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Study on resist sensitivities for nano-scale imaging using water window X-ray microscopy

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ABSTRACT

The sensitivities of deep-UV resist TDUR-P722 (Tokyo Ohka Kogyo Co., Ltd.) and two types of electron beam (EB) resists ZEP520A and ZEP7000 (ZEON Co.) to soft X-rays in the water window region (284–532 eV) were investigated for the nano-scale imaging of the contact X-ray microscopy. At the periphery of the water window, there are absorption edges of main constituent elements of the resist materials, namely carbon and oxygen. It was found that the sensitivities varied widely along the range of X-ray energies used, which correlated with the X-ray absorption of the resists. Moreover for the first time, it was confirmed that K- and L-edge absorptions have a strong influence on the resist sensitivity. Among these resists, ZEP7000 had the highest sensitivity. It was suggested that water window X-ray imaging with nano-scale resolution would be possible with about 1/500 of the fluence, which has the same units (mJ/cm^2 or J/cm^2) as that of so-called dose/sensitivity in the field of resist research, compared with the previously reported method of using polymethylmethacrylate (PMMA). The details of the reaction mechanisms of the resists will be published elsewhere.

1. Introduction

Imaging techniques with nano-scale spatial resolution have been an extensive utility in various research fields, such as materials, chemical and biological sciences. X-ray microscopy is a promising analytical tool for this purpose, which has many attractive advantages, such as: higher resolution than the optical microscopy, longer depth of focus than the electron microscopy, ability to observe samples without microtoming or heavy metal staining, and so on. Moreover the distribution of specific elements can be visualized by the X-ray absorption differences when appropriate X-ray wavelengths are used (Kirz et al., 1995).

For the X-ray microscopy, there are several imaging modes, such as contact, projection and scanning. In principal, the contact method enables larger imaging fields with shorter exposure times than the other modes (Kirz et al., 1995). Also, it is better suited for high spatial resolution imaging, because it does not require condensing and objective optical devices, which limit the final resolution. However, the spatial resolution of currently available monitoring devices, such as CCD cameras and imaging plates are not enough for nano-scale imaging.

Therefore, using high resolution resist materials as a detection layer for imaging has been studied to realize nano-scale X-ray imaging (Gowa et al., 2009). By placing a resist behind the object and irradiating with X-rays, the object's profile and X-ray absorption information can be recorded in the resist as the pattern and its depth (Yamamoto and Shinohara, 2002). The spatial resolution of the resist, which can be as high as 10 nm, is critical for achieving high spatial resolution X-ray microscopy (Sayre and Chapman, 1995). Therefore, by choosing appropriate X-ray wavelengths and examining the resist surface with suitable profilometers, such as an atomic force microscope (AFM), nano-scale imaging and elemental mapping would be possible.

Of particular interest for X-ray microscopy is the X-ray region between the K-shell absorption edges of carbon (4.37 nm/284 eV) and oxygen (2.33 nm/532 eV) (Henke et al., 1993), known as the "water window" (Fig. 1). There, the absorption coefficient of water is much less than those of biologically and chemically important elements, such as carbon and nitrogen. Hence, X-ray analysis, using the water window X-rays enables the carbon/nitrogen elemental mapping of wet materials, e.g., cells and bio-polymers, without requiring dehydration of samples (Kirz et al., 1995; Schneider, 1998).

PMMA is typically used as the resist for X-ray lithography, and there have been some previous reports of X-ray imaging with PMMA, using synchrotron radiation (SR) and laser plasma X-ray sources (McGowan et al.,1979; Yamamoto and Shinohara, 2002). However, the sensitivities of all resists (materials/polymer) for soft X-rays in the water window region, especially for monochromatic X-rays, have not been evaluated yet. In light of the radiation

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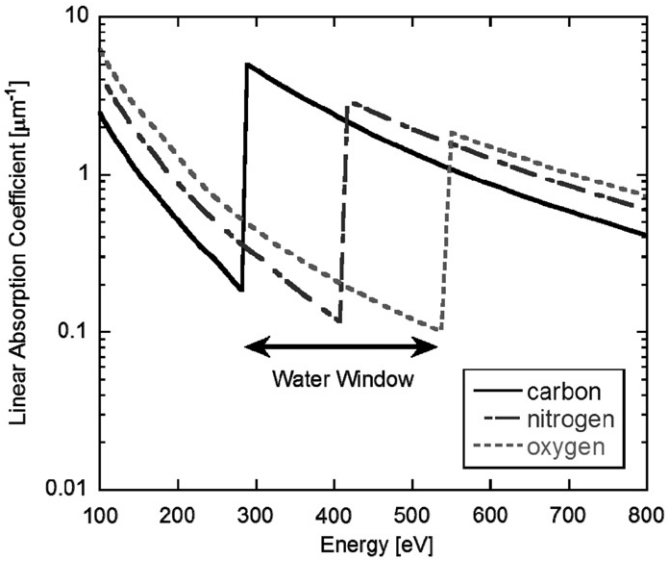

Fig. 1. Plots of linear absorption coefficient versus energy for carbon, nitrogen and water.

damage to objects during X-ray imaging, it is required to choose resists with high sensitivity to minimize the fluence received during imaging. Also, if the required X-ray flux is reduced, it will be possible to take images with laboratory type compact light sources, such as inverse Compton X-rays (Kashiwagi et al., 2005; Gowa et al., 2007; Sakaue et al., 2008).

In this study, to investigate the applicability of commercially available deep-UV and EB resists for X-ray microscopy, the sensitivities of the resists to soft X-rays, in the vicinity of the water window region, were evaluated. For the X-ray source, quasi-monochromated X-rays produced by an SR were used.

2. Experimental procedure

2.1. Resist materials

A positive deep-UV photo resist TDUR-P722 (Tokyo Ohka Kogyo Co., Ltd.), and two types of positive EB resists, ZEP520A and ZEP7000 (ZEON Co.), were selected for use in the experiments.

TDUR-P722 is a chemically amplified resist (CAR), which is comprised of polyhydroxystyrene (PHS) based polymer resin and photo-acid generator (PAG) molecules. The reaction mechanisms of TDUR-P722 that result from an exposure to deep-UV and X-ray irradiation are very different. The excited states of PAG are mainly produced by deep-UV irradiation and they result in decomposition of the PAG to generate acids. On the other hand for X-ray irradiation, ionization of resists mainly occurs and acids are generated through dissociative electron attachment and geminate recombination (Kozawa et al., 1992; Tagawa et al., 2000). Acids are generated in both deep-UV and X-ray irradiated CARs (Tagawa et al., 2000). After acid generation, during the post exposure bake (PEB) step, the generated acids diffuse and induce deprotection reactions of functional groups in the resist polymer, which makes the polymer soluble in 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, ZEP520A and ZEP7000 are non-chemically amplified, chain-scission type resists. They consist of copolymers of α-chloromethacrylate and α-methylstyrene with different molecular weights (Nishida et al., 1992; Yamaguchi et al., 2004). It has been reported that ZEP resists have an excellent resolution, as high as 10 nm (Kurihara et al., 1995), which is almost comparable to PMMA. In the chlorinated resist materials, there are positive-type resists (ZEP and EBR-9 (TORAY)) and negative-type resists (chloromethylated polystyrene (CMS) and chloromethylated poly-α-methylstyrene (αM-CMS)). The detailed reaction mechanisms of CMS and αM-CMS have been reported (Tabata et al., 1985; Tagawa, 1986). In all cases of X-ray irradiated EBR-9, ZEP, CMS and αM-CMS, the initial step is ionization, and then dissociative electron attachment occurs.

2.2. Preparation and development processes

TDUR-P722 was spin-coated onto silicon wafers (525 μm thick, Shin-Etsu Chemical Co., Ltd.) under ambient conditions at 25 °C, and post-apply 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, a PEB step was performed at 140 °C for 90 s, and the samples were developed by an alkaline aqueous solution based developer, NMD-3 2.38% (Tokyo Ohka Kogyo Co., Ltd.), for 65 s. Then, they were rinsed with 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, using a spin speed of 4000 rpm for 60 s, and post-apply baked at 180 °C for 180 s. After irradiation, they were developed at 25 °C for 60 s with ZED-N50 (n-amyl acetate 100%) and ZED-500 (3-pentanone 50%, diethyl malonate 50%) (ZEON Co.), and rinsed with ZMD-B and ZMD-D at 25 °C 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, using atomic force microscopy (AFM, SPI3800: SII NanoTechnology Inc.). TDUR-P722 was about 600 nm thick, and ZEP520A and ZEP7000 were approximately 350 and 150 nm thick, respectively.

2.3. Exposure and measurement conditions

Soft X-ray irradiation was carried out at the soft X-ray beamline, BL12, of the SAGA Light Source (SAGA-LS). The SAGA-LS is a 1.4 GeV storage ring, which has an average stored current of 200 mA. At BL12, quasi-monochromated X-rays from 40 to 1500 eV are obtained through a varied line spacing plane grating monochromator. The energy resolution ($E/\Delta E$) is over 2000 and the flux at the sample position is over 1e+9 photons/s/mm^2 in the water window region (Kyushu Synchrotron Light Research Center, (last accessed 16.07.09). The total fluence was obtained by integrating the flux, which was estimated by measuring photocurrent at an Au mesh. Then, the actual fluence at the samples was recalculated considering the spatial distribution of the X-ray beam. The base pressure in the irradiation chamber was below 1e−6 Pa. The X-rays used in the experiment were 250, 320 and 400 eV (5.0, 3.9 and 3.1 nm). Of about 70 μm square Ni mesh masks were placed on the resist samples to facilitate pattern transfer.

After development, the resist profiles were measured with an AFM. The resist sensitivity and the contrast were evaluated from the obtained sensitivity curve, which indicates the normalized remaining resist thickness for the exposure dose used. The sensitivity is defined by the dose required to clear the resist to the wafer ($E_{70\,\mu m}$), and the resist contrast (γ), the tangent of the sensitivity curve slope, was estimated by a straight-line approximation.

3. Results and discussion

The sensitivity curves are shown in Figs. 2–4. All the resist materials exhibited high sensitivities to soft X-rays, and clear patterns were obtained. It is interesting to observe that the