Study of Pattern Collapse for Freezing Free Litho-Litho-Etch Double Patterning

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Pattern collapse becomes one of the serious issues for critical patterning process below 45nm half pitch. Many reports have been published in recent days to investigate pattern collapse mechanism. There are factors such as capillary force, hardness, swelling, and pattern profile that can cause pattern collapse.

On the other hand, Litho-Litho-Etch (LLE) without freezing process has been recognized as a promising candidate because of its cost effectiveness among double patterning processes. The materials using 2nd resist formulation is totally different from the one on 1st resist because it is necessary that 2nd resist solution doesn't dissolve 1st resist during 2nd litho process. Therefore, pattern collapse mitigation on freezing free LLE process can pose considerable challenges.

In this report, the improvement of pattern collapse on 2nd resist will be discussed by focusing on the surface free energy and the swelling during its development process.

Keyword: Double Patterning, Litho-Litho-Etch, Freezing Free, Pattern Collapse, Solubility Parameter, Surface Free Energy, Swelling

1. Introduction

Pattern collapse has become one of the serious issues for critical patterning process as CD size is being shrunk. Mechanism of pattern collapse is very difficult to fully understand because it is caused by a complexity of factors such as capillary force, hardness, swelling, and pattern profile.[1-15] We have proposed a freezing free Posi/Posi process as LLE process for 32nm half pitch node and below.[16] Two different resists were used to establish Posi/Posi process so that it was necessary to understand the mechanism of pattern collapse for the two different resist platforms used in Posi/Posi process.

For Posi/Posi process, minimization of interaction between 1st and 2nd resists is important. By using Hansen parameter simulation, base polymer of 2nd resist was

designed to have just enough solubility from specific alcohol solvent that could not dissolve 1st resist. Base polymer of 2nd resist has a specific structure that enhances the solubility for alcohol solvent. This specific structure causes lower surface energy than that of 1st resist, therefore pattern collapse of 2nd resist easily occurs on BARC substrate. And by using Quartz Crystal Microbalance (QCM) we also investigated pattern swelling of 2nd resist during its development since pattern swelling could be a possible cause leading to pattern collapse.

In this report, design of resist materials for freezing free Posi/Posi process will be discussed to minimize pattern collapse from the stand point of surface free energy and pattern swelling.

2. Experimental

2.1. Hansen Solubility Parameter (HSP) Analysis

Solubility parameter, a relative number, is commonly used as a measure of solubility of a material. Although in past, it was difficult to measure polymer solubility, in recent years however, Hansen Solubility Parameter (HSP) has been introduced to specify the solubility for polymer.[17] HSP can be divided into dispersion (δ_D) element, polar (δ_P) element, and hydrogen (δ_H) element that are treated as components of a 3D vectors. HSP is also used to calculate Relative Energy Difference (RED) where it gives possible solubility of a polymer into each solvent.

For this work, 5wt% polymer solutions with more than 15 kinds of solvents were prepared. A mixture of polymer and solvent was stirred for 10 minutes and then set aside for a while. It is preferred that selection of solvent be carried out based on how much difference of HSP. Polymer solubility was determined by simple observation with unaided eyes. As for these results, polymer solubility parameter (SP value) was simulated by HSPiP application, which could simulate details of SP values, such as δ_D , δ_P , δ_H and RED. Suitable base polymer can then be chosen for 1st resist and 2nd resist, mixture or single solvent.

2.2. Surface Free Energy Measurement

Correlation between surface free energy and adhesion of resist pattern has been reported.[12,18] Surface free energy (γ) can be expressed as a sum of dispersion (γ^d) element and polar (γ^p) element.

$$\gamma = \gamma^d + \gamma^p \quad (1)$$

The adhesion work (W_A) between substrate and resist pattern in the air can be presented by the following equation.

$$W_A = 2(\gamma_S^d \gamma_P^d)^{1/2} + 2(\gamma_S^d \gamma_P^p)^{1/2} \quad (2)$$

The intrusion energy (W_I) of liquid on the interface between resist pattern and substrate can be estimated by the following equation.

$$W_I = W_{SL} + W_{PL} - 2\gamma_L \quad (3)$$

On the other hand, the adhesion energy (W) between resist pattern and substrate in the liquid can be obtained as follows.

$$W = W_A - W_I \quad (4)$$

In this work, adhesion energy of 1st resist and 2nd resist between each substrate were checked. Surface free energy was measured by contact angle method. Also, surface energy of BARC substrate after the 1st resist process was measured in order to investigate 2nd resist adhesion on BARC, represented same condition as in Litho-Litho-Etch double patterning.

2.3. QCM Measurement

In earlier the swelling behavior during the development process have been investigated by QCM.[19,20]

Resist was coated on a 1-inch QCM substrate followed by a 90°C bake for 60 seconds. The resist film was exposed with different doses (1.0 ~ 8.0 mJ) with VUVES-4500 followed by a 90°C post exposure bake (PEB). The sample crystal was set in the sensor probe and immersed in TMAH 2.38wt% aq. at a temperature of 23°C. The resonance frequency was measured as a function of development time.

2.4. Dual Line Patterning with Freezing Free Posi/Posi Double Patterning Process

For imaging below 32nm hp dual line, a 38nm thick film of ARC95 (Nissan chemical) was applied on Zero maker wafer. The 1st resist was then coated with a 80 nm thick film followed by a 120°C softbake for 60 seconds. The resist film was then exposed by ASML XT1900Ei using annular polarized illumination with 1.35NA. The make for 32nm line was 56nm line with 128nm pitch with 6% transparent attenuated phase shift mask. PEB for 1st resist was performed at 110°C for 60 seconds followed by a 10 seconds develop with TMAH 0.26N aq. and 30 seconds distilled water rinse using ECO nozzle. The resist with developed pattern was then run through a 150°C hardbake for 60 seconds to remove residual solvent and water from the film. Then a 2nd lithography processed was carried out similar to the 1st litho process. Here, unlike the 1st resist, the PEB conditions were 90°C and 60 seconds. The 2nd litho process thus resulted in defining a dual line pattern below 32 nm half pitch. For CD measurement, S-9380 and CG-4000, produced by Hitachi were used.

3. Results and Discussion

3.1 Material Investigation of Solubility Parameter

To establish a freezing free Posi/Posi process the

integrity of the 1st resist pattern must be maintained during the 2nd resist process. Table 1 shows HSP and RED (calculated by HSPiP) of 1st and 2nd resist base polymers where the polymers can be easily dissolved in the solvent, when values for RED are smaller than 1.

Table 1. Hansen solubility parameter

Material	HSP			RED	
	δD	δP	δH	1st Solvent	2nd Solvent
General 1st polymer	17.05	11.04	8.57	0.78	1.16
General 2nd polymer	16.40	10.35	9.26	0.52	0.83

On the other hand, 1.0 and larger RED numbers indicate that the polymers cannot be dissolved in the solvent. Therefore, RED represents a readiness of polymer solubility into its solvent. Calculated RED between 1st resist polymer and 2nd resist solvent is 1.16. This means that 1st resist pattern cannot be easily dissolved during a 2nd resist lithography process. On the other hand, calculated RED between 2nd resist polymer and 2nd resist solvent is about 0.83. This means that 2nd resist polymer has adequate solubility for 2nd resist solvent. The RED gap between 1st resist polymer and 2nd resist polymer to 2nd resist solvent indicates less interaction of 1st resist pattern during 2nd resist process, so both 1st resist pattern and 2nd resist pattern can be obtained without any freezing treatment for 1st lithographic process.

3.2 Surface Free Energy Analysis

Table 2 summarizes the energy properties of these organic materials, such as BARC, 1st resist, and 2nd resist. Fig.1 shows component map of surface free energy for BARCs before and after the 1st lithography, 1st resist, and 2nd resist. They exhibit very similar properties. Based on component map, it can be expected that adhesion of 2nd resist is worse on BARC substrate than that of 1st resist. Table 3 shows calculation results of adhesion between BARC and resist pattern in water. There is no apparent difference among the samples from the 1st or 2nd resists. However, a comparison between 1st resist and 2nd resist shows a clear trend that the 2nd resist has less adhesion capability. Therefore, there is a potential that 2nd resist pattern can collapse more easily than 1st resist pattern.

Table 2. Surface free energy

Material	(mJ/m ²)		
	Dispersion component γ^d	Polar component γ^p	$(\gamma^d + \gamma^p) \gamma$
BARC-A	36.9	11.4	48.3
BARC-B	35.9	13.7	49.6
BARC-A after 1st lithography	34.9	17.4	52.3
BARC-B after 1st lithography	34.2	21.1	55.3
1st resist-i	38.1	8.1	46.2
1st resist-ii	37.1	10.0	47.1
1st resist-iii	38.1	8.1	46.2
2nd resist-iv	36.5	6.2	42.7
2nd resist-v	36.9	6.9	43.8
2nd resist-vi	37.7	6.4	44.1
Deionized water	21.8	51.0	72.8

Figure 1. Component map of surface free energy of the materials

3.3 QCM Evaluation

The weight shift for the resist film during its development step was measured using two 2nd resists with different protecting groups. Fig. 2 showed contrast curves of the two resists. X-axis means normalized sensitivity relative to Dose-to-clear (ETH), and Y-axis is

Table 3. Adhesion energy

Material	(mJ/m ²)		
	Adhesion energy W_A	Intrusion energy W_I	($W_A - W_I$) W
1st resist-i	94.2	57.6	36.6
1st resist-ii	95.4	61.4	34.0
1st resist-iii	94.2	57.6	36.6
2nd resist-iv	92.2	61.1	31.0
2nd resist-v	93.7	63.4	30.3
2nd resist-vi	93.7	62.6	31.0

remaining film thickness. Drastic thickness change was observed in the range from 80% to 100% of ETH.

Figure 2. Contrast curve of Resist A

Fig. 3 is a QCM spectrum of Resist A where X-axis is development time and Y-axis is frequency difference. The frequency values are inversely proportional to the film weights. Neither dissolution nor swelling occurred since no weight change was observed at 50% energy of ETH (ETHx50%). On the other hand, small weight increase, which suggests swelling behavior, can be seen at 70% energy of ETH (ETHx70%). Moreover, slight weight increase was observed until 5 seconds

Figure 3. QCM spectrum of Resist A

Each plots show spectrum of ETHx50%, ETHx70%, ETHx80% and ETHx100% which are indicated as 50%, 70%, 80%, and 100% of dose energy ratio of ETH

from start dipping and then loss in weight was observed at 80% energy of ETH (ETHx80%). At 100% of ETH, dissolution behavior mainly occurred so that swelling was not observed. As of these results, energy from ETHx70% till ETHx80% would be a suitable range to investigate swelling of resist film. From this experiment, QCM spectrums of Resists A and B, when they are exposed at 70% and 80% of ETH are shown in Figs. 4 and 5. Here apparent increment in film weight can be seen on Resist B film in comparison to Resist A film. This means that Resist B can exhibit more swelling behavior than Resist A.

Next we checked lithographic characteristics of 2nd Resists A and B.

Figure 4. QCM spectrum 70% x ETH

Figure 5. QCM spectrum 80% x ETH

3.4 Lithographic characteristics result

Lithographic characteristics of Resists A and B were evaluated by ArF immersion on the process of freezing free Posi/Posi double patterning process. Figure 6 shows SEM images of 32 nm hp resist pattern. The 2nd Resist A shows better pattern collapse stability than the 2nd Resist B with the same combination of the 1st resist. Minimum CD just before the collapse of Resist A was 27.2 nm line on 64 nm pitch. On the other hand, minimum CD for the 2nd Resist B was 30.7 nm. Moreover, Resist C which was an optimized version of Resist A showed 25.5 nm minimum CD on 64 nm pitch before a collapse.

Figure 6. Collapse comparison for 32nm HP
Eop means the dose where target feature size can be obtained and Ecol. means the dose where minimum feature size can be achieved without any pattern collapse

4. Conclusions

Polymer design for freezing free Posi/Posi process was clearly shown with the use of HSP. Based on the measurement results of surface free energy the 2nd resist due to poor adhesion appeared to collapse more easily than the 1st resist on BARC did. When the two different behaviors of 2nd resist during the development process by QCM analysis were evaluated on a double patterning process, the resist, which indicated small weight change, showed better pattern collapse stability. It was believed that pattern collapse was caused by the combination of many factors. However, it was found that surface free energy and swelling contributed significantly to pattern collapse.

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