A wet-silylated and dry-developed resist process for proximity X-ray and broad-band EUV lithographies are performed using a synchrotron radiation (SR) light source from the beamline (BL-A1) at theSORTEC ring, and those for broad-band EUV lithography are performed using 32:1 reduction Schwarzschild optics illuminated with the SR light source from the beamline (BL-D2). The silylation solution consists of B[DMA]DS (bis(dimethylamino)dimethylsilane) or HMCTS (hexamethylcyclotrisilazane) as the silylating agent, MCA (methyl cellosolve acetate) as the diffusion promoter and a solvent xylene. Silylation characterization and determination of the optimum composition of the silylation solution have been performed using Fourier transform infrared spectroscopy (FTIR) measurement. Using the optimal wet-silylation and dry-developed resist system, 0.08-µm lines and spaces of a 0.5-µm-thick resist (aspect ratio = 6) in proximity X-ray lithography, and 0.1-µm lines and spaces of a 0.55-µm-thick resist (aspect ratio = 5.5) in broad-band EUVL can be successfully delineated. High resolutions of ≤0.1 µm show that the silylation process for proximity X-ray and EUV lithographies is applicable to sub-0.1-µm lithography with a single-resist scheme.

1. Introduction

The finest resolution of X-ray lithography (XRL) using synchrotron radiation can be brought down to 0.1-µm features and even below. However, in order to delineate such fine patterns with conventional resist processes, it is necessary to overcome the serious problem in which fine patterns with a high aspect ratio are apt to collapse during wet-development [1]. Several approaches have been proposed and have proved effective for 0.15-µm level patterns [2]. However, application to much finer patterns will encounter growing difficulties because these approaches are based on wet development. A dry-developed resist process is considered to be a promising alternative for delineating sub-0.1-µm patterns. Another issue limiting the resolution in XRL is a decrease in the proximity gap latitude mainly due to diffraction and the waveguide effect [3]. If the pattern width is finer than 0.05 µm, this latitude becomes narrower than about 0.5 µm.
One possible solution to relax this constraint and make the ultimate resolution finer appears to be introduction of a surface imaging technique.

On the other hand, in extreme ultraviolet lithography (EUVL) using a reflection optics system, a broad band as an exposure beam can be applied because reflection optics intrinsically has no color aberration. If a broad band is used as the exposure beam, exposure intensity could increase much more than that of a narrow band such as 13 nm. However, using the broad band as the exposure beam, the resolution degrades and the absorption coefficient of resists becomes much larger because the exposure beam contains a longer wavelength. To overcome this problem, one approach is to use a top surface imaging resist technology. A silylated and dry-developed resist process has been widely studied as a top surface imaging technique in several lithography [4-6].

In this work, a wet-silylated and dry-developed resist process for X-ray and broad-band EUV (13-40 nm) lithographies is investigated in order to overcome pattern collapse during wet development and to delineate fine-pitch and high-aspect-ratio patterns. In particular, applicability to sub-0.1-μm patterning is discussed.

2. Experimental

Proximity X-ray Lithography

Imaging experiments were performed using a synchrotron radiation (SR) light source from the beamline (BL-A1) at the SORTEC ring [7]. The peak wavelength of the SR beam is 0.7 nm. Two different types of X-ray masks were used. One is composed of a 2-μm-thick SiN membrane and 0.8-μm-thick W patterns [8]. The other mask was prepared to estimate the applicability of the silylated resist to sub-0.1-μm features. This mask contains an 1.9-μm-thick step having a smooth sidewall anisotropically etched into silicon (110) substrate, as shown in Fig. 1. On the sidewall are deposited alternate layers of 0.07-μm-thick tantalum, an X-ray absorber, and 0.09-μm-thick silicon, which absorbs fewer X-ray [9].

EUV Lithography

Imaging experiments were performed using 32:1 reduction Schwarzschild optics illuminated with an SR light source from the beamline (BL-D2). The exposure was done through a quartz plane mirror at a grazing angle of 4°, a 0.1-μm-thick SiN membrane as a vacuum window and Mo/Si multilayer coated optics [10]. A transmission mask was used for pattern replications. The mask consists of a 0.05-μm-thick SiN membrane and lines and spaces made of a 0.2-μm-thick Au absorber.

In the reduction imaging, a broad band was used as the exposure beam. Figure 2 shows the calculated spectra of the broad band EUV without a Be filter and the narrow-band of 13 nm with a Be filter [11]. The beam of wavelength longer than 40nm is negligible because of the absorption of
Fig. 1 A model mask is fabricated by Si (110) anisotropic etching and Ta shadowing techniques.

Fig. 2 Calculated spectra of exposure beam at the broad band without a Be filter and the wavelength of 13 nm with a 1-µm-thick Be filter.

Fig. 3 Modulation function curves of Schwarzshild optics at 13, 20 and 40 nm with incoherent illumination.
the 0.1-µm-thick SiN vacuum window. The exposure intensity on the wafer at the broad-band EUV of 13~40 nm was 20 times larger than at the wavelength of 13 nm.

Figure 3 shows the modulation transfer function (MTF) curves of the Schwarzschild optics at each wavelength of the broad band with incoherent illumination [10]. The average MTF value for 0.1-µm lines and spaces exposed to the broad-band EUV is estimated at about 40%. This value is too small to obtain the resolution of 0.1 µm using a conventional resist process. To achieve the resolution of 0.1µm, a silylation process as a top surface imaging resist technology is required.

Resist and Silylation Processes

We used SAL601 (Shipley) resist which is composed of a novolac resin, a melamine crosslinker and a photo-acid generator. The resist was spin-coated on silicon wafers and pre-baked at 120 °C for 120 seconds. The exposed resist was post-exposure-baked at 105 °C for 120 seconds.

A wet-silylation process was chosen because the silicon concentration of a wet-silylated resist layer is much higher than that of a dry-silylated resist layer [4]. After the imaging, the resists were silylated at room temperature for 120 seconds in a liquid phase with a xylene solution containing silylating reagent and MCA (methyl cellosolve acetate) as the diffusion promoter. We used B[DMA]DS (bis(dimethylamino)dimethylsilane) and HMCTS (hexamethylocyclotrisilazane) which are well-known wet-silylating reagents. The concentration of silylating reagent was fixed at 5 vol. %. In order to find the optimum composition of the silylation solution, the concentration of MCA and xylene were varied in vol. %.

The silylated resist was dry-developed in a conventional O2 RIE system (PK1441 Plasma-Thermo). The O2 gas pressure and RF power are 1.33 Pa and 100 W, respectively.

Silylation characterization and the optimum composition of the silylation solution were examined by Fourier transform infrared spectroscopy (FTIR, PERKIN ELMER SYSTEM 2000) measurement.

Resist film thickness was measured using Alpha-step 200 (Tencor), and cross-sectional views of the dry-developed resist patterns and the silylated resist layer were observed using a scanning electron microscope (SEM), S-900 (Hitachi).

3. Results and Discussion

Characterization and optimization of silylation process

FTIR spectra of the resists after silylation and O2 RIE [12] are shown in Fig. 4. In the case of HMCTS, the absorbances corresponding to Si-N-H structure (\(\sim 1190\text{cm}^{-1}\)), Si-N-Si structure (\(\sim 930\text{cm}^{-1}\)) and Si-O-aryl structure (\(\sim 950\text{cm}^{-1}\)) are very large, and that of Si-O-Si structure, i.e., siloxane structure (\(\sim 1050\text{cm}^{-1}\)), is very small after silylation [13]. However, in the case of B[DMA]DS, the absorbance corresponding to siloxane structure is very large after silylation. These results show that polymerization of B[DMA]DS occurred during silylation, which formed siloxane
Fig. 4 FTIR spectra of the SAL601 resist after silylation and O$_2$ RIE.

(a) HMCTS

(b) B[DMA]DS

Fig. 5 Silylation depth and incorporated silicon content obtained from the FTIR peak height (Si-O-Si structure) normalized by the silylation depth.

Fig. 6 O$_2$ RIE selectivity between exposed-silylated and unexposed-silylated resist for 5 minutes from RIE starting time.
structure on each phenolic -OH group of the novolak resin [4,14], while polymerization of HMCTS was not appreciable [15]. This siloxane in the silylated layer has more than one silylating molecule bonded to each phenolic -OH group. Therefore, in the case of B[DMA]DS, much higher O₂ RIE resistance of the silylated layer is expected.

In the case of HMCTS, the absorbance corresponding siloxane structure increases and those of Si-N-H structure, Si-N-Si structure and Si-O-aryl structure decrease after O₂ RIE. In the case of B[DMA]DS, however, the peaks corresponding to siloxane structure and Si-O-aryl structure are almost unchanged even after O₂ RIE. These FTIR spectra show that most of the siloxane structure was formed during silylation in the case of B[DMA]DS, whereas most of the siloxane structure was formed during O₂ RIE in the case of HMCTS. Moreover, these FTIR spectra show that the contraction and reduction in the film thickness of the silylated layer in the case of HMCTS occurred during O₂ RIE, which might degrade the resolution of the silylated resist, while those of the silylated layer in the case of B[DMA]DS were not noteworthy because of the high concentration of siloxane structure which formed in the resist during silylation. An ideal silylated resist for obtaining high resolution should have high silicon concentration to obtain high O₂ RIE resistance and a thin silylated layer to prevent swelling and flow of the silylated layer. O₂ RIE resistance depends very strongly on the siloxane structure concentration in the resist. These results show that the resist silylated by B[DMA]DS has a higher O₂ RIE resistance than resist silylated by HMCTS; thus B[DMA]DS is preferable to HMCTS as a wet-silylation reagent for obtaining high resolution. We therefore chose B[DMA]DS as the wet-silylation reagent.

Figure 5 shows the silylation depth as measured under the SEM, and the incorporated silicon concentration obtained from the FTIR peak height of siloxane structure (\(\sim 1050\text{cm}^{-1}\)) normalized by the silylation depth as a function of MCA concentration [12]. The silylation depth increased radically above the MCA concentration of 10 vol. % due to diffusion of the silylating reagent enhanced by a concentrated MCA solution. These plots indicate that an optimum concentration of the diffusion promoter to achieve maximum silicon concentration exists. A diffusion promoter that is too concentrated gives the silylated resist a low incorporated silicon concentration. In this case, the maximum silicon concentration was obtained at the MCA concentration of 10 vol. %.

O₂ RIE selectivity between exposed-silylated and unexposed-silylated resist for 5 minutes from O₂ RIE starting time as a function of MCA concentration is shown in Fig. 6. At the MCA concentration of 10 vol. %, the maximum O₂ RIE resistance was obtained. This result agrees with the incorporated silicon concentration mentioned above.

Proximity X-ray lithography

0.2-μm line-and-space patterns dry-developed by O₂ RIE for various MCA concentrations [12] are shown in Fig. 7. The proximity gap in imaging was 15 μm. In the case of 5 vol. %, the pattern is destroyed because of under-silylation, while in the cases of 12.5 and 15 vol. % the
Fig. 7 0.2-μm lines and spaces of the B[DMA]DS wet-silylated and dry-developed resist in proximity X-ray lithography.

Fig. 8 An SEM micrograph of 0.08-μm lines and spaces of 0.5-μm-thick resist. The aspect ratio is 6.

Fig. 9 0.1-μm lines and spaces (0.55-μm-thick) of the B[DMA]DS wet-silylated and dry-developed resist in broad-band EUV lithography.
patterns have a constricted profile between silylated layer and unsilylated layer because of oversilylation. Rectangular patterns were obtained at the MCA concentration of 7.5 or 10 vol. %. Moreover, replicating the model mask as shown in Fig. 1, 0.08-µm lines and spaces of a 0.5-µm-thick resist (aspect ratio = 6) can be successfully fabricated [12], as shown in Fig. 8. B[DMA]DS, MCA and xylene concentration of the silylation solution is 5, 10 and 85 vol. %, respectively. The proximity gap in imaging was 7 µm. This pattern shows steep sidewalls, and has a fine pitch and high aspect ratio which can never be obtained with the conventional wet-development process due to pattern collapse.

EUV lithography

Figure 9 shows an SEM micrograph of 0.1-µm lines and spaces of the B[DMA]DS wet-silylated and dry-developed resist using broad-band EUV lithography. This pattern shows steep side-walls, and has a high resolution (≤0.1 µm) and high aspect ratio (5.5). However, the issue of the edge roughness of the fine-pitch silylated pattern after dry development still remains.

4. Conclusions

A wet-silylated and dry-developed resist process for proximity X-ray and EUV lithographies is a promising technology for delineation of fine-pitch and high-aspect ratio patterns. Moreover, the high resolution of ≤0.1 µm shows that the silylation resist system is applicable to sub-0.1-µm lithography with a single-resist scheme. However, the issue of the edge roughness of the fine-pitch silylated pattern after dry development still remains. Silylation with a much higher concentration of silicon, and silylation selectivity between the exposed and the unexposed area are required.

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