Exploring the ultimate resolution of positive-tone chemically amplified resists: 26 nm dense lines using extreme ultraviolet interference lithography

V. N. Golovkina, P. F. Nealey,^{a)} F. Cerrina, and J. W. Taylor
Center for Nanotechnology, University of Wisconsin-Madison, 3731 Schneider Drive,
Stoughton, Wisconsin 53589

H. H. Solak, C. David, and J. Gobrecht
Laboratory for Micro- and Nanotechnology, Paul Scherrer Institute, 5232 Villigen PSI, Switzerland

(Received 1 July 2003; accepted 17 November 2003; published 14 January 2004)

Interference lithography (IL) [Yen *et al.*, Appl. Opt. **31**, 2972 (1992)] based on reflective optics, and utilizing extreme ultraviolet (EUV) light from an electron storage ring, can be used to pattern structures with periods below 70 nm [Solak *et al.*, Appl. Phys. Lett. **75**, 2328 (1999); Ali *et al.*, Microelectron. Eng. **65**, 454 (2003)]. Previously achromatic interferometers with EUV transmission diffraction gratings were also used for this purpose [Wei *et al.*, J. Vac. Sci. Technol. B **12**, 3648 (1994)], and recently we have printed sub-50 nm high quality periodic structures in poly(methylmethacrylate) exposed with transmission-grating EUV interference lithography (EUV-IL) [Solak *et al.*, Microelectron. Eng. **61**, 77 (2002); Solak *et al.*, *ibid.* **67-68**, 56 (2003)]. With this technique, two-dimensional patterns are easily achievable using multiple diffraction gratings. Both types of EUV-IL have been implemented on one of the undulator beam lines at the University of Wisconsin-Madison Synchrotron Radiation Center electron storage ring because this undulator source provides a tunable and coherent beam of radiation well suited for IL studies. In this article, both exposure methods were applied to explore the ultimate resolution of two positive-tone chemically amplified resists supplied by the Shipley Corporation. We have demonstrated the printing of features as small as 26 nm line and space in Shipley XP9947W-100 resist. The present results demonstrate the fine quality of the above-mentioned EUV-IL techniques to test resist formulations for high-resolution patterning, and we provide the experimental setup and discuss the observed results. © 2004 American Vacuum Society. [DOI: 10.1116/1.1640402]

I. INTRODUCTION

Extreme ultraviolet (EUV) lithography has been selected as a promising next generation lithography (NGL) technology, but presently there are few experimental data with respect to developing EUV resists because of the scarcity of sources and imaging systems. EUV interference lithography (EUV-IL)^{1,2} is particularly appealing technology because it produces high-resolution images without the need for complex optical systems and it is well suited to study materials properties such as resist properties and resist processing. Thus EUV-IL can be used to provide critical information on exposures and exposure conditions in the development of EUV as a means to fill this gap in the development of the technology.

The objective of the work reported here is to utilize EUV-IL to explore the ultimate resolution of Shipley XP9947W-100 and XP99146-V, two promising positive-tone chemically amplified resists. In this article we describe new exposure studies, which allowed us to image the former resist to 26 nm line/space patterns using the transmission-grating EUV interferometer we have recently built and tested.^{1,2}

II. EXPERIMENTAL SCHEMES AND RESIST EVALUATION

The EUV exposures were conducted on the Center for NanoTechnology (CNTech) EUV beamline at the University of Wisconsin-Madison Synchrotron Radiation Center.³ This beamline is equipped with an undulator to generate photons with energy of 92.5 eV (13.4 nm), and it has two branches to deliver the EUV photons into the exposure chamber. In the first branch, monochromatized light from the undulator is diverted up into the chamber by a 45° Mo/Si multilayer mirror. A spherical grating monochromator provides spatially coherent light and narrow spectral bandwidth of 0.1%.⁴ The exposure times vary from 20 to 60 s depending on the beam current in the ring. In the second branch, undulator light is directed into the exposure chamber after three consecutive reflections from 45° Mo/Si mirrors. A wider bandwidth (of about $\Delta\lambda/\lambda = 2\%$) EUV transmitted radiation through this system has advantageously higher flux.² A power density of 20 mW/cm² allows exposure of 100-nm-thick Shipley UV-6 resist film in 2 s. The series of multilayer mirrors has peak reflectivity at 13.4 nm and consists of 40 pairs of Mo/Si periodic layers for each mirror.

Two different exposure methods were employed in this study, namely reflective EUV-IL and transmission-grating EUV-IL. In the first technique, a simple Lloyd's mirror interferometer is used to deliver a variable-pitch interferogram. An adjustable incidence angle gold mirror folds the radiation

^{a)}Electronic mail: nealey@nanotech.wisc.edu

FIG. 1. Schemes for (a) two-beam and (b) four-beam EUV interference lithography. The picture is taken from Solak (Ref. 2).

incoming from an undulator onto itself, thus creating an interference pattern with a period adjustable in the range from 38 to 350 nm. In the second configuration an achromatic interferometer, based on transmission gratings, delivers a 50 μm field image. Figures 1(a) and 1(b) explain the design² for creating both one- and two-dimensional images that are line/space and square lattice patterns. In Fig. 1(a) two beams of light diffracted by a grating overlap at the center where an interference pattern is created. In order to create two-dimensional patterns, multiple beam IL is necessary. Interference of four beams schematically shown in Fig. 1(b) creates an array of holes on a square grid. The final image has higher resolution than the gratings, by a factor of 2 for linear gratings, $\sqrt{2}$ for square grid patterns (four wave interference), and 1.5 for hexagonal patterns (a beam diffracted by triangular gratings interferes to give hexagonal dot arrangement). Using this interferometer we have printed 26 nm line/space patterns (52 nm period) in Shipley XP9947W-100, a chemically amplified positive-tone photoresist.

The Shipley XP9947W-100 positive-tone chemically amplified photoresist series consists of a phenolic polymer base with a high-activation energy blocking group and was developed by Shipley primarily as an electron-beam resist system. The XP9947W-100 is a resist with high sensitivity. In all cases for chemically amplified resist, the high absorption of the materials at the EUV wavelength of 13.4 nm requires the use of extremely thin resist films. In order to meet this thickness requirement with high sensitivity, the Shipley

XP9947W-100 formulation was chosen. However, the processing conditions recommended by the supplier (Table I) had to be modified to work appropriately under EUV exposure conditions. The parametric optimization of the XP9947W-100 resist was first completed with normal x-ray exposures at 0.9 nm using the CNTech Karl Suss model 200/2M stepper exposure tool. Later, x-ray processing conditions were adjusted and a set of conditions was identified to meet EUV-IL requirements. The modified process conditions were not optimized after the resist thickness was changed. The decrease in thickness might require shorter time in the developer. We note from this optimization that thickness is not a major variable from the optimization data. In the original optimization the developer time was not a variable, and we have noted that the time in the developer varies 15% for every 20 nm of the resist thickness. However, the initial processing conditions were applied. These are shown in Table II and were derived by determining the exposure behaviors of four sets of the photoresists.

The absorbance of the resist has been calculated from data

TABLE I. Recommended processing conditions by Shipley Inc. for XP9947W-100 electron-beam photoresist.

Photoresist	XP9947W-100, 100 nm thick
Spin speed	3000 rpm
Spin time	30 s
Postapply bake (PAB)	140 °C/90 s
Postexpose bake (PEB)	130 °C/90 s
Developer type	LDD-26W or MF-26A
Development	45 s puddle

FIG. 2. EUV contrast curve of Shipley XP9947W-100 positive tone chemically amplified photoresist (sample No. 4).

TABLE II. EUV lithography processing conditions used for Shipley XP9947W-100 positive-tone chemically amplified resist (developer used was MF-26A).

Sample No.	Spin speed (rpm)	PAB (temp, °C)	PAB time (s)	Thickness (nm)	PEB (temp, °C)	PEB time (s)	Contrast	Clearing dose (mJ/cm ²)
1	2500	120	75	100	140	75	7.7	1.8
2	3500	120	105	98	120	75	5.9	2.0
3	3000	130	90	111	130	60	4.4	2.1
4	3000	120	105	108	140	45	5.8	1.7

supplied by Shipley. In addition, we have computed transmission and optical density of Shipley XP9947W-100 in 125 nm films at 13.4 nm wavelength. The transmittance of the resist was found to be 0.599, absorbance 0.222, and optical density 1.78/ μm . As shown in Table II the exposure doses were varied to generate normalized remaining thickness (NRT) curves. The sensitivity was determined experimentally for each set of conditions by exposing regions of resist of known thickness to different radiation doses and measuring the film thickness remaining after development for each exposed region. In positive resists, the film thickness of the exposed area decreases after development until it is completely removed at a critical dose D_0 . The contrast is derived from the plot of the remaining film thickness normalized to the original thickness as functions of exposure dose,⁵ as illustrated in Fig. 2, where a typical EUV contrast curve is shown for sample No. 4. In this case the resist with a post-apply bake (PAB) of 120 °C and a postexposure bake (PEB) of 140 °C demonstrated high sensitivity (D_0) and a clearing dose of less than 2 mJ/cm².

The resolution of a resist is directly proportional to its contrast. For XP9947W-100 chemically amplified resists being tested the highest resolution pattern was printed in sample No. 2. We noticed that PAB and PEB temperatures and time factors significantly affect the quality of the EUV pattern as well as the clearing dose and contrast and need to

be carefully controlled. The exposure conditions used by an electron beam differ from EUV, which requires the adjustment of the processing conditions for a particular wavelength used at the exposure tool.

The EUV exposures were done on Si wafers spin-coated with ~ 100 -nm-thick photoresist. Prior to the film coating, the wafers were processed with hexamethyldisiloxane (HMDS) for 60 s to ensure uniform coating and adhesion of the resist film. The resist thickness was measured using a thin-film optical analyzer Filmetrics F-20. All samples were developed in Shipley MF-26A for 45 s. The scanning electron microscopy (SEM) images were obtained using the LEO 1550 VP system.

Three out of four sets of XP9947W-100 were later chosen for EUV patterning due to relatively high resist contrasts, i.e., samples No. 1, No. 2, and No. 4. Due to the high absorption of all materials in EUV we decided to further decrease the thickness of the resist film. The original spin time was doubled to 60 s for all samples in order to get ~ 70 –80 nm resist thickness that turned to be more suitable for EUV-IL patterning in terms of image quality. Depending on the electron-beam current in the storage ring, typical exposure time never exceeded 20 s for the Lloyd's mirror exposures and 60 s for the transmission-grating EUV-IL, respectively.

The resolution and EUV-IL patterning abilities of Shipley XP99146-V chemically amplified resist were tested as well. This resist was spun at 2500 rpm for 60 s onto HMDS primed Si wafers in order to get the supplier specified 125 nm film thickness and baked at 130 °C both before and after exposure for 60 s and 90 s, respectively. The sample was developed in Shipley MF-26A for 45 s as it was done for the XP9947-W-100 resist. The XP99146-V resist processing

FIG. 3. SEM image of a 77 nm period pattern formed in Shipley XP9947W-100 chemically amplified resist using "reflective" EUV-IL.

FIG. 4. One-dimensional patterns created in Shipley XP9947W-100 resist with transmission-grating EUV-IL: (a) 50 nm L/S dense lines, and (b) 30/70 nm lines/spaces.

FIG. 5. SEM images of a 26 nm line/space pattern exposed in Shipley XP9947W-100 photoresist with transmission-grating EUV-IL.

conditions given by the manufacturer have not been optimized in this test.

III. RESULTS

Figure 3 shows the SEM image of 77 nm period patterns printed in Shipley XP9947W-100 89-nm-thick resist using “reflective” EUV-IL. A nonuniform distribution of EUV light caused by possible beam-line optical elements surface contamination and/or defects has resulted in a variation of EUV dose delivered to the wafer. The SEM images in Fig. 3 display the consequential pattern imperfections. The two SEM images in Figs. 4(a) and 4(b) demonstrate EUV exposures using gratings printing 50 nm line and space (L/S) dense lines and 30/70 nm lines/spaces, respectively. In this case, printed structures are almost defect-free due to the smaller number of EUV optical elements that the light gets reflected from on its way to the sample. The SEM image in Fig. 5 shows a 26 nm line/space pattern exposed in Shipley XP9947W-100 80-nm-thick photoresist with transmission-grating EUV-IL. We have calibrated our LEO SEM against an atomic force microscope (AFM) calibration standard us-

FIG. 6. Two-dimensional square grid with 56 nm period exposed in Shipley XP9947W-100 resist.

FIG. 7. Transmission-grating EUV-IL 50 nm line/space pattern printed in Shipley XP99146-V resist.

ing a Thermomicroscopes Autoprobe M5 AFM. In the specific case, we calibrated the LEO 1550 VP SEM against 30/70 nm features. We believe that the accuracy of our LEO SEM tool would allow us to claim 26 nm line/space features because the difference between the calibration and the measured 26 nm line/space features are reasonably close. The difference between the calibrations of lines in the image is 1.02%. Good quality SEM imaging is difficult to achieve with very thin resist films, however, a substantially reduced SEM extracted voltage of 0.5 keV or less improves image contrast. An attempt to print two-dimensional 56 nm square grid structures patterned in the same resist is shown in Fig. 6. Figure 7 shows the SEM image of a 50 nm line/space pattern exposed in Shipley XP99146-V 125-nm-thick photoresist using transmission-grating EUV interference lithography. The quality of the achieved results indicates that it is possible to use EUV interferometric lithography for printing of high-resolution grating patterns in chemically amplified resists.

IV. SUMMARY AND CONCLUSIONS

The present results demonstrate that the EUV-IL techniques can be used to test resist formulations for high-resolution sub-30 nm L/S patterning. Two resists, Shipley XP9947W-100 and Shipley XP99146-V are seen to be capable of imaging at the 26 and 50 nm L/S level, respectively. For XP9947W-100, the resist thickness required to achieve the high resolution was ~ 80 nm whereas the XP99146-V resist film was 125 nm thick.

ACKNOWLEDGMENTS

This work was supported by DARPA Grant No. MDA 792-01-1-0039. The Synchrotron Radiation Center, University of Wisconsin-Madison, is operated under NSF Grant No.

DMR-0084401. The authors would like to thank R. Brainard (Shipley Company) for valuable suggestions on the resist choices and the formulations for this demonstration, as well as D. Malueg (CNTech, UW-Madison) for the parametric optimization of the XP9947W resist using x rays at the 0.9 nm wavelength.

Presented at the 47th International Conference on Electron, Ion, and Photon Beam Technology and Nanofabrication, Tampa, FL, 27–30 May 2003.

¹H. H. Solak, C. David, J. Gobrecht, L. Wang, and F. Cerrina, *Microelectron. Eng.* **61**, 77 (2002).

²H. H. Solak, C. David, J. Gobrecht, V. Golovkina, F. Cerrina, S. O. Kim, and P. F. Nealey, *Microelectron. Eng.* **67-68**, 56 (2003).

³H. H. Solak, W. Li, D. He, J. Wallace, and F. Cerrina, *AIP Conf. Proc.* **521**, 99 (2000).

⁴H. H. Solak, D. He, W. Li, S. Singh-Gasson, F. Cerrina, B. H. Sohn, X. M. Yang, and P. Nealey, *Appl. Phys. Lett.* **75**, 2328 (1999).

⁵L. F. Thompson, C. G. Willson, and M. J. Bowden, *Introduction to Microlithography* (American Chemical Society, Washington, DC, 1994).