ArF excimer-laser lithography is one of the most promising optical lithography technologies after KrF excimer-laser lithography. However, conventional phenolic polymer-based resist cannot be used as single layer resists at this wavelength (193 nm) due to the extremely high photo-absorption of their phenyl ring structure. To solve this problem, single layer chemically amplified resists based on transparent methacrylate polymers have been intensively investigated [1, 2, 3]. Top surface imaging systems and bilayer resist systems have also been introduced to avoid some of the limitations of single layer resist processes, such as substrate reflection and resist pattern collapse [4, 5, 6]. Furthermore, an all-dry photolithographic process utilizing plasma-polymerized organo-polysilane has been introduced for ArF excimer-laser lithography [7].

We have recently shown that polyhydroxybenzyl silsesquioxane (HSQ) acts as a high resolution negative tone resist for ArF excimer laser exposure and that the obtained patterns can be used as a mask in etching underlying polysilicon films [8].

This suggests the possibility of a new process, shown in Fig. 1, which we call direct formation of hard-masks process. In this process, a directly patterned SiO₂-like thin resist film is used as a hard-mask for dry-etching metals or silicon. Except for the film thickness, this very simple process resembles conventional single-layer resist process. It is therefore likely to represent a cost-effective alternative to more complex proposed process.

Silsesquioxane polymers are attractive for resist materials using this process because of their SiO₂-like structure and their spin-coatable and aqueous base soluble characteristics [9, 10]. We have investigated photo-reactions for various silsesquioxane polymers under ArF irradiation. In our previous work, however, excessively high photo-absorption in HSQ limited the photo-sensitivity and the possible resist thickness.

Figure 1 Process scheme of direct hard-mask formation.

In this paper, we describe a new ArF excimer-laser irradiation-induced photochemical reaction in which a positive-tone image is obtained using standard aqueous-base developer. We discuss the positive working mechanisms of polyphenylmethyl silsesquioxane, compared with the previously reported negative working mechanisms of HSQ.

2. Experimental

Polyphenylmethyl silsesquioxane (PMSQ) was obtained from Showa Denko Co. under the trade name GR-100 and polyhydroxybenzyl silsesquioxane (HSQ) was supplied by Hitachi Chemical Co.. Their chemical structures are shown in Fig. 2. The PMSQ and HSQ coating solvents were, respectively, propylene glycol 1-monomethylether 2-acetate and ethyl cellosolve acetate. A commercially available aqueous base developer NMD-3 (tetramethylammonium hydroxide (TMAH), Tokyo Ohka Co.) was used as the developer.

Exposure characteristics were obtained by using an ArF excimer laser (EMG 201 MSC, Lambda Physik). Sample films were coated onto silicon wafers (thickness: 50-100 nm), and baked at 90 °C for 180 s on a hot plate. The film thickness was determined with an Alpha Step-200 profilometer (Tencor Inst.). Infrared (IR) spectra were measured with a Fourier-transform IR spectrometer, JEOL JIR-100. X-ray photoelectron spectrometry (XPS) was performed for the PMSQ films before and after ArF laser exposure with a Shimazu-KRATOS XSAM800.

Figure 2 Chemical structures of polyhydroxybenzyl silsesquioxane (HSQ) and polyphenylmethyl silsesquioxane (PMSQ).

3. Results and discussion

3.1 Basic characteristics

We have examined various kinds of silsesquioxane polymers as resists for the direct formation of hard-masks process. Since the phenyl ring shows strong absorption at 193 nm, the phenyl ring structure itself can be a photo-active group in the resist materials. Exposure characteristics of two examples (PMSQ and HSQ) are shown in Fig. 3. As shown in the figure, HSQ acts as a negative resist, whereas PMSQ acts as a positive resist when aqueous-base development is used. PMSQ is insoluble in the aqueous-base developer, however, and the ArF exposed area became aqueous-base soluble by NMD-3 2.38 wt. % at doses above ~100 mJ/cm².

The observed contrast of PMSQ was promising, as shown in the figure. HSQ is aqueous-base soluble due to the phenolic moiety at the side chain of its ladder siloxane structure. ArF irradiation can destroy the phenolic structure and form siloxane networks to cause aqueous-base insolubility in the exposed area.

3.2 IR and XPS analysis

To investigate the positive working nature of PMSQ, IR spectra of films before and after exposure were measured (Fig. 4). The silanol group is known to be an aqueous base soluble moiety [11]. As can be seen in Fig. 4, ArF excimer-laser irradiation resulted in an increase of the silanol moiety in the PMSQ film. However, the absorption spectra due to the silanol group showed a small increase at the dose of 600 mJ/cm², at which a positive tone had already been obtained.

Figure 3 Exposure characteristics of HSQ and PMSQ
initial film thickness, HSQ: 50-nm, PMSQ: 70-nm, development time: 45 s

Figure 4 IR spectra of PMSQ films before and after ArF excimer laser exposure.

To evaluate the degree of photo-oxidation, we applied XPS analysis to PMSQ before and after the ArF exposure at 100 mJ/cm². The results are summarized in Table 1. The atomic ratio of oxygen to silicon in PMSQ films was 1.7 before exposure, and became about 2.0, the same as silicon dioxide, after exposure. Therefore, photo-oxidation induced by ArF excimer-laser irradiation proceeds effectively even at a dose of 100 mJ/cm².

Table 1. Elemental fraction of PMSQ before and after ArF excimer laser exposure.

atomic ratio	Si	O	C
before exposure	16.6	27.2	56.3
after exposure	17.4	35.2	47.5

exposure dose: 100 mJ/cm²

3.3 Chemical reaction

The aqueous-base solubility of resists depends not only on the concentration of base-soluble moieties but also on their orientation or positions in the resist matrix[12]. Though the PMSQ film was not soluble in standard aqueous-base developer, as we explained, it did have some silanol before exposure, as shown in

Fig. 4, and was soluble in a stronger aqueous base solution with a TMAH concentration of over 3 wt. %. From these results, the following dissolution inhibition and promotion mechanism of PMSQ is proposed. The PMSQ film is potentially soluble in an aqueous-base solution since it contains hydrophilic silanol moieties. However, organic sites (phenyl and methyl groups) form hydrophobic regions that block the hydrophilic base-soluble regions from the aqueous base solution, and inhibit film dissolution in the developer. ArF excimer-laser irradiation induced photo-oxidation breaks the phenyl-Si bond to form a polar oxide structure, such as silanol pendants, and makes the hydrophobic regions in the film smaller. That exposes the hydrophilic base-soluble regions to the aqueous base solution and promotes the film dissolution. In this scheme, the photo-oxidation acts as the switch that turns on the film dissolution.

3.4 Resolution capability

The result of a preliminary lithographic application of PMSQ as a resist for direct formation of hard-masks is shown in Fig. 5. The 0.2 μm -pitch-L/S PMSQ patterns were successfully obtained. The initial film thickness was 70 nm, the film was pre-baked at 90 °C for 180s, and patterns could be formed by ArF excimer-laser exposure. We were also able to delineate a 0.2- μm HSQ pattern, though the pattern was not well-defined because of the strong photo-absorption.

Figure 5 SEM micrograph of PMSQ-based resist patterns formed by using an ArF excimer laser with a holographic mask.

4. Summary

Polyphenylmethyl silsesquioxane (PMSQ) showed positive tone characteristics when exposed by ArF excimer laser radiation followed by development with aqueous-base developer, while polyhydroxybenzyl-silsesquioxane (HSQ) exhibit negative tone characteristics. Infrared (IR) spectra and X-ray photoelectron spectrometry (XPS) suggests that a major mechanism of the pattern formation is the polarity change in PMSQ, while it is crosslinking in HSQ. PMSQ showed high resolution capability, resolving features as small as 0.1 μm .

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