High sensitivity nanocomposite resist materials for X-ray and EUV Lithography

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ABSTRACT

Novel positive nanocomposite photoresists for X-ray lithography (XRL) and Extreme Ultraviolet lithography (EUVL) have been developed. In this work, resists containing acrylate monomers, organic-inorganic hybrid nanoparticles and a photo acid generator (PAG) were prepared by varying the compositions of the components. It was observed that the nanophotoresists were suitable for XRL and EUVL. The new resists exhibit all characteristics for NGL viz. defect free thin film formation <100 nm and show high sensitivity (1.0 - 1.2 mJ/cm^2) and contrast (γ = 4.9). This significant increase in sensitivity should lead to an enormous cost reduction of the XRL and EUVL processes as well as high-resolution sub-100 nm features.

Key words: Polymers; Photolithography; EUV; XRL; NGL; Nanocomposites photoresist; Photo Acid Generator (PAG).

1. INTRODUCTION

Within the next decade the microelectronic industry requires a lithographic process capable of mass-producing integrated circuits with sub-70 nm critical dimension (CD), even ever-smaller features [1, 2]. This challenge is unlikely to be met by evolutionary steps. A drastic departure from the current optical lithographic technology is mandatory both in the development of desirable resists materials and exposure tools. Extreme ultraviolet (EUV), X-ray, electron beam (EB) and ion beam (IB) lithographies therefore have emerged as promising candidates for next generation nanofabrication, as it is widely accepted that the shorter the radiation wavelength the finer the theoretical resolution [2]. Extreme ultraviolet lithography (EUVL) is regarded as a continuation of the optical lithography trend, and is targeted to enter into the production of 70 nm critical dimensions (CD) [3]. Therefore EUV lithography is a leading candidate for next generation lithography (NGL) technology for fabricating integrated circuits (IC) with a features size of 70 nm or below [4-7]. This presents a challenge for the imaging layer, so that surface imaging resist schemes [8] particularly ultrathin films or top-surface imaging [9-10] resists are considered to be desirable in order to achieve high resolution fidelity. Beside resolution and sensitivity, the photoresist material must also be able to resist the aggressive environment of plasma processing (reactive ion etching. The use of composite materials may represent a solution to these problems, by separating the imaging characteristics from the imaging issues. On the contrary, X-ray lithography (XRL) uses powerful collimated X-ray beams emitted by synchrotron radiation (SR) sources to expose a thick resist layer through an X-ray mask. Due to the high penetration depth of X-rays, thick layers of the polymer can receive enough doses to allow the chemical etching of deep structures.

To meet these objectives our current focus is thus on the synthesis and characterization of novel nanocomposites resists [11] for NGL. In this paper we report the initial evaluation of a novel chemically amplified nanocomposite photoresist [11-14,17,18] for NGL. We investigated the lithographic properties of this positive ultrathin resist upon exposure to EUV radiation with respect to defect free thin film formation, sensitivity, contrast and pattern development. In order to characterize the exposure properties, we have also employed other techniques such as X-ray Lithography (XRL, 1 nm wavelength).

2. EXPERIMENTAL

2.1 Materials

The components of the nanocomposite photoresist (nanoRT-3b) were: *tert*-butyl methacrylate (*t*-BMA), methyl methacrylate (MMA), methyl methacrylic acid (MAA), polyhedral oligosilsesquioxane methacrylate (POSS)^{TM} and a

proprietary photo acid generator (PAG) [18]. NanoRT-3b was synthesized through a free radical polymerization process using AIBN as initiator. This polymerization process was similar as described by us earlier [13,18].

2.1 Resist evaluation

Photoresist samples (5% solution in PGME) were spin coated on 3 inch. silicon wafers @ 3000 rpm and 4000 rpm for 60 sec. Coated wafers were post-applied baked (PAB) at 120 ^{0}C for 120 sec., providing film thicknesses of ~ 100 nm measured using a Tencor Instrument Alpha-step 200.

Exposures were conducted at the Synchrotron Radiation Center (SRC) the Center for NanoTechnology (CNTech), University of Wisconsin-Madison [7, 15]. The schematic view of the EUV experimental set-up is shown in Figure 1 [16]. Figure 2 shows the schematic view of the of the Lloyds' mirror interferometer set-up. Gold coated planar mirror were used to reflect part of the beam which then interferes with the direct beam to form a pattern on the wafer surface [15].

After the exposure, a post exposure bake (PEB) was performed at 120 ^{0}C for 60 sec on a hot plate. Exposed samples were developed using 0.26 N TMAH for 60 sec. and rinsed using deionized water (DI) for 15 sec. The adhesion of the resist was sufficient to observe the difference in exposed resist thickness as a function of exposure dose. The dose range for EUV of 0.1 mJ/cm^2 – 2.0 mJ/cm^2 was chosen for this experiment. The normalized resist thickness remaining after development versus exposure dose (NRT) were used to determine resist sensitivity and contrast. It was found that the critical dose (dose to clear) was about 1.4 mJ/cm^2 for 100 nm resist thickness in the quoted development conditions – a very good value in comparison to other resist systems. The dose range for X-ray of 50 mJ/cm^2 –150 mJ/cm^2 was chosen for the XRL evaluation. NRT were used to calculate resist sensitivity (100 mJ/cm^2) and contrast (4.8) for 200 nm thick films. Lithographic results were evaluated using a Hitachi S-6180 CD-SEM scanning electron microscope at 20 K magnification. Line edge roughness was characterized by SEM as well as by AFM.

3. RESULTS AND DISCUSSION

3.1 Preparation of NanoRT-3b

NanoRT-3b was prepared by a polymerization process described by us previously [18]. The objective of this copolymerization was to prepare a novel chemically amplified nanocomposite photoresist. *Tert*-butyl methacrylate (t-BMA) was used as a protecting group for NanoRT-3b. Polyhedral oligosilsesquioxane methacrylate (POSS) was incorporated to achieve higher plasma etch rate required for pattern transfer [17]. It has been previously demonstrated that incorporation of POSS into methacrylate based CA resists could improve their plasma etch resistance [13,17]. However, the most important idea and technique is the incorporation of PAGs within the molecular architecture of the resist as depicted in **Scheme 1** [13,18]. This is necessary in order to significantly enhance the sensitivity of the resist. Note that PAG also could function as a dissolution promoter due to its solubility in bases.

PAGs play an important role in a CA resist system [19]. PAGs are almost exclusively used in their monomeric forms. Small molecule PAGs usually have limited compatibility with the polymer matrix [20]. The resulting problems include phase separation, non-uniform acid distribution and migration during temperature fluctuations, such as in the baking processing. These problems frequently lead to an undesirable, premature and non-uniform deprotection reaction in the CA resist film. To alleviate these problems, it is proposed that photoacid generating units be incorporated in the resist chains, rather than adding monomeric PAGs into the resist polymers. We *hypothesize*, based on our promising preliminary results for low voltage e-beam resist systems [13,18], that a combination of the following mechanism(s) can operate to facilitate extremely high sensitivity for film thickness ranging from 100 to 250 nm. We have also confirmed this by determining that the acid generation [18] during exposure is independent of the microstructure when the PAG is chemically bonded to the polymer resist backbone. Due to a high concentration (~10%) of PAGs, even within the first 50 nm of the exposed film, the concentration of the hydrogen ions generated is large enough to promote controlled diffusion within the underlying layers of the film, i.e., below the initial 50 nm. During the post bake processing, deblocking and change in solubility of the resist in the exposed areas is obtained.

^{1}H-NMR spectrum in Figure 3 was used to estimate the polymeric compositions in NanoRT-3b. From the NMR spectrum (δ 1.4), we inferred that the protecting ratio (i.e., t-BMA) of NanoRT-3b is ~ 38 % (wt.%). The adhesion promoter (MAA) group, -COOH attributed at δ 10.0 of the resist material. The absorptions between δ 7.5 and δ 8.5 estimated the sensitivity ratio (i.e., PAG composition) of NanoRT-3b is ~ 5% (wt.%). The sensitivity of the resist is tunable based on PAG incorporation.

3.2 Lithographic Evaluation

The lithographic evaluation of the NanoRT-3b was investigated under EUV (13.4nm) and X-ray (1nm) exposure. The results are summarized in Table 1 and Table 2 respectively, which contains the sensitivity and contrast for NanoRT-

3b under the lithographic process conditions. Sensitivity was also calculated based on the normalized thickness (NRT) curve for NanoRT-3b shown in Figure 4 and Figure 5. The new nanocomposite photoresist (NanoRT-3b) thus demonstrated high sensitivity in the EUV range of 1-1.5 mJ/cm^{2,} compared to current commercial resists (Table 1). Beside EUV exposure, the NanoRT-3b was also evaluated for X-ray other lithographic techniques. Initial exposure to X-ray of 1 nm wavelength (XRL) indicated that the sensitivity of the nanocomposite resist (NanoRT-3b) is 60-80 mJ/cm^2, considerably higher than that of the EUV exposure because of the much lower absorption coefficient in the X-ray region. The resist sensitivity for X-ray is very good in comparison with conventional X-ray resists (**Table 2**) such as TDUR-N908 (150mJ/cm^2) and UVII-HS (190mJ/cm^2)[21].

Figure 6 shows scanning electron (SEM at 10 K resolution) micrographs of 480 nm period grating patterns (L/S 240 nm) in NanoRT-3b resist under X-ray exposure. The resist was ~ 100 nm thick and was processed according to the conditions specified above. The SEM image in Fig. 6 display S = 240 nm wide lines printed in the new resist. The period in this case was 480 nm. Fig. 7, shows SEM micrograph of 300 nm pattern (period) in NanoRT-3b resist under EUV exposure at seizing dose 1.0 mJ/cm^2. These are the first attempts to print nanoscale features on the new resist NanoRT-3b.

Atomic force microscope (AFM) images of the same patterns with appropriate cross section (3D) are shown in Figures 8. Both SEM micrographs and AFM analysis display grating patterns. We will attempt to fabricate sub-100 nm patterns using EUV interferometry technique and measure their properties. The modifications in PEB conditions should result in a higher aspect ratio as well. Initial variation of PEB indicates that contrast of 4.9 to 5.2 is achievable.

4. Conclusion

In this paper we have reported initial results for novel nanocomposite resist materials for NGL technologies. These new materials exhibit extremely high sensitivity. The development of further improvement of the contrast is underway to demonstrate high-resolution sub-100 nm features.

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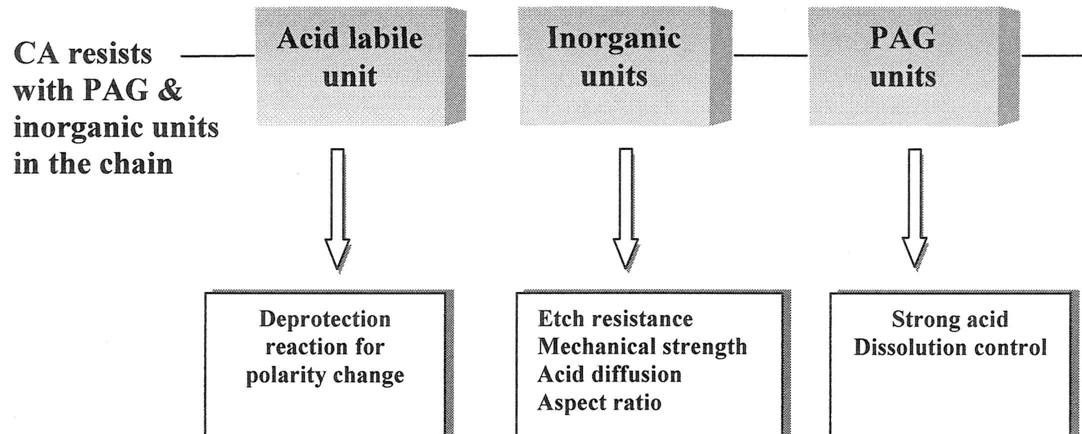

Scheme 1. Molecular architecture of nanocomposite resist.

Table 1. NanoRT-3b evaluated under EUV lithography.

Resist	Formula	Thickness nm	Density g/cm^3	Absorption coefficient μm^{-1}	Sensitivity, mJ/cm^2	Contrast γ
NanoRT-3b	$C_{68}H_{104}O_{23}Si_{08}S_{02}F_{03}$	**100**	**1.0**	**3.6**	**1-1.5**	**3.0**
UV-6	$C_{8323}H_{9026}O_{1015}S_5I_5F_{14}N_1$	118	1.042	3.61	6-7	4.0
*SAL-605	$C_{744}H_{74O143}N_{23}Br_{12}$	90	1.1	4.1	1.0	2.0
PMMA	$C_5H_8O_2$	90	1.11	4.85	40	2.8

* Negative resist

Table 2. NanoRT-3b evaluated under X-ray lithography.

Resist	Formula	Thickness nm	Density g/cm^3	Sensitivity mJ/cm^2	Contrast γ
NanoRT™	$C_{68}H_{104}O_{23}Si_8S_2F_3$	**100**	**1.0**	**< 100**	**4.8**
PMMA	$C_5H_8O_2$	**<100**	**1.1**	**> 300**	**3.0**
UV6	$C_{8323}H_{9026}O_{1015}S_5I_5F_{14}N_1$	**180**	**1.04**	**180**	**4.1**
TDUR-N908	-	-	-	**> 150**	-
UVII-HS	-	-	-	**190**	-

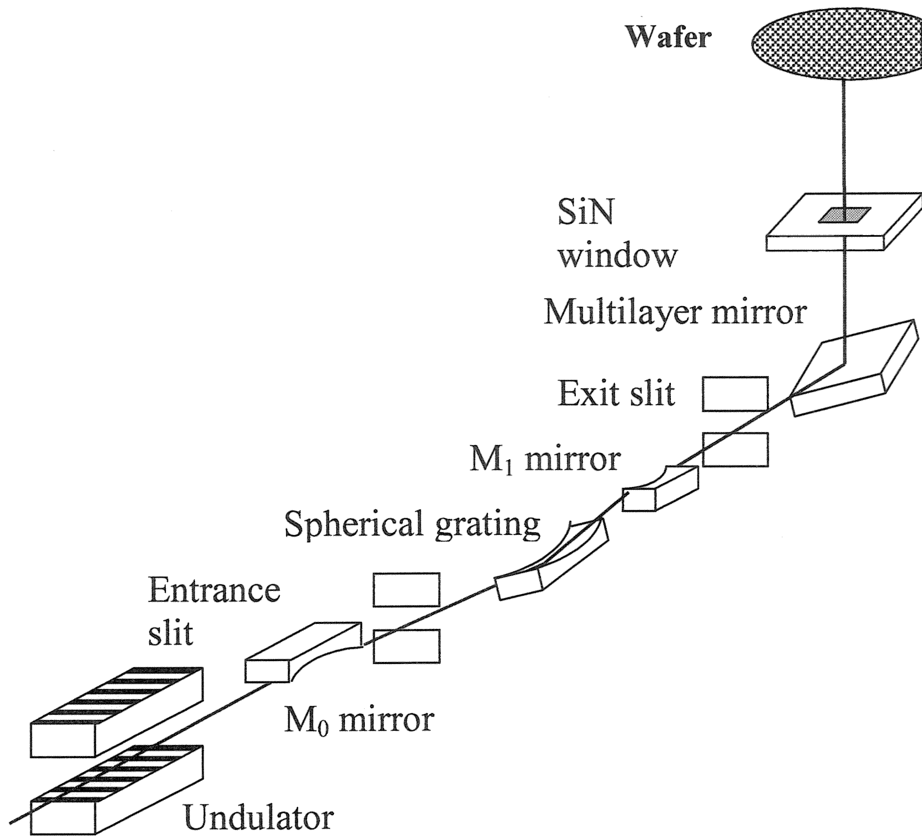

Figure 1. The schematic view of the EUV experimental set-up.

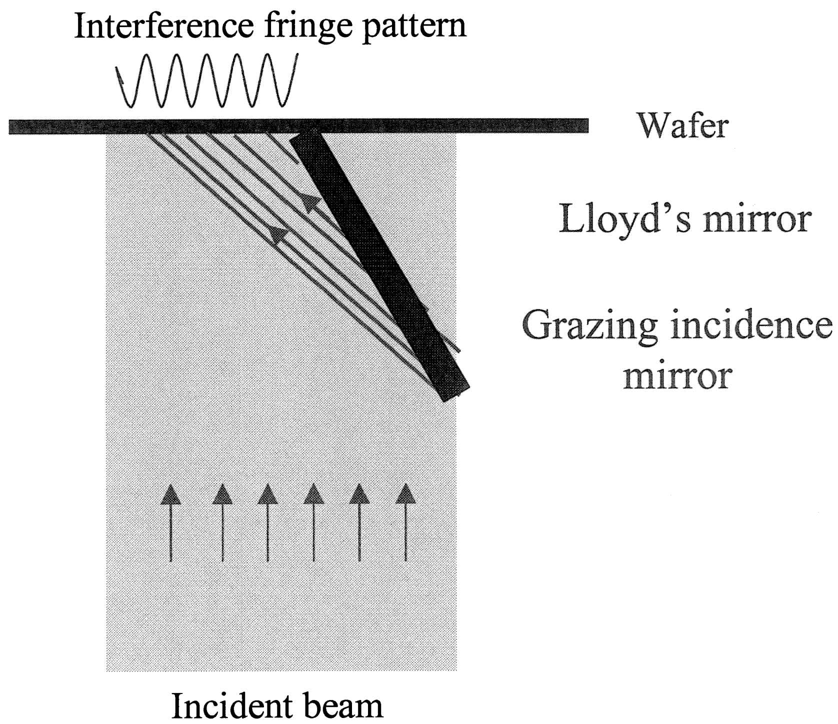

Figure 2. Lloyd's mirror interferometer scheme.

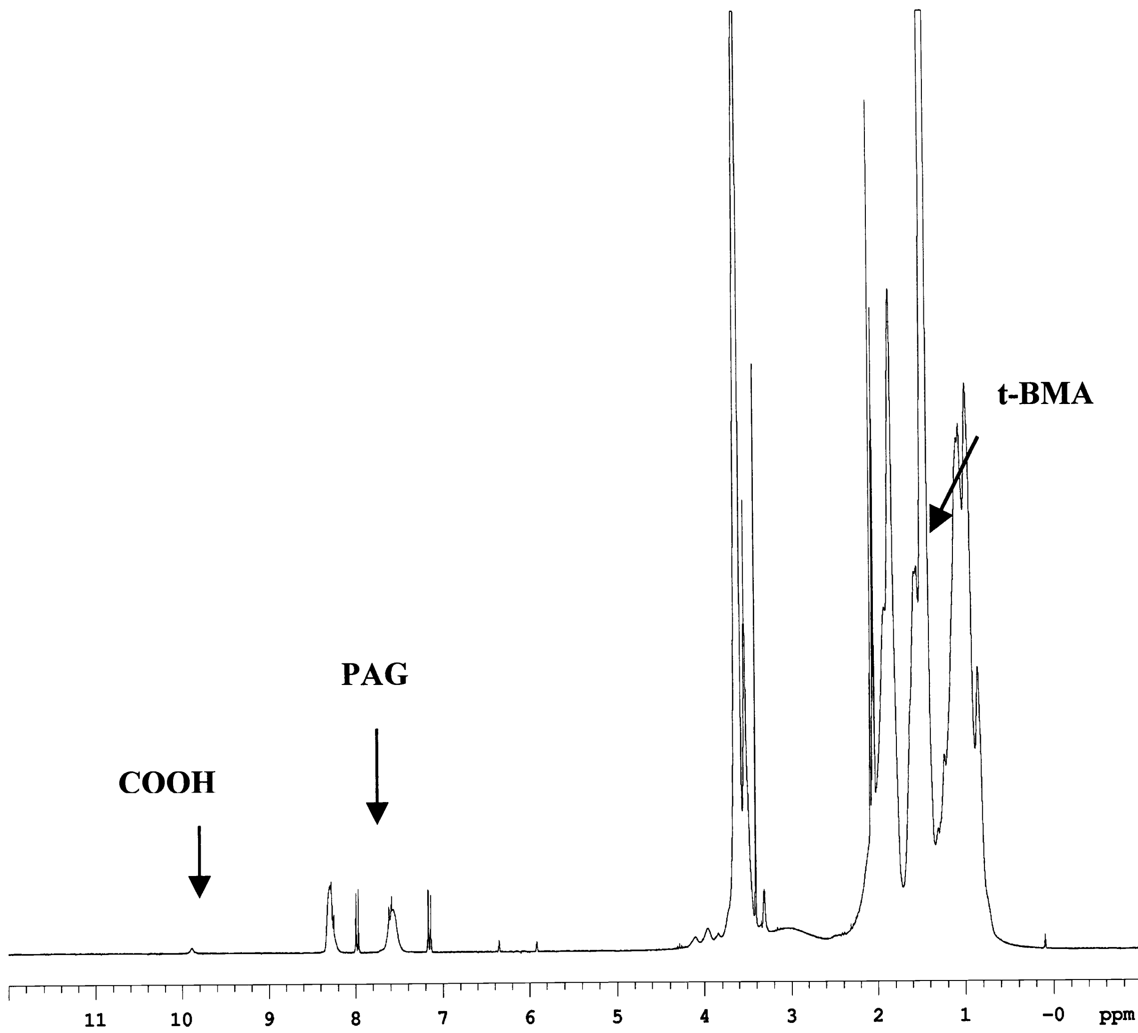

Figure 3: ^{1}H-NMR spectrum of nanocomposite resist NanoRT-3b.

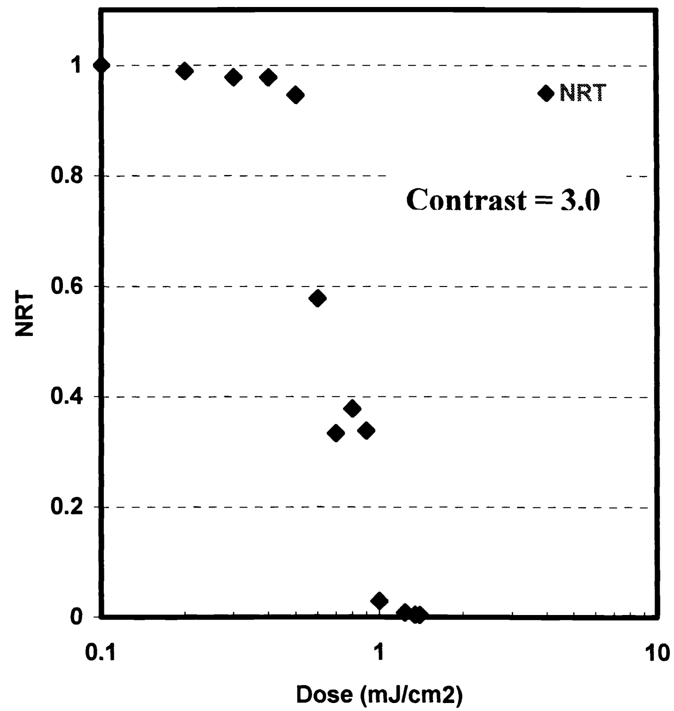

Figure 4. Sensitivity curve obtained from EUV exposure experiments.

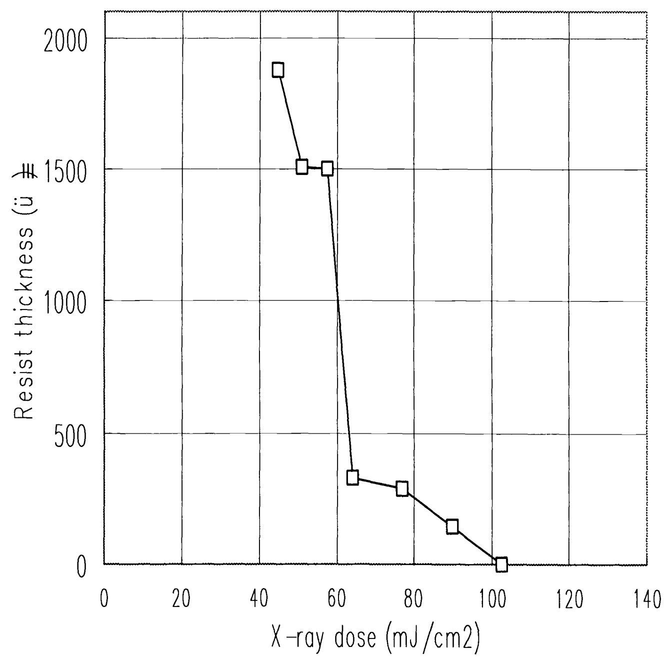

Figure 5. Sensitivity curve obtained from X-ray exposure experiments.

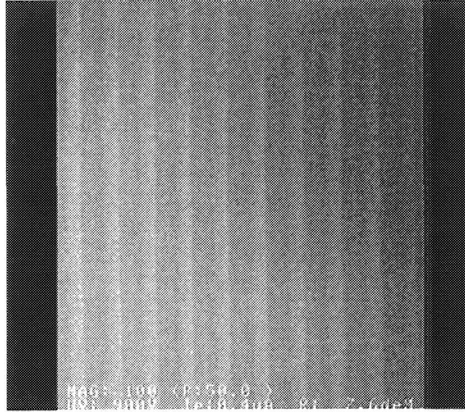

Figure 6: SEM image (line pattern) L/S 480 nm of X-ray
(@ < 100 mJ/cm^2) for sample NanoRT-3b.

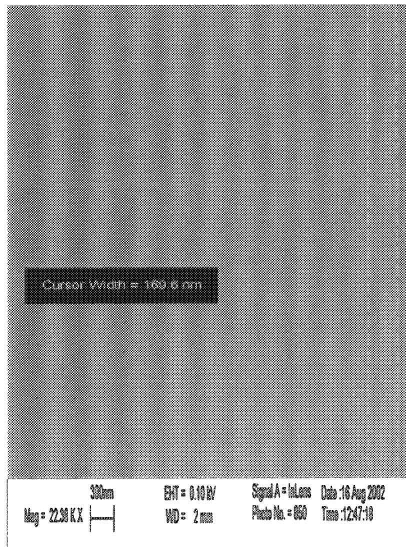

Figure 7. SEM of EUV pattern L/S (300 nm) for sample NanoRT-3b resist @ dose (1.0 mJ/cm^2).

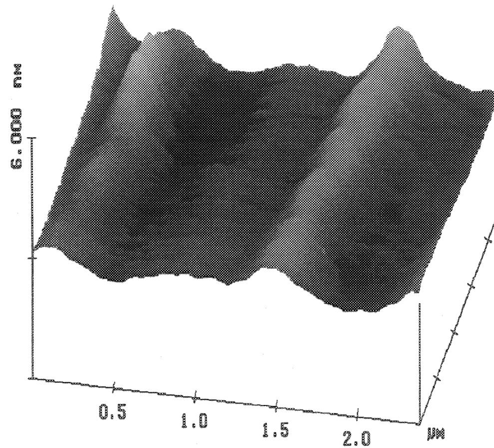

Figure 8. AFM of EUV pattern L/S (300 nm) for sample NanoRT-3b resist @ dose (1.0 mJ/cm^2).