Study on Irradiation Effects by Femtosecond-pulsed Extreme Ultraviolet in Resist Materials

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ABSTRACT

Irradiation effects of poly(methyl methacrylate) (PMMA) induced by femtosecond-pulsed extreme ultraviolet (EUV) were investigated using Soft X-ray free electron laser (SXFEL) for realization of next generation extreme ultraviolet free electron laser (EUV-FEL) lithography. The sensitivity of PMMA upon exposure to femtosecond-pulsed SXFEL was much higher than that measured for conventional nanosecond-pulsed EUV source. The sensitivity enhancement upon exposure to femtosecond-pulsed SXFEL is similar to the result obtained using laser-induced-plasma based Soft X-ray laser (SXRL) (picosecond-pulsed EUV). This result speculates the reactions induced by femtosecond-pulsed SXFEL and picosecond-pulsed XRL were almost same, but it was different from those induced by nanosecond-pulsed EUV.

Keywords: Extreme Ultraviolet, Resist materials, Free-electron laser, Poly(methyl methacrylate), X-ray laser

1. INTRODUCTION

It is essential for our lives to use electronic devices. Lithography technique is very important for producing them. ArF immersion lithography has mainly used for the high-volume production of the forefront of electronic devices.1, 2 However, ArF immersion lithography has reached the limit of nanofabrication and thereby a new technique has been urgently required.3

Extreme ultraviolet (EUV) lithography, whose wavelength is 13.5 nm, has been recently adopted by the semiconductor industry as the advanced lithography technology to achieve further device scaling. However, EUV lithography also has approached the limits imposed by single exposure. Therefore, we must replace EUV with next generation lithography candidates including High-NA EUV lithography,4 next generation EUV with the wavelength of 6.λ,5 extreme ultraviolet free electron laser (EUV-FEL) lithography,6, 7 and so on. Among them, it is thought that high power EUV-FEL will improve both nano fabrication cost and throughput.5 One of the important characteristics of EUV-FEL is its short temporal pulse duration, which arises from the interaction between the ultrashort electron bunch and electromagnetic field. Recently, FEL which generates pulsed soft X-ray (EUV) such as SPring-8 Angstrom Compact FEL (SACLA) has been developed all over the world.8

Main-chain-scission-type resists have been widely used for the fabrication of nano-devices because they could fabricate in principle ultrafine structures to the dimensions of the monomers they consist of. Among them, poly(methyl methacrylate) (PMMA) is a typical main-chain-scission-type resist.8-13 PMMA has the capability for fabricating sub-10 nm half-pitch, although its applications are limited due to its poor etch resistance.14, 15 The reaction mechanism of
PMMA upon exposure to radiation and electron beam has been reported as follows.\textsuperscript{16-18} Upon exposure to radiation such as EUV and electron beam, PMMA molecules are ionized and their radical cations results in. After the detachment of side chains from the radical cations, β-scission of PMMA molecules occurs. However, the irradiation effects induced by EUV with a short pulse width and high power intensity in PMMA have not yet been elucidated.

In order to make clear the irradiation effects by EUV with a short pulse width and high power intensity, the morphological and chemical changes in PMMA induced by picosecond-pulsed EUV were investigated using a laser-induced-plasma based Soft X-ray laser (SXRL) in Kansai Photon Science Institute (KPSI).\textsuperscript{19} It has been reported that the sensitivity of PMMA upon exposure to picosecond-pulsed SXRL was much enhanced in comparison with using conventional EUV sources.\textsuperscript{20} The short-pulsed ionizing radiation causes a unique reaction because of the high dose rate.

Further investigation of short-pulsed EUV-induced reactions in resist materials are strongly needed for realizing EUV-FEL lithography. An important feature of EUV-FEL is the short pulse width on the order of femtoseconds. Because EUV with a pulse width of less than picoseconds is a novel light born in recent scientific and technological developments, physical events and chemical reactions in resist materials induced by the short-pulse EUV are not sufficiently understood. Therefore, it is very important for EUV-FEL resist design to understand femtosecond-pulsed EUV-induced reaction in PMMA.

In this study, the sensitivity of PMMA upon exposure to femtosecond-pulsed EUV was investigated by using soft X-ray free electron laser (SXFEL) in SACLA in order to make clear whether the resist sensitivity of PMMA enhances or not upon exposure to femtosecond-pulsed-EUV.

\section{EXPERIMENTAL}

Ultrashort-pulsed soft X-ray of SACLA BL1 was used as femtosecond-pulsed EUV source.\textsuperscript{21} SXFEL is generated by 800 MeV electron beam passing through an undulator. The pulse width was 70 fs and the energy was 92 eV, which is equal to wavelength of 13.5 nm. The horizontal spot size was 4.47 μm and vertical spot size was 3.67 μm (FWHM). Because the maximum fluence on target is approximately 100 J/cm\textsuperscript{2}/shot, SXFEL was attenuated below the ablation threshold. The SXFEL shots were attenuated to suitable intensity by using Zr filters having various thicknesses (0.1, 0.2, 0.5, 1.0, and 2.0 μm thickness or these combination). Details of the system have been reported elsewhere.\textsuperscript{22-24}

PMMA (Sigma-Aldrich, Mw = 350,000) were dissolved in toluene, spin-coated on Si wafer chips at 2500 rpm (min\textsuperscript{-1}), and baked at 220 °C for 15 minutes in air. The thicknesses of the spin-coated PMMA samples can be controlled by changing the concentration of PMMA solution. The samples with the thickness of approximately 66 nm and 350 nm were prepared. PMMA films were exposed to femtosecond-pulsed EUV. The irradiated samples were developed in a developer (methyl isobutyl ketone (MIBK): isopropyl alcohol (IPA) 1:3) for 60 s at room temperature (22 °C).

The surface change due to development was observed by using atomic force microscope (AFM) (AFM5300E, Hitachi High-Tech Science Corporation) in the atmosphere. The three-dimensional profiles of PMMA surface were obtained.

\section{RESULTS AND DISCUSSION}

SXFEL-irradiated PMMA surface was observed without attenuation as already reported.\textsuperscript{23} Large craters with several tens of μm were produced on samples as shown in Fig. 1 and used as a mark to search the position of development experiment.

Subsequently, in order to investigate resist performance of PMMA, SXFEL was attenuated to suitable intensity by using Zr filters. PMMA samples (initial thickness: 350 nm) were irradiated by one shot of SXFEL and total exposure dose was change by the combination of Zr filters. We confirmed no holes or damages was observed with microscope on the irradiated PMMA surface when the intensity was attenuated to about 1/1000 using Zr filters. Then, the sample was developed in for 60 s at room temperature (22 °C). Small holes were observed after development. The holes appeared after development on the irradiated PMMA sample as shown in Fig. 2. Also, AFM image of the hole on the 66 nm thick sample are shown in Fig. 3. Relatively well-formed profiles were obtained after development by using SXFEL. The hole size was consistent with SXFEL spot size.
The EUV pulse width of SXFEL in SACLA is approximately 80 fs, which is much shorter than conventional EUV and laser-induced-plasma based SXRL pulse widths. In order to confirm whether the resist sensitivity of PMMA enhances or not upon exposure to femtosecond-pulsed-EUV compared with conventional EUV and SXRL, we evaluated the resist performance of PMMA. Sensitivity of PMMA for SXFEL irradiation was measured. Fig. 4 shows sensitivity curve of PMMA with 66 nm film thickness after development. The sensitivity of a positive-tone resist is defined as the dose required to entirely remove the resist layer after development. The sensitivity of PMMA for femtosecond-pulsed SXFEL was determined to be approximately 6–8 mJ/cm$^2$. It has been reported that the sensitivity of PMMA for typical EUV and SXRL was approximately 50 mJ/cm$^2$ and 2 mJ/cm$^2$, respectively.\textsuperscript{19, 20} PMMA can be developed with lower energy deposition for femtosecond-pulsed SXFEL than typical EUV. On the other hand, the sensitivity enhancement upon exposure to femtosecond-pulsed EUV is similar to the result obtained using laser-induced-plasma based SXRL. Surprisingly, the sensitivity enhancement is common to result obtained using picosecond-pulsed SXRL. It has been already reported that SXRL irradiation induced the decomposition of both the main and side chains in PMMA.\textsuperscript{20} In femtosecond-pulsed SXFEL, the same reaction in PMMA as SXRL might be induced, so that the sensitivity of PMMA for SXFEL irradiation was enhanced compared with using typical EUV sources. Further investigation of these detailed mechanisms are in progress.
4. CONCLUSION

In order to investigate the physical and chemical reactions in resists for next generation lithography using short-pulsed EUV-FEL, irradiation effects by femtosecond-pulsed SXFEL in PMMA were performed. When using SXFEL with a pulse width of femtoseconds, PMMA film was removed by development after exposure of only 6–8 mJ/cm². Sensitivity of PMMA for SXFEL was much higher than the value that measured for conventional EUV. The sensitivity enhancement is common to result obtained using picosecond-pulsed SXRL. These results suggest the importance of a specific resist design for next-generation EUV-FEL lithography, which is short-pulsed EUV.

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