High Selective Plasma Etching of PMMA to PS

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Polymethylmethacrylate (PMMA) and polystyrene (PS) are important materials for nano pattern fabrication processes such as the directed self-assembly (DSA) lithography. In this paper, the high selective etching of PMMA to PS films is presented by use of $O_2 + C_4F_8$ mixed gas plasmas. Although both etch rates for the PS and PMMA films decrease by increasing the C_4F_8 content, the PS etch rate decreases faster than the PMMA one. The etching selectivity reaches to 6 when the C_4F_8 content is 65 %. The aspect ratio of nano pattern is enhanced by use of the high selective PMMA etching. The 250 nm depth trench pattern of the 80 nm width is successfully obtained from the 80 nm depth trench pattern.

Keywords: Polymethyl methacrylate , polystyrene, dry etching, C_4F_8

1. Introduction

Nanoimprint lithography [1] is superior nanofabrication process because of extremely high resolution and relatively low cost. Polystyrene (PS) and polymethylmethacrylate (PMMA) are very famous resists for the thermal nanoimprint lithography (T-NIL) [2]. Recently, directed self-assembly (DSA) lithography is one of the powerful candidates for nano pattern fabrication around 10 nm [3, 4]. A block copolymer of PS and PMMA (PS-*b*-PMMA) is the most popular block copolymer for the DSA lithography. PS and PMMA are very important materials for nano pattern fabrication processes.

It is very important that the PMMA etch rate is larger than the PS one for oxygen plasmas. In the DSA lithography, PS pattern can be obtained by use of the etch rate difference between PMMA and PS resists. The molecular formulas of PS and PMMA are $(C_8H_8)_n$ and $(C_5O_2H_8)_n$, respectively. Gokan et al. showed that resist etch rates for O_2 plasmas greatly depended on the numbers of C atoms and O atoms in a monomer unit [5]. Since no O atoms contain in the monomer unit of PS, the PS etch rate for O_2 plasmas is low. The etching selectivity of PMMA to PS films is usually 2~3. Yamamoto showed that the high selective PMMA etching to PS was obtained by CO plasma [6].

In this paper, C_4F_8 is added to O_2 plasma in order

to obtain a high selective etching of PMMA to PS. C_4F_8 is widely used for CF film deposition [7]. A resist etch rate is reduced by the film deposition. Since O atoms contain in the PMMA monomer (internal O atoms), the deposited film on the PMMA can be partially removed by the internal O atoms. On the other hand, since no oxygen atoms contain in the PS monomer, no film etching by the internal O atoms is induced. Therefore, it is expected that the PS etch rate decreases faster than the PMMA one as increasing the C_4F_8 content, and the selectivity of PMMA to PS increases. The selectivity of PMMA to PS is shown for various C_4F_8 contents. Next, the pattern aspect enhancement process is proposed by use of the high selective etching.

2. Experiment

2.1 High selective etching of PMMA to PS

For the resist etching, a commercial ICP etcher (ULVAC, NE550) is used in our experiments. The RF powers to the antenna coil, P_{ANT} , and the sample stage where samples are placed, P_{BIAS} , are fixed at 600 W and 10 W, respectively. P_{BIAS} is adjusted to a relatively small value. Since the incident ion energy to samples is mainly controlled by P_{BIAS} , the incident ion energy is small for low P_{BIAS} . Then, the physical sputter etching, which has low material selectivity, must be suppressed.

Fig. 1 Process flow of aspect ratio enhancement process.

We use the mixed gases of Ar, O₂, and C₄F₈. This gas chemistry is widely used for SiO₂ selective etching over Si [8]. O₂ is the most commonly used gas for a resist etching. C₄F₈ induces the CF film deposition, and the etching selectivity of PMMA to PS films can be enhanced. Ar is used for the dilute gas. In our experiments, the Ar flow rate is fixed at 50 sccm and the flow rate of O₂ + C₄F₈ mixed gas is always kept to 50 sccm.

The etch rates of PMMA and PS films are measured. Cyclohexanone is used as the solvent for PMMA (Mw=120K) and PS (Mw=350K) resins. The PMMA and PS films are fabricated on a Si wafer. The films are etched by the ICP etcher for 1 min. The film thicknesses before and after the etching are measured, and the etch rates are obtained.

2.2 Aspect ratio enhancement process by the selective etching

Since the etch rate of PS film is smaller than that of PMMA film, PMMA patterns with high aspect ratio can be obtained when PS patterns are used as the PMMA etching mask (aspect ratio enhancement process). The aspect ratio enhancement process is shown in Fig. 1.

(a) The bi-layer film of PS/PMMA is fabricated. The thicknesses of the PS film and the PMMA film are 80 nm and 1.2 μ m, respectively. (b) The nano pattern of the 80 nm trench is fabricated to

Fig. 2 Relation between PS, PMMA etch rates and C₄F₈ content.

the PS film by T-NIL. The pressure and the temperature are 10MPa and 140 °C, respectively. c)The PS residual layer is removed (PS residual remove process) and the PMMA film are etched (PMMA etching process).

3. Results and Discussion

3.1 High selective etching of PMMA to PS

The etch rates of the PMMA and the PS films for various C₄F₈ gas contents are shown in Fig. 2. The etch rates for both films decrease rapidly by increasing the C₄F₈ content. Note that the etch rate reduction of the PS film is faster than that of the

Fig. 3 Relation between selectivity of PMMA to PS and C₄F₈ content.

Fig. 4 PS pattern fabricated by NIL

Fig. 6 Fabricated pattern after 60 s PMMA etching process.

PMMA film. The selectivity, which is the ratio of the PMMA etch rate to the PS one (PMMA/PS), is shown in Fig. 3. For a pure O_2 plasma (C_4F_8 content=0 sccm), the selectivity is about 2. The selectivity increases as the C_4F_8 content increases. The selectivity becomes about 6 for the $C_4F_8/O_2 = 32.5$ sccm/17.5 sccm.

3.2 Improvement of aspect ratio of nanopatterns by the selective etching

Figure 4 shows the PS pattern after T-NIL. The trench width and depth are 80nm, that is, the aspect ratio is unity. For the PS residual remove process, the C_4F_8 content of 10 sccm is used because the PS film should be etched by a moderate etching speed. Although it is difficult to determine the PS residual layer thickness from Fig. 4, the etching time is chosen for 10 s. Figure 5 shows the fabricated pattern after the PS residual remove process. Since the trench depth of 120 nm is larger than the initial PS thickness of 80 nm, the PS residual layer must be removed. After the PS

Fig. 5 Fabricated pattern after the PS residual remove process.

residual remove process, the PMMA film is etched by the high selective etching. The gas chemistry of $O_2/C_4F_8=27.5$ sccm/22.5 sccm is used for the PMMA etching process. Figure 6 shows the fabricated pattern after the PMMA etching process of 60 s. The trench depth is 150 nm. The trench can be enhanced from that of 120 nm after the PS residual layer remove process. However, the etching depth during the PMMA etching process is only 30 nm. Since the PMMA etch rate is 180 nm/min as shown in Fig. 2, the value of 30 nm is much smaller than the value expected from the etch rate measurement. This value is similar to the PS etch rate of 50 nm. Figure 7 shows the fabricated pattern after the PMMA etching process of 120 s. It is clear that the trench depth is almost unchanged, but the roughness of PS layer becomes very large.

3.3 Process with osmium barrier layer

In our experiments, both the PMMA and PS resins are dissolved by cyclohexanone. It is

Fig. 7 Fabricated pattern after 120 s PMMA etching process.

Fig. 8 Fabricated pattern after 120s PMMA etching process with osmium barrier layer.

afraid that the mixing layer of the PMMA and PS resins is formed during the PS and PMMA bi-layer film fabrication. Moreover, the mixing layer may be generated during the T-NIL process, because the imprint temperature is higher than the glass transition temperatures of the PMMA and the PS films. The formation of the mixing layer should be suppressed. A barrier layer between the PMMA and the PS films must be effective in order to avoid the mixing layer formation. Thin osmium film is used as the barrier layer. The osmium film is deposited by a commercial osmium coater for SEM sample preparation (Neoc-pro supplied by Meiwafoysis co. ltd). It is considered that osmium film is suitable for the barrier film by the following reasons. No damage must be induced in the osmium film by the PS spin coating, because the osmium film is tough to organic solvents such as cyclohexanone. Since the osmium film can be easily removed by O_2 contained plasmas, no additional etching process is necessary. Moreover, the deposition process is easily carried out (the total time for the deposition process is shorter than 10 min). The sample preparation process is same as the bi-layer film fabrication except that the osmium deposition process is inserted between the PMMA and PS film fabrication processes. The deposition time of osmium is 10 s. The etching conditions for the PS residual remove and the PMMA etching processes are same as those

described in the section 3.2. Figure 8 shows the fabricated pattern after the PMMA etching process of 120 s. The trench width and depth are 80nm and 250nm, respectively. Clearly, the trench depth is deeper than that in Fig. 7 where the etching conditions are same. However, the etching depth is only 100 nm although the expected PMMA etching depth for 120 s is 360 nm. The osmium barrier layer is effective for the suppression of the PS and PMMA mixing, but the PS and PMMA mixing cannot be removed completely.

4. Conclusions

The PMMA and PS film etch rates are examined for $O_2 + C_4F_8$ mixed gas plasmas in order to obtain the high selective etching of PMMA to PS films. When the C_4F_8 content is increased, the etch rates for both films decreased. The PS etch rate decreases faster than the PMMA one, and the etching selectivity reaches to 6 at 65 % C_4F_8 content. A fine pattern aspect ratio is enhanced by use of the high selective PMMA etching. The 250 nm depth trench pattern of the 80 nm width is successfully obtained from the 80 nm depth trench pattern when osmium barrier layer is used.

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