A Surface-Silylated Single-Layer Resist Using Chemical Amplification for Deep-UV and Vacuum-UV Lithography

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1. Introduction

The increasing packaging density and shrinking critical dimension of electronic devices require resist systems with enhanced performance, including high resolution of an image delineated in a thin uniform layer, and high dry-etching durability enabled by a thick and flat layer covering the topography. Further, pattern transfer with the light of shorter wavelength is preferable for high resolution from the optical limitation, and high transmittance of the imaging layer is also required for the formation of a resist pattern of high aspect ratio.

The contradicting requirements for resist thickness can be released by surface imaging (SI). SI is a promising technology to expand the resolution limit of photolithography toward a half of or finer than the wavelength of the transfer-ring light. However, in the SI based on selective silylation in the exposed or in the unexposed area of the surface sublayer of the single thick layer, the selectivity is not always perfect, which causes unwanted partial silylation in the non-image area and a tapered depth profile of the silylated sublayer at the image/non-image boundary. As the results, the unwanted silylation must be removed by break-through etching prior to dry blanking of the thick bulk layer, and the linewidth of the silylated sublayer pattern depends on the duration of the break-through etching. Further, image expansion during silylation brings about resolution deterioration, i.e., line broadening or trench narrowing.

As a new type of SI, we proposed in recent

papers [1-4] "Surface-silylated Single-layer Resist (SSS Resist)" prepared by uniform, pre-exposure silylation of a thick single layer of conventional resist polymer containing photoacid generator (PAG) to form a bilevel structure composed of a surface-silylated sublayer and an unsilylated bulk layer, instead of spin-coating with a Si-containing resist. Since the structure is quite similar to that of a bilayer scheme which uses a Si-containing resist, the SSS Resist was patterned similarly. The patterning scheme is illustrated in Fig. 1: imagewise exposure to generate acid from the PAG, postexposure bake (PEB) for chemically amplified desilylation, alkaline development of the sublayer, and dry blanking of the bulk layer by O_2 RIE to form a positive pattern.

In the previous paper [4], we reported preparation of SSS Resists composed of the surface-silylated sublayer of around 200 nm thickness and the unsilylated bulk layer of 900-1,100 nm, and clear pattern formation with a deep UV sensitivity of 7 mJ/cm².

However, patterning of this resist with vacuum and extreme UV radiation should be considered for the development of photolithography in near future. Since transmittance of a poly(vinyl phenol) (PVP) resist layer of 100 nm thickness is 19% at 157 nm [5] and 68% at 13 nm [6], the SSS Resist may be useful for VUV and EUV lithography, if the sublayer is thinner than 100 nm.

In this paper, we studied silylation of the surface-sublayer as thin as possible, by optimizing the silylating conditions.

Fig. 1 Patterning process of SSS Resists.

2. Experimental

2.1 Specimen preparation

PVP ($M_w = 8,000$) from Aldrich Co. was formulated with 8 wt% of triphenylsulfonium hexafluoroantimonate ($\text{TPS} \cdot \text{SbF}_6$) in diethyleneglycol dimethyl ether (DGM). The resist layer was spin-coated from the PVP solution to an initial thickness of 1.0-1.2 μm on a Si substrate, and soft-baked at 80 °C for 20 min.

2.2 Silylation

Silylation was carried out in liquid phase by dipping the specimen in a solution containing 15-30 vol% of hexamethyl-disilaxane (HMDS), 1-2 vol% of DGM, and 69-83 vol% of n-decane at 75-95 °C for 20-50 sec and rinsed twice in n-decane for 1 min.

2.3 O₂ RIE

The etch study was carried out in a parallel-plate etcher (electrode: 100 mm ϕ , distance: 40 mm) equipped with a water-cooling system under operating conditions of 50 W/13.56 MHz net power and O₂ pressure of 150 mTorr, at around 20 °C for 3-10 min. The etched depth was measured with a surface roughness analyzer, Kosaka Labs. SE3500.

The O₂ RIE experiments were performed for two purposes: (1) the SSS Resist before imagewise exposure was etched with overlaying a metal mask partly over the specimen to estimate the durability and thickness of the surface-silylated sublayer, and (2) the SSS Resist after wet development was dry-blanked to the substrate in the exposed area by using the surface-silylated sublayer in the unexposed area as an etch mask (Fig. 1, Step 5).

2.4 Exposure, PEB and wet development

The specimen was irradiated with a low-pressure 8W mercury lamp, Toshiba GL-05, through a mesh mask, and baked in an air-circulating oven at 120 °C for 5 min with a beaker containing hot water at 75-80 °C. Then, it was wet-developed in a 1.0-1.5 wt% aqueous tetramethyl-ammonium hydroxide (TMAH)

solution at 23-26 °C for 1-10 sec. [In the case of large specimens for SEM pictures, TMAH concentration was a little higher and the duration was longer, i.e., 2-6 min.]

3. Results and Discussion

3.1 O₂ RIE durability and sublayer thickness of SSS Resists

Preparation of 1- μm thick SSS Resists with 100-nm thin sublayers is the target of this study. However, O₂ RIE durability, which is represented by the reciprocal ratio of the etching rate of the silylated sublayer to that of unsilylated layer etched simultaneously, should be high. The minimum requirement of silylation for preparing the surface sublayer to function as an effective etch mask is as follows:

$$(\text{Sublayer thickness}) \times (\text{O}_2 \text{ RIE durability}) \geq (\text{Initial thickness}) - (\text{Sublayer thickness}) \quad (\text{i})$$

Then, the minimum value of the durability is calculated to be 9, but a part of the silylated sublayer was found to dissolved into the developing solution. As a consequence of thickness reduction, the durability necessary for pattern formation was 20 or higher.

After SSS Resist #34 which was reported in the previous paper [4], more than 15 times of silylation were studied in order to form a thin surface sublayer with high durability, revising the experimental conditions: concentrations of HMDS and DGM were increased and decreased, respectively; temperature of the silylating solution was raised, while the duration was once lowered and then raised with decreasing the DGM concentration.

Among them, patternable SSS Resists were prepared under the conditions cited in the upper half of Table 1. O₂ RIE durability was 28-43, and thickness of the silylated sublayer was 100-130 nm (SSS Resist #34 is cited for comparison [4]). Typical etching rate dependence on the layer depth for Resist #50 is shown in Fig. 2.

Table 1 Silylation, patterning conditions, and resist performance

SSS Resist No.		#34	#44	#46	#47	#50
HMDS conc.	(vol%)	15	30	30	30	30
DGM conc.	(vol%)	5	1.5	1.5	1.0	1.0
Silylating temp.	(°C)	72~74	76~80	76~80	75~78	90~95
Silylation time	(sec)	60	20	20	20	50
Sublayer thickness	(nm)	220	120	100	130	100
O ₂ RIE durability		x38	x28	x33	x43	x30
PEB temp.	(°C)	120	120	120	120	120
Hot water temp.	(°C)	80	80	80, 75	75	75
TMAH conc.	(wt%)	1.5	1.5	1.5, 1.0	1.0	1.0
Develop. time	(sec)	2	1	1, 3	10	10
O ₂ RIE	(min)	7	9	9	6	10
Pattern height	(μm)	1.1	1.0	0.5, 1.1	1.1	1.0
Sensitivity	(mJ/cm ²)	7	20	7	7	7

Fig. 2 O₂ RIE characteristics of SSS Resist layer #50 before (○) and after (●) silylation.

3.2 Patterning of SSS Resists

The SSS Resists were patterned under the conditions indicated in the lower half of Table 1. When Resists #44 and #46 were exposed to DUV light of 7 mJ/cm², steam-baked at 120 °C with hot water at 80 °C, and developed with 1.5 wt% aqueous TMAH for 1.0 sec, the exposed area of #44 was not blanked, while that of #46 was observed to be covered with traces of white powder. The reason was considered that the silylated sublayer was not removed completely by wet development in the former case, and that a part of the silylated sublayer turned into alkaline insoluble compound by reaction with excess steaming. The second specimen of Resist

#46 was similarly patterned just replacing the hot water at 75 °C, and the bulk layer was blanked, but pattern height observed was 500-600 nm.

This result was ascribed to loss of the silylated sublayer during O₂ RIE. In this way, strict control of sublayer thickness after wet development with concentrated solution is very difficult especially with a thin silylated sublayer. The third specimen of Resist #46 was steam-baked with hot water at 75 °C, and developed with 1.0 wt% aqueous TMAH for 3.0 sec, and a 1.1 μm high pattern was formed with DUV sensitivity of 7 mJ/cm².

SSS Resists #47 and #50 were successfully patterned under the conditions cited in Table 1.

Fig. 3 DUV exposure characteristics of SSS Resist #50 after wet development (●) and after O₂ RIE (○).

Around 1 μm -thick resist layers were observed to be blanked in the area exposed to DUV light of 7 mJ/cm^2 . The wet-developed depth and the depth amplified by O_2 RIE with SSS Resist #50 are plotted against the DUV dose in Fig. 3. Another large specimen of SSS Resist #50 was DUV exposed through a pattern mask for SEM, and treated similarly, though the conditions of wet development were with 1.5 wt% TMAH for

5 min or 6 min. The SEM pictures are shown in Fig. 4. In the exposed area of the pattern formed after wet-development for 5 min, slight residue of white powder was observed, while in the case of that formed after prolonged development for 6 min, the residue was not observed at all, and the border of exposed and unexposed areas was quite sharp.

(a)

(b)

Fig. 4 SEM pictures of SSS Resist #50 patterns after wet development with 1.5 wt% TMAH and O_2 RIE: development (a) for 5 min; (b) for 6 min.

This SSS Resist process can be regarded as a hybrid of the bilayer resist and the surface imaging based on selective silylation or unsilylation in the exposed area. Therefore, it is expected to retain the merits of both processes, i.e., a simple single-layer process without using the Si-polymer prepared by many steps of complicated reaction, uniform and thin top imaging sublayer formation without spin-coating even on a wavy, not always flat, bottom layer, minimum pattern deterioration caused by low T_g of Si-polymers, no need for break-through etching after wet development under appropriate conditions. In particular, pre-exposure silylation eliminates the resolution deterioration caused by image expansion during silylation. Further, acid-catalyzed hydrolysis of silylether during PEB is employed for solubilization of the exposed area of the silylated sublayer, and, namely, an enhanced sensitivity can be attained by the chemical amplification.

4. Conclusion

A SSS Resist with a thin silylated sublayer of 100 nm thickness, which has high transmittance to 157 nm and 13 nm radiation, formed a clear 1- μm high pattern with a DUV sensitivity of 7 mJ/cm^2 . It has attained the targeted performance necessary to extend the limit of DUV lithography toward the next generation.

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