Wavelength Dependence of Poly(p-hydroxystyrene) Ablation by Mid-Infrared Free-Electron Laser

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Ablation of polymer thin films for resists was studied using a mid-Infrared (IR) Free-Electron Laser (FEL). Irradiation fluence of the IR light in the mid-IR region (5.6 to 8.0 μm) to a thin film of poly(p-hydroxystyrene) (PHOST) on a silicon wafer increased to cause PHOST ablation. The ablated spot size was smaller than the irradiated area calculated by wave optics, because the ablation is a multiphoton absorption process. The ablation threshold energy was determined using the irradiation area calculated by the wave optics. The threshold energy depended upon the film thickness of PHOST and irradiation wavelength of FEL. The threshold energy of thin PHOST film with 61 nm increased at the wavelength of vibrational modes of phenyl ring. It associates the durability of phenyl ring to photon decomposition.

Keywords: Mid-infrared free-electron laser, Photoresist, Multiphoton absorption, Poly(p-hydroxystyrene), Vibrational mode

1. Introduction

Polymer thin films have been used as base materials in semiconductor resist materials. With continued decrease of resist feature size, the thickness of a resist film has been decreased in order to mitigate the pattern collapse and increase the resist resolution. One of the important factors to achieve the high resolution is the homogeneity of the structure and composition of a thin polymer film, because the inhomogeneity may deteriorate the resist resolution and line edge roughness of resist patterns. In fact, the correlation between the inhomogeneous distribution of the composition and reactivity in the polymer film have been confirmed by the time-resolved total-internal-reflection experiment [1], X-ray reflectivity [2] and gas-cluster ion-beam Time-of-flight secondary ion mass spectrometry [3]. It has been also measured that the glass transition of the thin film is different from the thick film by the local thermal analysis [4]. Instead of polymer matrix, molecular resists were intensively investigated to improve the resist resolution because smaller molecules are expected to form the smaller pixels. However, the inhomogeneity of components was indicated by mesoscale simulation [5] and molecular simulations [6,7] and scanning transmission electron microscopy and electron-energy loss spectroscopy [8,9]. Studies on the structure and inhomogeneity of resist films are now essential to realize the advanced lithography such as single-nanometer lithography.

The mid-Infrared (IR) Free-Electron Laser at Tokyo University of Science (FEL-TUS) [10] is a high-power pulsed laser with an oscillation wavelength in the mid-IR region (5 to 14 μm), which enables us to excite specific vibrational modes of resist materials. FEL-TUS has a ca. 2 ps pulse width and produce non-linear effects more efficiently than continuous or ns pulsed IR lasers. FEL-TUS has been so far widely used for basic as well as applied research in universities, government institutes and industries [11-13].

In the current experiment, the light from FEL-TUS was focused on thin films of polymer samples to induce an ablation phenomenon at the
The threshold energy for ablation was calculated using the irradiation area derived from geometrical optics. On the other hand, the estimation of an irradiation area by geometrical optics may not be suitable in the vicinity of the focal point due to a large diffraction effect. In this paper the irradiated area was evaluated by wave optics and the more accurate ablation threshold was calculated. The effect of the irradiation wavelength and film thickness dependences on the ablation threshold energy of poly(p-hydroxystyrene) thin films will be also discussed.

2. Experimental

2.1. Materials, preparation and characterization

Poly(p-hydroxystyrene) (PHOST, $M_w = 20,666$) was purchased from Sigma-Aldrich and diethylene-glycol diethyl ether (diglyme) was purchased from Tokyo Chemical Industry Co., Ltd.

PHOST was dissolved in diglyme to yield polymer solutions. Film samples were fabricated by spin-coating the polymer solution on a silicon substrate. The thin films were baked for 10 min at 120°C on an oven to remove residual solvents. The film thickness was measured by Ellipsometer M-2000 (J. A. Woollam, Co.).

The ablated spots of the polymer film on the substrate were observed by the microscopy IRT-7000 (Jasco, Co.).

2.2. Mid-IR FEL ablation apparatus

The mid-IR FEL experiments were carried out by using the facilities at the FEL Research Center, Research Institute for Science and Technology, Tokyo University of Science. Details of the FEL-TUS are described elsewhere [14,15]. The FEL-TUS delivers macro-pulses at 5 Hz. Each macro-pulse is ca. 2 μs long and consists of ca. 6,000 micro-pulses of ca. 2 ps duration, where the interval of adjacent micro-pulses is 350 ps, which corresponds to the RF frequency (2,856 MHz) employed for the linear accelerator. In this experiment, the laser wavelength of FEL-TUS system was tuned over the range of 5.6 - 8.0 μm with the energies of 5 - 10 mJ/macro-pulse.

The FEL-TUS system was coupled to the home-made ablation system as shown in Fig. 1. The output beam of FEL-TUS was focused by a barium-fluoride lens (Pier Optics, Co., Ltd.) to the sample film. The sample was held on the XY-axis stepping-motor stage. FEL light propagated parallel to the X axis of the stage to irradiate the sample through a pinhole and the focusing convex lens along the X axis. The FEL fluence or intensity per area irradiating the sample was varied with moving the sample along X stage. Simultaneously the wafer sample was translated along the Y axis which produced a row of irradiated spots with fluence variation. Intensity of FEL light was detected by Joulemeter ED-500 (Gentec Electro-Optics, Co.) and measured by Digital oscilloscope TDS3052 (Tektronix, Inc.). All equipments were controlled and recorded by a computer with a software LabVIEW (National Instruments, Co.).

2.3. Calculation of the irradiation area by wave optics

Wave optics was used to calculate the irradiated area of a focusing FEL light. All traveling light produced in phase by a unit-amplitude point source on focusing lens was propagating at the plate of a defocus plain where the irradiated area should be calculated. The light amplitude at the defocus plain is given by the summation of amplitudes of spherical light waves originating from the lens, of which curvature is the focal length, as follows;

$$\sum \frac{E_0 e^{-i(k \cdot \vec{r})}}{r}$$  \hspace{1cm} (1)

where $E_0$ is the electrical field vector, $k$ is the wavevector, $\vec{r}$ is the distance vector from the lens and $i$ is the imaginary unit. The light intensity across the defocus plain is defined as the absolute square of its complex amplitude.

2.4. Vibration analysis by quantum chemical calculations

Quantum chemical calculations were used to investigate the vibrational modes of PHOST. 4-sec-Butylphenol was used as a model molecule of
PHOST. The molecular structure and vibrational frequencies were obtained by B3LYP/cc-pVTZ using Gaussian 09W (Gaussian, Inc.) [16]. The calculated vibrational frequencies were corrected by using the scaling factor of 0.965 [17]. The vibrational mode of the PHOST model molecule was displayed by GaussView5.0 (Gaussian, Inc.).

3. Results and discussion

3.1. Irradiation area calculated by wave optics

In order to confirm the accuracy of the numerical calculation by wave-optics, the calculated absolute amplitude of light across the focal plane was compared with the Fraunhofer diffraction pattern as shown in Fig. 2. The cross sectional plots by wave-optics calculation are well consistent with that by Fraunhofer diffraction as shown in Fig. 2(b).

The irradiation area is defined as the area of a circle of which diameter is the full width at half maximum (FWHM) of the light intensity calculated by wave optics. The ablation threshold energy calculated by the wave optics was 47% on average from that by geometrical optics reported previously [13].

Figure 3 shows the micrograph of ablated spots by irradiating a 203-nm thick PHOST film with 6.6-μm FEL light. The first spot where ablation started was observed by the microscope and its diameter was measured as 112 μm. The diameter of the circle at FWHM obtained from the light profile calculated by the wave optics under the same conditions was 204 μm as indicated by the dashed circle. The spot size of the mid-IR FEL ablation was smaller than the irradiation diameter calculated by wave optics. It indicates that the mid-IR FEL ablation is a multiphoton absorption process [13].

3.2. Wavelength dependence of ablation threshold energy

The irradiation area determined as described above was used to recalculate the ablation threshold energy of PHOST by FEL-TUS reported previously [13]. Figure 4 shows the wavelength dependence of ablation threshold energy. When the film thickness of PHOST is greater than 106 nm, the ablation threshold energy is not dependent much upon the FEL irradiation wavelength. No clear dependence of vibrational modes of PHOST in Table 1 is seen. It is interesting to note that the threshold energy of a thin 61-nm-thick PHOST film increases as the wavelength decreases. As shown in Table 1, these shorter wavelengths involve the vibrational modes of the aromatic ring which has the stable structure to photodecomposition and radiation decomposition. The characteristic may be effective in ablation of the thin film. In addition to structural effect, thermal effects from the substrate also increase as the film becomes thinner. Thermal effects should be also considered. Further study is necessary to understand the ablation phenomena of polymer thin films.
4. Conclusion

Laser ablation of poly(p-hydroxy styrene) (PHOST) film was studied using mid-Infrared (IR) free-electron-laser (FEL). The accurate irradiation area was estimated by wave-optics calculations. The ablation threshold energies of thick PHOST films did not depend on the irradiation wavenumber of mid-IR FEL. Thin PHOST films with 61 nm thicknesses have higher threshold energy with decreasing wavelength of mid-IR FEL.

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Table 1. Vibrational modes of PHOST model, 4-sec-butylphenol.

| Wavelength [μm] | 5.6 | 6.2 | 6.6 | 7.3 | 8.0 |
|-----------------|-----|-----|-----|-----|-----|
| Assigned vibration mode | C=C stretch | C=O-H bend | C=C stretch | C-O stretch | C-O-H bend |
|                  | C-O stretch | C=C stretch | C-O-H bend | C-O stretch | C=C stretch |

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