Development of a Compact X-ray Source and Super-sensitization of Photo Resists for Soft X-ray Imaging

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A compact soft X-ray source via inverse Compton scattering has been developed at Waseda University. The energies of the generated X-rays are within “water window” region (250 - 500 eV) and development of a soft X-ray microscope is expected which can get the elemental mapping of carbon and/or nitrogen without dehydration. We have studied to develop a high resolution soft X-ray imaging system with photo resists for nanoscale observation. However, the yield of generated X-rays had been too small for the practical use of the soft X-ray microscopy. To enhance the X-ray yield, we have upgraded the generation system and succeeded in increasing the detected photons 10-fold. Total generated photons were estimated to be over 1.5×10^5 photons/s. Also, super-sensitization of photo resists has been attempted to reduce the required X-ray amount. By irradiating quasi-monochromatic X-rays in the water window region from synchrotron radiation at BL12 of the SAGA-LS, the sensitivity of a deep-UV photo resist, TDUR-P722 (Tokyo Ohka Kogyo Co., Ltd) was evaluated. After UV light (including 254 nm) exposure up to the sensitivity threshold and baking as PEB process, it was found that the resist becomes more sensitive. This UV “pre-exposure” method reduced the required 400 eV X-ray amount by over 65 %.

Keyword: photo resist, inverse Compton scattering, soft X-ray microscope

1. Introduction

Short-pulse soft X-ray sources are now widely required in various fields, such as medical, biological, chemical and material science. A compact soft X-ray source via inverse Compton scattering using a photo-cathode RF-gun and a picosecond laser system has been developed at Waseda University [1, 2]. Inverse Compton scattering is the inverse energy transfer process of general Compton scattering between

Figure 1. Inverse Compton scattering in the laboratory and electron rest frames

relativistic electrons and low energy photons such as a laser light. The laser light, which collides with high energy electrons, is scattered as X-rays by gaining its energy [3].

Figure 1 shows the coordinates of the inverse Compton scattering in the laboratory and electron rest frames. When the electron rest mass (m_e), the electron energy (E_b), Lorentz factor γ ($E_b = \gamma m_e c^2$), and the incident laser photon energy (E_p) are defined in the laboratory frame, the energy of scattered photons (E_s) is given as

$$E_s = \frac{m_e c^2 \gamma^2 (1 + \beta \cos \phi)(1 + \beta \cos \theta) E_p}{m_e c^2 + \gamma(1 + \cos \theta)(1 + \beta \cos \phi) E_p} \quad (1)$$

where θ is the scattered angle in the electron rest frame and ϕ is the crossing angle in the laboratory frame.

Using a Nd:YLF (1047 nm) laser beam and a 5 MeV class electron beam generated from a photo-cathode RF-gun system, we have already succeeded in generating inverse Compton X-rays [2]. The energies of the generated X-rays are within so-called “water window” region (250 - 500 eV) where the X-ray absorption coefficient of water is much less than those of carbon and nitrogen as shown in Figure 2 [4]. Hence, development of a soft X-ray microscope is expected which can get the elemental mapping of a living cell or hydro-gels without dehydration [5]. As described in Equation (1), the X-ray energy is tunable by changing the electron beam energy and/or the collision angle. In addition, quasi-monochromatic X-ray beam can be

obtained by selecting the scattered angle. Its short pulse length and compactness of the instruments are also important advantages of inverse Compton X-rays [2].

For the soft X-ray microscopy, there're several imaging types: contact, projection, scanning and so on [5]. We have studied to develop a contact microscope with photo resists as the detector, which is the conceptually-simplest and expected to have high resolution [6]. By placing the resist behind the object and irradiating X-rays, the object's profile and X-ray absorption information can be transferred to the resist as the pattern and its depth. The resolution of the resist, which is as high as several nm, is critical for the spacial resolution of the contact microscopy [7]. Therefore, by examining the resist surface with suitable profilometers such as an atomic force microscope (AFM), nanoscale imaging and the elemental mapping will be possible.

For the practical application to the X-ray microscopy, it is estimated that about $1\text{E}+11$ photons/mm² are required to get an absorption contrast image of hydrated specimens with resolution of 100 nm [8, 9]. However, at Waseda University, the yield of generated X-rays had been too small. Therefore, we have tried to solve this problem through two approaches: the enhancement of the generated X-ray yield by upgrading the generation system and the reduction of the required X-rays for the imaging by super-sensitization of the resists.

2. Experimental

2.1. X-ray Generation Setup

Figure 3 shows a schematic diagram of the experimental setup of inverse Compton X-ray generation in the present study [10, 11]. The system is constructed on a $2.5 \times 2 \text{ m}^2$ optical table, including all the beam lines and a picosecond Nd:YLF laser system (Pulrise-V: Sumitomo Heavy Industry Co.). The RF-gun is composed of BNL-type 1.6 cells S-band RF cavities and copper cathode. The Nd:YLF fundamental IR laser (1047 nm) is used as the incident laser for the scattering, and its 4th harmonic UV laser (262 nm) is for generating electrons by irradiating the photo-cathode. The IR laser passes through a flash lamp pumped Nd:YLF amplifier system and an

Figure 2. The water window region [4] and calculated energy distribution of generated X-rays with 5 MeV electron beam and 1047nm laser collision ($\phi=20$ deg).

Figure 3. Schematic diagram of the experimental setup for the X-ray generation at Waseda University

optical delay stage which controls the timing of the electron-laser interaction. Since both IR and UV lasers are generated from the same laser system, the interaction timing is able to synchronize easily. We can choose the collision angle, *i.e.* X-ray energy, by tuning an IR mirror located before the collision point. For the X-ray detection, a micro channel plate, MCP (F4655-10: Hamamatsu Photonics K.K.), is installed after the electron beam is separated from the generated X-rays.

2.2. Resist Sample Preparation

For the soft X-ray imaging, both high sensitivity and high resolution are required for the photo resists. As one of the potential candidates, a positive deep-UV photo resist, TDUR-P722 (Tokyo Ohka Kogyo Co., Ltd) was selected. TDUR-P722 is a chemically amplified photo resist which is composed of a basic polymer resin and a photo-acid generator. In this study, the resist was spin-coated on the silicon wafers and pre-baked at 140 °C for 90 s on a hot plate. The thickness of the resist was approximately 600 nm when the spin-coating speed and duration time were 2000 rpm and 60 s, respectively. After the exposure, the post exposure bake (PEB) was performed at 140 °C for 90 s, and the samples were developed by alkaline aqueous based developer, NMD-3 (Tokyo Ohka Kogyo Co., Ltd), at 23 °C for 65 s. After that, they were rinsed by the de-ionized water for 30 s and post-baked at 100 °C for 60 s.

2.3. Exposure Condition

The photo sensitivity was obtained by the resist pattern depth dissolved in the developer measured with an AFM (SPI3000: SII). First, the sensitivity to the deep-UV light was measured, because the resist is originally made for the deep-UV lithography. As a light source, a low-pressure mercury vapor lamp (including 254 nm) was used, and all the processes from the spin-coating to the development were performed under ambient conditions. A 40 μm square pattern Cu mesh mask was set on the resist samples to transfer the pattern. The exposure amount was measured with an UV power meter (C9536, H9535-254: Hamamatsu Photonics K.K.).

Secondly, to evaluate the sensitivity to the water window region, the irradiation experiment was carried out at BL12 of the SAGA Light Source (SAGA-LS). The SAGA-LS is a 1.4 GeV storage ring which average stored current is 200 mA [12]. At BL12, quasi-monochromatic X-rays from 40 eV to 1500 eV are obtained through a varied line spacing plane grating monochromator. The flux at the sample position is over $1\text{E}+9$ photons/s in the water window region. In this experiment, the total fluence was obtained by integrating the flux which is estimated by the photocurrent from Au mesh. Then, the actual fluence on the samples was recalculated considering the spacial distribution of the X-ray beam. In the irradiation process, a 70 μm square pattern Ni mesh was set as a mask. The base pressure in the irradiation chamber

was below $10\text{E-}6$ Pa, and the sample preparation and the development were performed under ambient conditions.

3. Results and Discussion

3.1. Soft X-ray Generation

At Waseda University, we achieved a first observation of the inverse Compton X-rays in 2004 [2]. Since that time, we have been upgrading our system to improve the X-ray quality with an incident laser amplification system, background reduction, an electron beam optimization and so on [10, 11]. The recent parameters of both electron and laser beams at the collision point are summarized in Table 1. With these modifications, the X-ray photons detected by the MCP have increased 10-fold to reach $1.6\text{E}+3$ photons/s. The maximum energy of generated X-rays was calculated to be about 370 eV. Good signal to noise ratio 6.2 ps (RMS) short pulse X-rays was obtained, and the number of total generated X-rays was estimated to be over $1.5\text{E}+5$ photons/s. Moreover, we succeeded in generating soft X-rays stably over 12 hours [11].

Table 1. Recent experimental parameters of the electron beam and the laser beam at the collision point

Electron beam		Laser beam	
Energy	4.6 MeV	Wavelength	1047 nm
Bunch Charge	350 pC	Pulse energy	36 mJ
Size (horizontal)	251 μm	Size (horizontal)	42 μm
Size (vertical)	56 μm	Size (vertical)	42 μm
Bunch length	10 ps (FWHM)	Pulse duration	10 ps (FWHM)

Still, the generated X-rays are not enough for the soft X-ray microscopy. Therefore, we are planning to develop a multi-pulse inverse Compton scattering system [13]. With multi-pulsed electron and laser beams, the generated X-rays would increase about 7000-fold in simulations. For the multi-bunch electron beam generation, we have already installed a new RF-gun with Cs_2Te cathode which has 100-fold higher quantum efficiency than the copper cathode.

3.2. Sensitivity Measurement

Figure 4 shows a sensitivity curve of the resist indicating the normalized depth of the pattern formed on the resist in relation to the deep-UV light exposure. The error bars indicate the standard deviation of the

measured value for five samples.

The resist has the threshold of exposure for dissolving in the developer, *i.e.*, obtaining the image. As shown in Figure 4, the sensitivity threshold to deep-UV light was approximately 2.6 mJ/cm^2 . This result shows relatively high sensitivity because the mask pattern is as large as $40 \mu\text{m}$ square and it can be considered as a flat-exposure. The oxidation would also be a factor since the experiment was carried out under ambient conditions.

Figure 4. Sensitivity curve of TDUR-P722 to 254 nm deep-UV light exposure

In the same way, the sensitivity to the water window region was evaluated. Figure 5 shows the transferred mask pattern on the resist after irradiating 250 eV and 400 eV X-rays. Also, similar result was obtained for 500 eV X-ray irradiation, which means the resist is sensitive to throughout the water window region. In this study, the sensitivity at 400 eV was especially measured because the X-rays which can be stably generated with our present system are around 400 eV.

Figure 5. The resist surface observed with AFM after irradiating 250 eV (left) and 400 eV X-rays (right)

At 400 eV (3.1 nm in wavelength), the sensitivity threshold was approximately

$3.3\text{E}+11$ photons/ mm^2 , *i.e.* $2.1\text{ mJ}/\text{cm}^2$. On the other hand, to 250 eV (4.96 nm), the threshold was over $3.0\text{E}+12$ photons/ mm^2 , *i.e.* $13\text{ mJ}/\text{cm}^2$. The sensitivity to the 400 eV X-rays is about 10-fold higher than to the 250 eV. This can be explained by the X-ray absorption coefficient of carbon which is the main constituent element of the resist. This result indicates that the required irradiation amount varies widely in the water window region which contains the K-shell absorption edge of carbon. The detail of this difference in sensitivity and its reaction mechanisms will be reported in the near future.

3.3 UV Pre-Exposure Method

Higher sensitivity is necessary for the resist materials to reduce the required X-rays because the yield of generated X-rays is still inadequate. Even if the generated X-rays will be enough for the imaging, higher sensitivity is important because short exposure time will avoid image blurring. Also, considering the radiation damage to the objects, the required fluence should be reduced. Therefore, we attempted the super-sensitization of the TDUR-P722.

After the UV light exposure up to the threshold and baking as PEB process, we found that the resist becomes more sensitive to the deep-UV light. The exposure up to the threshold, “pre-exposure”, generates certain amount of acid. During the baking process which is performed just like PEB, the generated acid would cause chemical reaction although it wouldn’t be enough for the resist to dissolve in the developer. This chemical reaction caused by the pre-exposure would raise the sensitivity of the resist.

Figure 6 shows the sensitivity curve of the $2.0\text{ mJ}/\text{cm}^2$ UV pre-exposed resist samples, in comparison with that of without pre-exposure (blank). The photo sensitivity to the deep-UV light was successfully improved. The threshold became approximately $0.4\text{ mJ}/\text{cm}^2$, which means the required exposure reduced by over 80%.

Figure 6. Sensitivity curve of $2.0\text{ mJ}/\text{cm}^2$ UV pre-exposed TDUR-P722 samples to deep-UV light

Figure 7. Sensitivity curve of $2.0\text{ mJ}/\text{cm}^2$ UV pre-exposed TDUR-P722 to 400eV soft X-ray exposure

This UV pre-exposure method was also confirmed very effective to the soft X-ray irradiation. After $2.0\text{ mJ}/\text{cm}^2$ pre-exposure of the deep-UV light, the required irradiation amount of 400 eV and 250 eV X-rays reduced to about $1.0\text{E}+11$ photons/ mm^2 ($0.7\text{ mJ}/\text{cm}^2$) and $1.4\text{E}+12$ photons/ mm^2 ($5.6\text{ mJ}/\text{cm}^2$), respectively. The required 400 eV X-ray amount successfully reduced by over 65 %. These results are adequate for contact microscopy with 100 nm resolution which is aimed at present, although the X-ray yield must be enhanced more for the practical use.

4. Conclusion

At Waseda University, we have been developing a short-pulse inverse Compton soft X-ray source in the water window region. For the application to the soft X-ray microscopy, we are developing high resolution imaging system with photo resists. Because the generated X-ray yield had been too small for the practical use of the soft X-ray microscopy, we have upgraded the generation system. The generated X-rays have successfully increased and the total generated X-rays were estimated to be over 1.5×10^5 photon/s. Also, to reduce the required amount of X-rays, the super-sensitization of photo resists has been attempted. The photo sensitivity of a chemically amplified deep-UV photo resist, TDUR-P722, was evaluated in this study. We found that the UV pre-exposure method is one of the powerful tools for the super-sensitization, and it reduced the required 400 eV X-ray amount by over 65 %.

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