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Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

High molecular weight polystyrene as very sensitive electron beam resist

Celal Con, Ripon Dey, Mark Ferguson, Jian Zhang*, Raafat Mansour, Mustafa Yavuz, Bo Cui

Waterloo Institute for Nanotechnology (WIN), University of Waterloo, 200 University Ave. West, Waterloo, ON, Canada N2L 3G1

ARTICLE INFO

Article history:

Available online 16 July 2012

Keywords:

Nanofabrication
Nanolithography
Electron beam lithography
Resist
Polystyrene

ABSTRACT

Previously we demonstrated ultra-dense patterning using 2 kg/mol polystyrene negative electron beam resist that has low sensitivity [16]. To drastically improve its sensitivity, here we studied the exposure behavior of polystyrene with molecular weight of 90 and 900 kg/mol. Very high sensitivity of $1 \mu\text{C}/\text{cm}^2$ was obtained for 900 kg/mol when exposed at 2 keV. The sensitivity for 90 kg/mol polystyrene is about one order lower. The resist has a contrast around 1.5 that is nearly independent of molecular weight for the current range of molecular weight. It can achieve fairly well-defined patterns of 150–200 nm period line arrays. Polystyrene is a simple and low-cost resist with easy process control and practically unlimited shelf life. It is also considerably more resistant to drying etching than PMMA. Therefore, the current high molecular weight polystyrene could be employed for applications that need moderate resolution but high sensitivity for a reasonable exposure time.

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1. Introduction

Electron beam lithography (EBL) [1], focused ion beam (FIB) lithography [2] and nanoimprint lithography (NIL) [3] are currently the three most widely employed nanolithography techniques. Among them, EBL is undoubtedly the most popular for R&D. Unlike NIL, EBL can generate arbitrary patterns without the need of fabricating a mold first. Though not as versatile as FIB, which can do both lithography using a resist and milling, EBL is capable of exposing thick ($>>100 \text{ nm}$) resist without ion contamination to the resist. In addition, it is faster than FIB exposure since the electron beam can remain well-focused below 10 nm beam size even with nA beam current, as is needed for fast writing. Nevertheless, the throughput of EBL is still very low compared to optical and nanoimprint lithography, which calls for highly sensitive resists and tools capable of exposure at tens of nA beam current.

Positive resist is typically used for EBL, largely because of the availability of the benchmark resist poly(methyl methacrylate) (PMMA) that offers high resolution with low cost and ease of process. With its higher sensitivity and etching resistance than PMMA, ZEP520 (positive-tone, Zeon Corp) is arguably the second most popular EBL resist. However, for some applications such as the fabrication of hole arrays in a metal film (the structure for extraordinary optical transmission [4]) by using liftoff, negative resist would offer substantially shorter exposure time, except when using a more complicated “resist tone reversal” process [5]. Unfortunately, there is no negative resist that gains similar popularity to PMMA

and ZEP520. Bilenberg et al. has selected four negative EBL resists and compared their performance: calixarene (Tokuyama Corp), ma-N 2401 (Microresist Technology), SU-8 (Microchem Corp) and mr-L 6000 (Microresist Technology) [6]. As chemically amplified resists, SU-8 and mr-L 6000 offer superior sensitivity, but with low contrast and resolution (more strictly speaking, half-pitch for dense periodic line array patterns) that is limited by the diffusion of the photoacid generator during post exposure baking. Ma-N 2401 has sensitivity comparable to that of ZEP520 resist, but with far inferior resolution. Among the four resists, calixarene offers the highest resolution. Calixarene has been studied as a candidate resist for fabricating using EBL bit-patterned recording media that have achieved areal density of 1.4 and 1.6 Tbits/in² (corresponding to a dot array of 20 nm period) [7,8] using very thin (sub-20 nm) film. However, it has low sensitivity despite being a chemically amplified resist, and the acid generated in the exposed area may diffuse into the unexposed area, blurring the latent image.

In recent years, hydrogen silsesquioxane (HSQ) probably attracted more attention than any other negative tone resist [9–11]. HSQ is an excellent inorganic EBL resist that has demonstrated the highest resolution of 9 nm period line array patterns [12], thanks to its small molecular size and lack of swelling during development [13]. However, in addition to its low sensitivity, HSQ is not suitable for liftoff unless using a double layer resist stack such as HSQ coated on PMMA. The development process is also self-limiting due to cross-linking of resist by the developer, leading to incomplete removal of unexposed resist, though a salty developer can minimize this effect [12,14]. More importantly, HSQ is unstable, so spin coating, baking, exposure and development must be done quickly (yet this is not possible if the exposure time is long) [15].

* Corresponding author. Tel.: +1 519 729 3582.

E-mail addresses: bcui@uwaterloo.ca, j242zhan@ecemail.uwaterloo.ca (J. Zhang).

In addition, all the above resists are commercially formulated with typically high cost and short shelf life. Therefore, it is desirable to have a negative resist like PMMA, which is a simple polymer with low cost and practically unlimited shelf life, and can be dissolved easily using various solvents to give desired film thickness. Polystyrene is such a resist, as it undergoes cross-linking when exposed to deep UV light or an electron beam. Previously, dense periodic patterns with 20 nm period lines and 15 nm period dots have been demonstrated using low molecular weight 2 kg/mol polystyrene resist [16]. However, the sensitivity of the 2 kg/mol polystyrene is very low, one order lower than the insensitive PMMA. Knowing that for negative cross-linking polymer resist the sensitivity is theoretically proportional to its molecular weight, here we investigate the exposure properties of high molecular weight (90 and 900 kg/mol) polystyrene, which demonstrated a very high sensitivity of $1 \mu\text{C}/\text{cm}^2$ when exposed at 2 kV. Besides its high sensitivity, polystyrene is more (by $\sim 3\times$) resistant to dry etching than PMMA. Its major drawback is low contrast and thus low resolution compared to PMMA.

2. Experiment

Polystyrene powder with a molecular weight of 90 and 900 kg/mol ($M_w/M_n = 1.10$) was dissolved in chlorobenzene with a concentration of 1.3 wt/vol.%, which gave a film thickness of 60–140 nm (measured by Dektak profilometer) depending on molecular weight and spin speed. The silicon wafer was cleaned using acetone and 2-propanol, followed by short exposure to oxygen plasma. After spin coating, the film was baked at 120°C for 5 min on a hotplate. Unlike the low molecular weight polystyrene that cannot form a continuous film on base silicon wafer, the current polystyrene was found able to form a uniform film, though its adhesion could be further enhanced by coating the silicon wafer with a mono-layer surfactant trichloro(phenyl)silane.

Exposure was performed using a LEO 1530 field emission SEM equipped with a Nabity nanometer pattern generation system (NPGS) at acceleration voltages of 20, 5 and 2 kV. The beam currents were 35–100 pA that depends on the acceleration voltage for an aperture of $20 \mu\text{m}$. For high resolution study, the periodic lines were exposed as single-pass lines with a beam step size of 12 nm. After exposure, the samples were developed using tetrahydrofuran for 2 min, followed by a 2-propanol rinse. Such a relatively long development time is necessary since high molecular weight polystyrene is less soluble in the solvent than the low molecular weight one. As cross-linked polystyrene is insoluble, in principle, all solvents that can dissolve (un-exposed) polystyrene can be used as developer, such as chlorobenzene, anisole and toluene.

3. Results and discussion

Fig. 1 shows the contrast curves for 90 kg/mol polystyrene resist exposed at 20 and 5 keV. The contrast for exposure at 20 keV, defined as $\gamma = [\log(D_{100}/D_0)]^{-1}$, is calculated to be 1.5, which is very close to the contrast at 5 keV exposure. The contrast is much lower than the popular chain-scission positive resist PMMA and ZEP-520A. For PMMA, a critical molecular weight around 10 kg/mol exists, below which the polymer becomes very soluble by the developer. For chain cross-linking resist polystyrene, apparently there is no such a critical transition point, and its solubility decreases gradually with the increasing degree of cross-linking. Nevertheless, the contrast is higher than the popular chemically amplified resist SU-8 ($\gamma \sim 1.0$) [17]. The sensitivity (defined as D_{50} , the dose to result in 50% remaining thickness) is $120 \mu\text{C}/\text{cm}^2$ and $26 \mu\text{C}/\text{cm}^2$ for 20 keV and 5 keV exposure, respectively. This

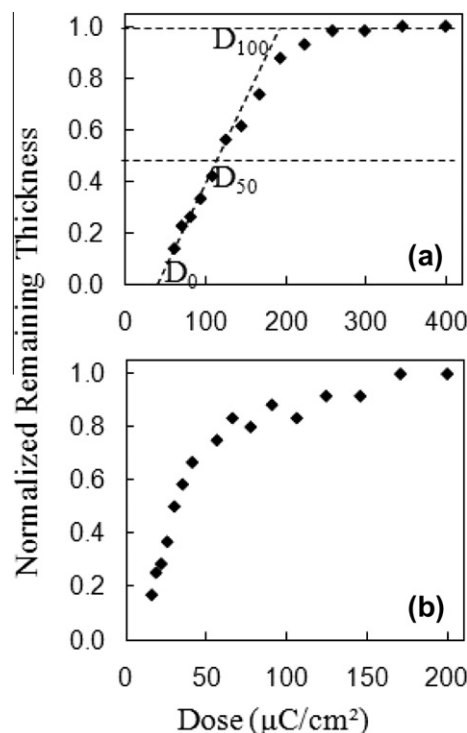


Fig. 1. Contrast curves for 90 kg/mol polystyrene exposed at (a) 20 keV and (b) 5 keV, and developed by tetrahydrofuran for 2 min.

is in good agreement with the fact that sensitivity is roughly inversely proportional to the beam energy (E) as predicted by the Bethe

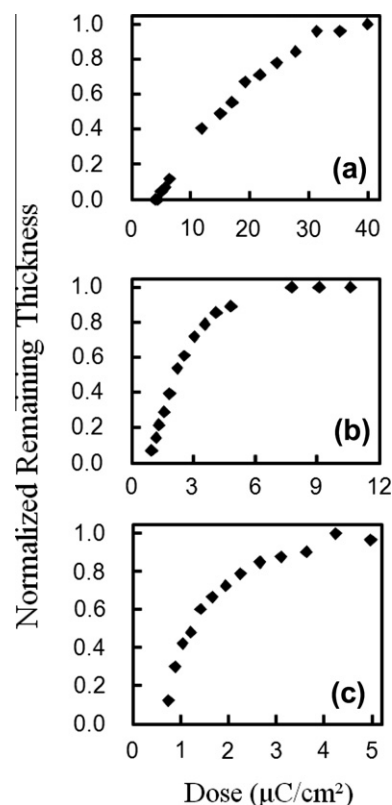


Fig. 2. Contrast curves for 900 kg/mol polystyrene exposed at (a) 20 keV, (b) 5 keV and (c) 2 keV, all developed by tetrahydrofuran for 2 min.

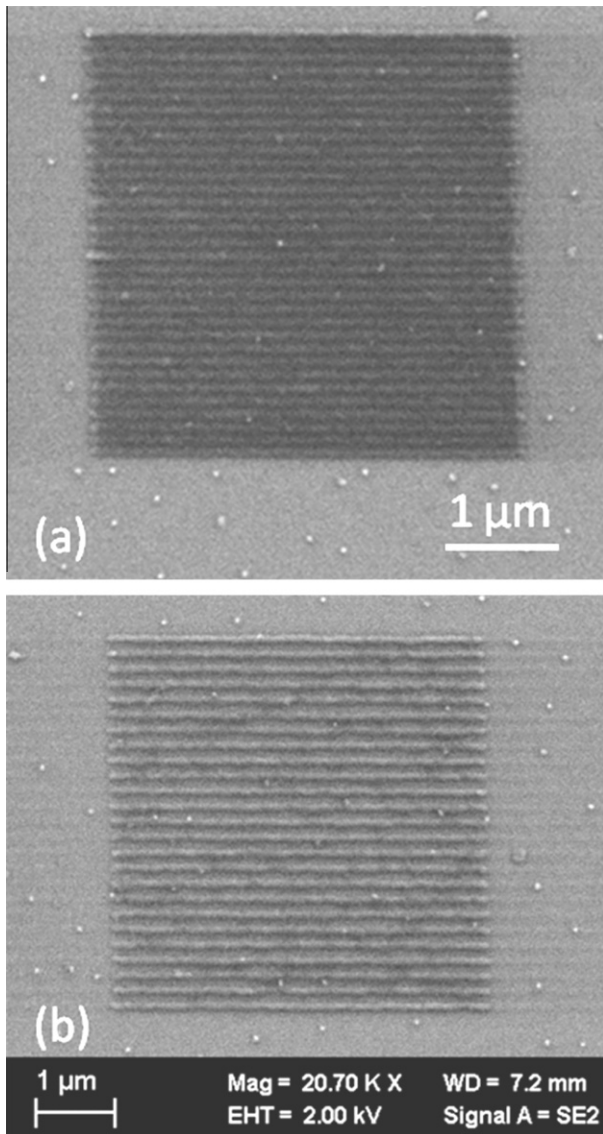


Fig. 3. SEM images of 90 kg/mol polystyrene line array exposed at 5 keV with line dose of 0.54 nC/cm, and developed by tetrahydrofuran for 2 min. (a) 150 nm period, (b) 200 nm period.

equation for electron energy loss (E_{loss}) in the resist: $E_{\text{loss}} \propto 1/E \cdot \log(\alpha E)$ with α being a constant. The threshold dose where the contrast curve starts to rise (D_0) is the “gel point” that is roughly inversely proportional to the molecular weight for simple negative polymer resists according to the Charlesby theory [18]. This is because the number of cross-linkings necessary to render the resist insoluble in the developer decreases with molecular weight. Contrary to the cross-linking negative resist, for positive resist based on chain scission such as PMMA, the sensitivity does not depend significantly on molecular weight, because for longer chains, though more chain scission is needed to render it soluble in the developer, it also receives proportionally higher exposure dose. The sensitivity for 2 kg/mol polystyrene at 5 keV exposure is $1170 \mu\text{C}/\text{cm}^2$ [16] that is $\sim 50\times$ lower than 90 kg/mol polystyrene, which is in good agreement with the Charlesby theory.

The contrast curves for 900 kg/mol exposed at different acceleration voltages are shown in Fig. 2. As expected, the sensitivity ($14 \mu\text{C}/\text{cm}^2$ and $2.1 \mu\text{C}/\text{cm}^2$ for 20 keV and 5 keV exposure, respectively) is roughly one order higher than that for 90 kg/mol polystyrene exposed at 20 and 5 keV. It is also much higher than ZEP-520A

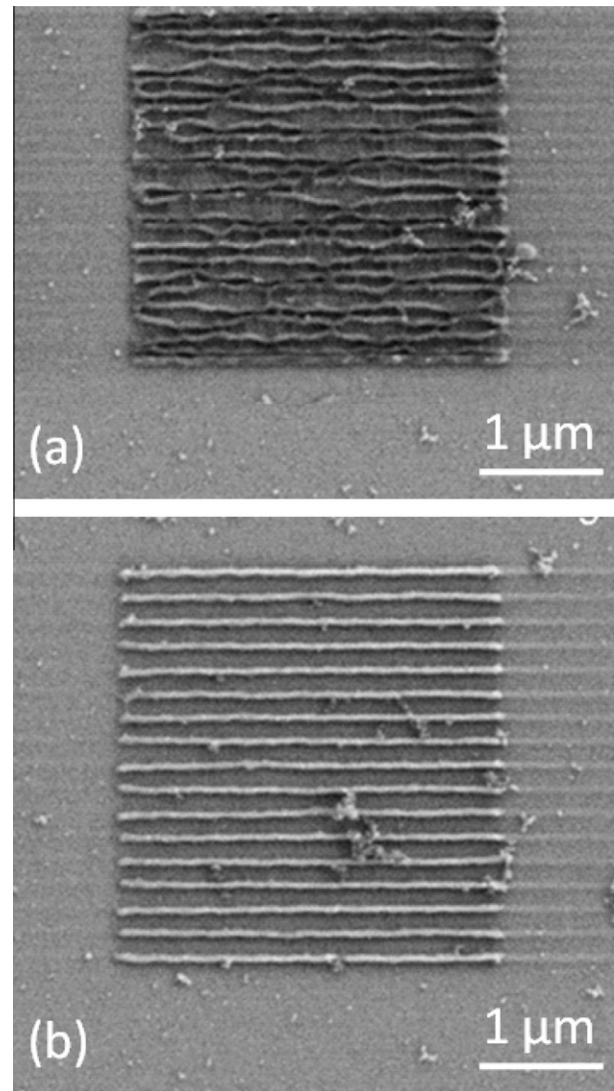


Fig. 4. SEM images of 900 kg/mol polystyrene line array exposed at 5 keV with line dose of 0.043 nC/cm, and developed by tetrahydrofuran for 2 min. (a) 200 nm period, (b) 300 nm period.

resist when using the standard amyl acetate developer, and comparable to ZEP-520A resist when using a stronger developer of methyl ethyl ketone:methyl isobutyl ketone = 40:60 [19]. The sensitivity can be further enhanced by exposure at lower acceleration voltage, here 2 keV, which resulted in a sensitivity of $1.1 \mu\text{C}/\text{cm}^2$. Further reduction of acceleration voltage would lead to more serious forward scattering and shallower resist penetration depth (e.g. 65 nm penetration for 1.3 keV exposure [20]), so was not experimented. Contrary to intuition and experience that high sensitivity generally comes with low contrast, the contrasts ($\gamma = 1.4, 1.6, 1.7$ for 20, 5 and 2 keV exposure, respectively) was found to be not noticeably worse than 90 kg/mol polystyrene. This might be explained by that the ratio of the exposure dose for full cross-linking (nearly insoluble in the developer) to the dose for partial cross-linking (e.g. 50% cross-linking, moderately soluble) should be independent of the molecular weight. However, this is not the case for very low molecular weight, as our previously study showed that the contrast for 2 kg/mol polystyrene is significantly higher [16].

To study the resolution capability of the polystyrene resist, we exposed periodic dense line arrays with periods 120, 150, 200 and 300 nm, all at 5 keV. For 90 kg/mol polystyrene, Fig. 3 shows

line array patterns of 150 and 200 nm period. Grating with 200 nm period was well defined, whereas the 150 nm one is fairly well defined. The next period (120 nm, not shown) was not resolved. For 900 kg/mol, as seen from Fig. 4, the lines for both 200 and 300 nm period were well defined. However, as the film thickness (140 nm) is about twice that of 90 kg/mol polystyrene, the capillary force is stronger, leading to line collapse during resist drying for the 200 nm period grating. We can conclude that the resolution capability for the two molecular weights are not significantly different, which agrees with the fact that the two resists have similar contrast. It is well known that denser pattern can be obtained when proximity effect is insignificant owing to small pattern area compared to the range of backscattered electrons or exposure on a thin membrane. Here the pattern area is larger than the proximity effect range for 5 keV exposure, hence similar resolution is expected when writing over larger areas. The resolution or half pitch for the current polystyrene resist is lower than the very low contrast resist SU-8 [17]. However, in that study the authors did not mention the pattern area as compared to the range of proximity effect for 100 keV exposure. In fact, when proximity effect is unimportant, very fine SU-8 line of only 24 nm wide has been obtained using 100 keV exposure [21].

Previously, Cord et al. has demonstrated robust undercut profile by using a bi-layer positive resist stack PMMA and PMGI [22] (more sensitive than PMMA when using aqueous basic developer, less sensitive than PMMA when using solvent developer [23]). Such a robust undercut profile could be realized readily by using a bi-layer polystyrene resist stack having higher molecular weight for the top layer. Similarly, by using a bi-layer stack with the top layer having lower molecular weight, two-level patterning could be achieved, which, after pattern transfer to a hard substrate, could be used to fabricate 3D mold for dual damascene process based on nanoimprint lithography [24].

4. Conclusions

We studied the exposure behavior of the negative EBL resist polystyrene with molecular weight of 90 and 900 kg/mol. Very high sensitivity of $1 \mu\text{C}/\text{cm}^2$ was obtained for 900 kg/mol when exposed at 2 keV. The sensitivity for 90 kg/mol polystyrene is about one order lower. The resist has a contrast around 1.5 that is nearly independent of molecular weight for the current range of molecular weight. The contrast is much lower than PMMA, but higher than the chemically amplified negative resist SU-8. The current resist

can achieve fairly well-defined patterns of 150–200 nm period line arrays. In addition to its high sensitivity, polystyrene is a simple and low-cost resist with easy process control and practically unlimited shelf life. It is also considerably more resistant to drying etching than PMMA. We believe polystyrene is a very promising negative resist with tunable sensitivity and resolution capability over a broad range simply by choosing different molecular weights. For applications that need only moderate resolution, it is desirable to use high molecular weight such as 900 kg/mol in order to take advantage of its very high sensitivity; whereas if ultra-high resolution is the primary goal, very low molecular weight such as 2 kg/mol would be the choice.

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