Performance of Supercritical Resist Drying in Improving Practical Resolution Limit

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We have studied the lithographic performance of resist pattern prepared by supercritical resist drying method. Patterns were exposed by proximity X-ray lithography and the supercritical resist drying was performed with CO₂ by 10MPa and 60°C. We found that 70-nm-L/S patterns were prepared with the exposure gap of 15 μm, though it had not been ever obtained without supercritical drying. The CD control and line-edge-roughness for those patterns are also measured.

Key words: pattern collapse, supercritical drying, X-ray lithography

1. Introduction

Recently resist pattern collapse is becoming one of a major problem in lithography. It is known that the pattern collapse occurs because of a capillary force of rinse solution left between resist patterns during drying procedure [1]. That force pushes the resist sidewall with the magnitude that increases in inverse proportion to the distance between the patterns. So the pattern collapse is more serious as the feature size decreases. In fact the resist thickness is becoming thinner partly to escape the collapse. In our previous study [2], the aspect ratio of 3.5 was not small enough in 100-nm-L/S patterns, and in 70-nm-L/S patterns we had to decrease it to 3 or less to keep patterns standing. It means that we might have to make the aspect ratio down to 2.5 and 1.5 in 50 and 30 nm patterns, respectively. If the dry etching stability of resists will not be increased strikingly, single layer resist will not be used any more because of pattern collapse. Thus a concern to a new method that can save patterns from collapse is increasing.

Supercritical CO₂ (sc-CO₂) drying is known as the method that can dry an object without giving the capillary force. It has been used to

prepare a sample of electron microscope when observing organic materials. Some pioneering workers have proved that this method is also effective to perform drying of resist pattern without collapse [3,4]. We also have confirmed the feasibility of this method in semiconductor process for several kinds of resists [2]. In this paper we reports additional findings in lithographic performance mainly focusing on 70-nm-node patterns.

2. System configuration and process

The instrument to perform sc-CO₂ drying, developed by Dainippon Screen MFG. co. Ltd. and Kobe Steel Ltd., is constituted from 3 main operating modules, i.e., aqueous process module for alkali development and rinse by DI water, solvent process module for development and rinse by organic solvents, and supercritical drying module, as shown in Fig.1. Wafers are transferred between these modules by a robot arm that keeps flat and smooth during transportation so as not to drop a processing liquid covering on the wafer. In case of alkali development resist sample, an exposed and post exposure baked wafer (200 mm φ) is developed in the aqueous

process module followed by the rinse by DI water, then moved to the solvent process module slowly with the surface covered by the water-cap. As the water must be removed before starting sc-CO₂ drying [4], for the water cannot be solved in sc-CO₂, it is replaced by 2 solutions sequentially in solvent process module. In the first replacement, the wafer is washed with a solution that scavenges water, and in the second replacement the surface of wafer is wrapped by a solution that is solved in sc-CO₂.

Fig.1 Configuration of the instrument.

In sc-CO₂ module, CO₂ gas of 60 °C is introduced at first into the chamber in which the sample is placed. In the experiments the pressure in the chamber was controlled as the chart shown in Fig. 2. As the temperature of CO₂ was kept to

Fig.2 Pressure control diagram during sc-CO₂ drying.

60°C during the process, supercritical condition was obtained without crossing the phase interface of gas and liquid, as shown in Fig.3. After the pressure reached 10 MPa, sc-CO₂ flow was kept for a certain period (5~20 min.) to remove the solvent wrapping the wafer. The flow rate was controlled with injection and drain valves equipped to the chamber. Finally pressure in the chamber was decreased to atmospheric level, by

closing the injection valve, then the dried wafer was returned to the wafer cassette.

Fig.3 Process condition of CO₂ in phase diagram.

3. Results and discussions

3.1 Improvement of resolution in L/S pattern

In the experiments, we used proximity X-ray lithography (PXL) in pattern replication by using an X-ray stepper. In our previous study [5], 70-nm-L/S could be replicated when using the high resolution chemically amplified positive resist UV6 (Shipley Far East Ltd.) with the standard process condition by the mask-to-wafer gap of 10 μm. In that case the resist thickness had to be used with 0.23 μm to escape pattern collapse, and even with such a thickness the pattern collapse appeared when the exposure dose was out of the optimum window, as shown in Fig.4. With the gap of 15 μm, 70-nm-L/S could not be resolved with this resist in that

Fig.4 70-nm-L/S patterns by the resist UV6 with normal spin drying after rinse. Exposure dose shown on each photographs are given by the unit of D₀ (D₀: dose to clear).

thickness, as shown in Fig.5. When performing

sc-CO₂ drying, we found that the resolution of 70-nm-L/S was strikingly improved with the exposure gap of 15 μ m, as shown in Fig. 6. We confirmed that positive resist UVII-HS (Shipley)

Fig.5 70-nm-L/S patterns by the resist UV6 with normal spin-drying after rinse. Exposure condition is same as in Fig.3 except that the mask-to-wafer gap is 15 μ m.

Fig.6 70-nm-L/S patterns by the resist UV6 with the thickness of 0.35 μ m exposed with the gap of 15 μ m. Sc-CO₂ drying was performed for 20 min with 10MPa and 60°C.

is also capable to resolve 70-nm-L/S in this gap with high aspect ratio, nevertheless the resolution of UVII-HS is less than UV6 and this is the resist most likely to collapse in spin-drying among which we have ever investigated. Figure 7 shows the patterns of 70-nm-L/S by UVII-HS exposed by the gap of 15 μ m followed by sc-CO₂ drying with 10 MPa and 60°C for 20 min. It can be said that the sc-CO₂ drying has potential to increase practical resolution, by making the most of the intrinsic ability of resists to resolve.

Fig.7 70-nm-L/S patterns by the resist UVII-HS with the thickness of 0.4 μ m, exposed with the gap of 15 μ m by the dose of 1.06*D₀. Sc-CO₂ drying was performed for 20 min with 10MPa and 60°C.

3.2 The effect of scum cleaning

In the observation of L/S pattern in TDUR-N908 (Tokyo Ohka Kogyo Co., Ltd.), a negative tone chemically amplified resist, we

found an interesting phenomena, the possibility of scum cleaning by sc-CO₂. As the gamma value of negative resist is generally small compared to that of positive resist, scum sometimes appears between and at the terminal area of dense patterns. Figure 8 shows the comparison of 100-nm-L/S patterns and their terminal area with/without sc-CO₂ drying at the exposure dose of 2*D₀ (here D₀ is defined as the dose the sensitivity curve crosses the dose-axis with the residual thickness of 0). In the figure, scum is

(a) Spin-dry (b) Sc-CO₂ dry (10MPa, 60°C, 15min)

Fig. 8 100-nm-L/S patterns and peripheral area replicated in TDUR-N908 by the gap of 10 μ m with the exposure doses of 2*D₀. The thickness is (a)0.27 μ m and (b)0.63 μ m.

observed with the usual development condition. On the contrary, it is not observed in the patterns sc-CO₂ drying was performed. We found that the spin-dried pattern began to scum with the dose of 1.9*D₀ and sc-CO₂ dried pattern began to scum with the dose of 2.2*D₀. It indicates that sc-CO₂ drying might be effective to clean the scum. Figure 9 is the comparison of sensitivity curve with/without sc-CO₂ drying, i.e., residual thickness of the resist vs. exposure dose. As it can be seen in the figure, the residual thickness is slightly less in sc-CO₂ dried resist in the low dose region insufficient to make pattern. From these results we guess that sc-CO₂ is capable to clean a

Fig.9 Sensitivity curve of TDUR-N908 with/without sc-CO₂ drying.

scum caused by softly exposed TDUR resist. If it is true, it is advantageous to do sc-CO₂ drying in improving pattern quality and process margin.

3.3 Evaluation of CD uniformity and line-edge-roughness

In the previous discussion, we did not pay close attention on the effect of processing time, i.e., the period keeping a wafer in sc-CO₂, and applied 15 or 20 minutes without a certain basis. As 20 minutes of treatment is too long to use normally, we examined feasibility of 5 minutes as the time for a wafer in sc-CO₂ with 10MPa by 60°C. The checking points of feasibility were the uniformity of critical dimension (CD) and line-edge-roughness (LER) in 70-nm-L/S patterns, and they were compared between 5 and 20 minutes of process. In this evaluation we used the positive resist UV3 (Shipley) with a thickness of 0.35 μm , for this resist showed high resolution comparable to UV6 with relatively higher sensitivity, as shown in Fig. 10.

Fig. 10 70-nm-L/S pattern by UV3 with the thickness of 0.56 μm exposed by the gap of 10 μm . Sc-CO₂ drying was performed for 20 min with 10MPa and 60°C.

The CD pattern was exposed 13 shots in a wafer with a same dose by the gap of 10 μm and developed followed by the sc-CO₂ drying of 5 minutes for one wafer and 20 minutes for another. The measurement of CD and roughness were made by top-down SEM S8840 (Hitachi, Ltd.). The measured results are shown in Fig. 11 and 12, respectively. As it can be seen in the figures, the remarkable difference was not observed in both CD uniformity and roughness. From the results we can say that CD and LER is not sensitive with process time, and 5 minutes of sc-CO₂ drying is acceptable for UV3 with this thickness.

4. Summary

The supercritical resist drying, thought to be

Fig.11 Comparison of CD of 70-nm-L/S between the sc-CO₂ time of 5 and 20 min with the resist UV3.

Fig.12 Comparison of line-edge-roughness of 70-nm-L/S between the sc-CO₂ time of 5 and 20 min with the resist UV3.

the ultimate method to escape pattern collapse, was investigated in viewpoint of lithographic performance such that if it changes resolution, CD control, and roughness. Though the process optimization is not yet enough, we found that this method had the potential to improve practical resolution, and it had a pleasant robustness on process time without a particular disadvantage in CD control or roughness. A possibility of scum cleaning was also found in a negative tone resist.

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