Ion Beam Irradiation Effects on Resist Materials

Tomoko Gowa¹, Tomohiro Takahashi¹, Toshitaka Oka²,
Takeshi Murakami³, Akihiro Oshima⁴, Seiichi Tagawa¹,⁴, Masakazu Washio¹

¹: Research Institute for Science and Engineering, Waseda University,
3-4-1 Okubo, Shinjuku-ku, Tokyo 169-8555, Japan
²: Advanced Science Research Center, Japan Atomic Energy Agency (JAEA),
2-4 Shirakata-Shirane, Tokai-mura, Naka-gun, Ibaraki 319-1195, Japan
³: National Institute of Radiological Sciences (NIRS), 4-9-1 Anagawa, Inage, Chiba 263-8555, Japan
⁴: The Institute of Scientific and Industrial Research, Osaka University,
8-1 Mihogaoka, Ibaraki-shi, Osaka 567-0047, Japan

6 MeV/u ion beams such as Si¹⁴⁺, Ar¹⁸⁺, Kr³⁶⁺ and Xe⁵⁴⁺ and 30 kV Ga¹ focused ion beam (FIB) were irradiated to a chemically amplified deep-UV resist TDUR-P722 (Tokyo Ohka Kogyo) and electron beam (EB) resists ZEP520A and ZEP7000 (ZEON). Clear patterns were obtained on all resists for high energy ion beams, and it was confirmed that resist sensitivities were correlated with the energy deposition. In contrast, high flux FIB irradiation induced crosslinking reactions of resist polymers, and positive-negative inversion took place.

Keyword: resist, heavy ion beam, focused ion beam (FIB), positive-negative inversion, linear energy transfer (LET)

1. Introduction

Recently, there have been increasing interests in micro- and nano-scale fabrication techniques, in response to expanding demands for electronic devices, bio and medical components, optical devices, and so on. In addition to the fabrication size and accuracy, which determine the performances of these devices, high throughput is required for the mass-production. The fabrication capabilities and production speed are limited by the resolution and sensitivity of resist materials.

The reaction mechanisms of resist materials have been studied [1-3] and many improvements in resist resolution and sensitivity have been accomplished [4]. Besides the resist itself, irradiation source and its conditions should be also important.

In this study, fabrication of deep-UV and EB resist materials using 6 MeV/u ion beams and 30 kV focused ion beam (FIB) was demonstrated. The ion beam irradiation effects on resists were investigated, and compared with deep-UV and EB lithography.

It is expected that ion beam could achieve high spatial resolution because its reaction area along the beam axis in resist films is much less than those of electron beam (EB) and X-rays which are widely used in micro- and nano-scale fabrication industries. Also, high resist sensitivity can be expected for ion beams, since the high linear energy transfer (LET) may induce chemical reactions with higher efficiency [5].

2. Experimental

2.1. Resist Materials

A deep-UV photo resist TDUR-P722 (Tokyo Ohka Kogyo), and two types of electron beam (EB) resists, ZEP520A and ZEP7000 (ZEON), were selected in the experiments. All the resists are positive-type, i.e., irradiated areas will be chemically dissolved in suitable developers.
TDUR-P722 is a chemically amplified resist (CAR) which is composed of polyhydroxystyrene (PHS) based polymer resin and photo-acid generator (PAG) molecules. The deep-UV irradiation produces the excited states of PAG and they start the chemical reactions and generate acids in the resist. After the acid generation, during the post exposure bake (PEB), the generated acids diffuse and induce the deprotection reaction of the resist polymer, which makes the polymer soluble in the developer. Because a single generated acid has the capacity to catalyze hundreds of deprotection events, the CARs are known for high sensitivity.

On the other hand, selected EB resists ZEP520A and ZEP7000 are non-chemically amplified resists. They consist of copolymers of α-chloromethacrylate and α-methylstyrene with different molecular weights [6, 7]. They undergo main chain-scission upon irradiation, and the irradiated areas dissolve in the developers. It has been reported that ZEP resists have excellent spatial resolution as high as 10 nm [8].

TDUR-P722 was spin-coated on the silicon wafers (525 μm thick, Shin-Etsu Chemical) under ambient conditions at 25 °C, and pre-baked at 140 °C for 90 s on a hot plate. The spin-coating speed and its duration time were 2000 rpm and 60 s, respectively. After the exposure, the PEB was performed at 140 °C for 90 s, and the samples were developed by alkaline aqueous solution based developer, NMD-3 2.38 % (tetrethyl ammonium hydroxide 2.38 %) (Tokyo Ohka Kogyo), for 65 s. Then, they were rinsed by the de-ionized water for 30 s and post-development baked at 100 °C for 60 s. The development and rinse were performed under ambient conditions at 25 °C.

ZEP520A and ZEP7000 were spin-coated on the wafers with 4000 rpm for 60 sec, and pre-baked at 180 °C for 180 s. After the irradiation, they were developed with ZED-N50 (n-Amyl acetate 100 %) and ZED-500 (3-pentanone 50%, diethyl malonate 50 %) (ZEON) for 60 s, and rinsed with ZMD-B and ZMD-D for 10 s, respectively. The spin-coating, development and rinse were performed under ambient conditions at 25 °C. The thicknesses of the spin-coated resists were measured by an atomic force microscope (AFM, SPI3800: SII NT). TDUR-P722 was about 600 nm thick, and ZEP520A and ZEP7000 were approximately 350 nm and 150 nm thick, respectively.

2.2. Heavy Ion Beams at HIMAC

6 MeV/u accelerated high energy ion beams, such as Si^{14+} (168 MeV), Ar^{18+} (240 MeV), Kr^{36+} (504 MeV) and Xe^{54+} (792 MeV), from Medium Energy Experimental Port (MEXP) at Heavy Ion Medical Accelerator in Chiba (HIMAC) in NIRS were used in the experiment.

The irradiation was performed at room temperature and the base pressure of the irradiation chamber was below 2E-4 Pa. The ion fluence on a sample was estimated by the ion flux, which was detected by a Faraday cup set in the beam line. The period of the beam pulse was 1.65 s and the fluence was controlled by irradiation time and pulse duration. In this study, ion flux was about 1E+9 ions cm^{-2} pulse^{-1}. The beam size at the sample position was about 20 × 25 mm² ellipse, and 70 μm Ni mesh masks were placed on the resist samples to facilitate pattern transfer.

2.3. Focused Ion Beam (FIB)

The 30 kV focused Ga⁺ ion irradiation was carried out with a focused ion beam (FIB) equipment (SMI2050: SII NT, installed at ISIR, Osaka Univ.).

The Ga⁺ ions irradiate the desired patterns by a computer controlled scanning system which enables maskless direct etching. The selected beam currents and their beam spot sizes in FWHM were 9 pA (ϕ13 nm) and 47 pA (ϕ 23 nm). FIB provides continual beam, and the flux was estimated to be about 1E+13 ions cm^{-2} s^{-1}. The base pressure of the irradiation chamber was under 1E-4 Pa, and the irradiation was carried out at 25 °C. In the experiments, 70 μm patterns were directly irradiated in order to evaluate the resist sensitivities with the same fabrication size as ion irradiation at HIMAC.

2.4. Measurements

After the ion beam irradiation, the fabrication performances of each resist material were evaluated by the irradiated surfaces observed using the AFM. The resist sensitivity was evaluated from the measured resist depth. The sensitivity is defined by the fluence required for the remaining resist thickness of 0.
3. Results and Discussion

3.1. High Energy Ion Beam Irradiation

After each ion beam irradiation and the development processes, clear mesh patterns were obtained on all resist materials. Figure 1 shows the sensitivity curves, which plot the normalized thickness versus fluence, obtained for 168 MeV Si$^{14+}$ beam. It was found that ZEP7000 had the highest sensitivity, and TDUR-P722 and ZEP520A were in that order. Similar results were obtained for all ion beams used in the experiments.

Furthermore, it was found that the obtained sensitivities of resists varied depending on the irradiated ions, as summarized in Table 1. The heavy ion beams lose their energy depth-dependently from the sample surface (Bragg curve). Figure 2 shows the stopping powers of irradiated ion beams in PHS (the base polymer resin of TDUR-P722), which were simulated by SRIM-2008 [9]. Stopping power is defined as an energy deposition by an ion per unit weight and unit volume of the irradiated material. In Fig. 2, (e) means electronic and (n) means nuclear stopping power, respectively. The density of PHS was assumed to be 1.2 g/cm$^3$. Since the thicknesses of resist films are very thin as up to 600 nm, the average energy deposition in resists could be assumed to be equal to that at sample surface. The stopping powers at the resist surfaces, which were simulated by SRIM-2008, are summarized in Table 2. Although the detailed chemical structures have not been disclosed, in this study, ZEP520A and ZEP7000 were assumed to be 1:1 copolymer of α-chloromethacrylate and α-methylstyrene, and their densities were assumed to be 1.6 g/cm$^3$.

Figure 3 shows obtained resist sensitivities (i.e. fluence for remaining resist thickness of 0) versus stopping powers of each ion beam. Clear correlation between stopping power and resist sensitivity were demonstrated. Higher sensitivities were obtained with the higher energy deposition.

Figure 1. Sensitivity curves (normalized thickness versus fluence) of TDUR-P722, ZEP520A and ZEP7000 for 168 MeV Si$^{14+}$ beam.

Figure 2. Electronic and nuclear stopping powers of irradiated ions in PHS (base polymer of TDUR-P722).

| Table 1. Obtained resist sensitivities [ions/cm$^2$] for each ion beam. |
|-----------------|---------|--------|--------|---------|
|                 | Si$^{14+}$ | Ar$^{18+}$ | Kr$^{36+}$ | Xe$^{54+}$ |
| TDUR-P722       | 1.0E+11   | 8.3E+10   | 3.3E+10   | 2.0E+10   |
| ZEP520A         | 1.2E+11   | 1.0E+11   | 5.8E+10   | 4.2E+10   |
| ZEP7000         | 8.3E+10   | 6.6E+10   | 2.0E+10   | 1.1E+10   |

| Table 2. Ion beam energies and their stopping powers at resist surfaces. |
|-----------------|---------|--------|--------|---------|
|                 | Si$^{14+}$ | Ar$^{18+}$ | Kr$^{50+}$ | Xe$^{54+}$ |
| Ion beam energy [MeV] | 168     | 240    | 504    | 792     |
| Stopping power   | TDUR-P722 | 10.8   | 16.5   | 48.1    | 86.5    |
| [MeV/(mg/cm$^2$)] | ZEP resists | 10.4   | 15.9   | 46.3    | 83.4    |
As shown in Fig. 2, high energy ion beams mainly induce electronic effects. Therefore, it is considered that chemical reactions caused by high energy ion beams would be identical to EB and X-ray irradiation. In the case of CAR, TDUR-P722, the high energy ion beam irradiation would mainly cause the ionization of resists and acids are generated through dissociative electron attachment and geminate recombination [1, 3]. And the reactions in ZEP520A and ZEP7000 would be a main chain scission, which is identical to EB and X-ray irradiation.

3.2. FIB Irradiation

After the FIB irradiation, the resist thicknesses of the irradiated areas were decreased even without the development processes. It was indicated that resists were etched by ions. Figure 4 shows the etching depth of resists for irradiated fluence.

With the development processes, different surface patterns were observed depending on both ion fluence and beam current for all resists. Figure 5 shows FIB irradiated surfaces of ZEP520A which were observed using the AFM. For lower fluences (1E+12 and 1E+13 ions/cm²) with the beam current of 9 pA, the thickness of irradiated areas were decreased after the development, as normal reaction of positive type resists. The depths after the development were about 35 nm and 50 nm, respectively. Since the etching depth for 1E+12 ions/cm² was less than 1 nm, it can be considered that the chain scission took place through a depth of about 35 nm, and ZEP520A dissolved in the developer. Similar results were also obtained for TDUR-P722 and ZEP7000. These results agree with the simulated penetration ranges. Ga⁺ ions could penetrate a depth of 40 nm for TDUR-P722 and 31 nm for ZEP resists, as shown in Fig. 6. In the case of 1E+13 ions/cm² irradiation, the fabricated depth (~50 nm) should contain the effects of both etching and chemical reaction, which would be caused through to the penetration depths.

<table>
<thead>
<tr>
<th>Beam Current</th>
<th>Ion Fluence</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 pA</td>
<td>1E+12 ions/cm²</td>
</tr>
<tr>
<td>47 pA</td>
<td>49 nm</td>
</tr>
</tbody>
</table>

Figure 5. AFM images of ZEP520A surfaces after irradiation of 1E+12 to 1E+15 ions/cm² with the beam currents of 10 pA and 47 pA. (after development)
The irradiated area of the wide line (1) remained and only the surrounding sides were dissolved. In contrast, narrow lines (2), (3) and (4) were apparently fabricated. This is because the crosslinked irradiated areas were peeled off since the surrounding four sides were dissolved. The peeled fragments were found on the sample surface as marked in Fig. 7.

Figure 7. ZEP7000 surface after FIB irradiation and development (5E+14 ions/cm², 9 pA). Lines (2) (3) and (4) were peeled off as marked in the picture.

4. Conclusion
Several high energy ion beams with 6 MeV/u and 30 kV FIB were irradiated to photo and EB resist materials. In the case of high energy ion beams obtained at HIMAC, clear patterns were obtained on all resist materials, and it was confirmed that resist sensitivities were correlated with LET. In contrast, high flux FIB irradiation induced crosslinking reactions in resist polymers, and positive-negative inversion took place. It was suggested that the distance of spurs would determine whether resists react as positive type or negative-type. The detailed chemical reaction of resist materials will be studied in the near future.
Acknowledgments

This study was supported by research project with heavy ions at NIRS-HIMAC (19P186). The authors acknowledge staff members of HIMAC operation division and accelerator engineering company for the experiments using high-energy ion beam irradiation. A part of this work was conducted at Handai Multi-Functional Nanofoundry supported by “Nanotechnology Network Project” of MEXT. This work was supported by Grant-in-Aid for JSPS Fellows (21-04550) (T. Gowa) and JSPS Grant-in-Aid for Scientific Research (B)(2) 19340064.

References