Very high sensitivity ZEP resist using MEK:MIBK developer

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Low throughput is the major drawback for electron beam lithography. Chemically amplified resists that have high sensitivity are often used to keep the exposure time within practical limit. In this Letter the authors show that the popular non-chemically amplified electron beam resist ZEP-520A can achieve 2.6 μC/cm^2 sensitivity when using methyl ethyl ketone:methyl isobutyl ketone developer and 5 keV exposure, though at the cost of reduced contrast compared to standard developers xylene, *n*-amyl acetate or hexyl acetate. The achievable resolution was found to depend strongly on the resist's adhesion to the substrate or under-layer and thus obtained 40 nm half-pitch resolution using ZEP resist spun on a layer of anti-reflection coating that was treated by oxygen plasma.

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. Although not as versatile as FIB, which can do both lithography using a resist and milling, EBL is capable of exposing thick ($\gg$ 100 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. Desirable properties for EBL resist include high sensitivity, high contrast and high dry etching selectivity to the substrate materials. 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, ZEP-520A (positive-tone, Zeon Corp) is arguably the second most popular EBL resist.

Resist sensitivity depends mainly on the following three factors, the first being chemical composition of the resist. For example, chemically amplified resists making use of catalytic chain reaction during the post exposure baking step are generally very sensitive. On the other hand, for a negative resist based on polymer chain cross-linking such as polystyrene, its sensitivity increases proportionally with its molecular weight, as longer chain polymer needs few cross-links to render it insoluble by the developer. The second factor is developer strength, development time and temperature. Stronger developer and/or development at higher temperature lead to higher sensitivity for the positive resist, and vice versa for the negative resist. For example, PMMA is usually developed by a mixture of methyl isobutyl ketone (MIBK) and isopropyl alcohol (IPA), and its sensitivity increases considerably when the ratio of MIBK/IPA is increased from 1/3 to 1/1 since MIBK is a stronger solvent than IPA. Systematic studies on ZEP using 15 different developers demonstrated similar effect of developer's strength on resist's sensitivity [4, 5]. The same is true for development time: longer development time increases resist sensitivity for positive resist, even though the increase would be insignificant if the resist has a high contrast. The third factor is exposure condition and substrate material. Lower energy electron beam exposure results in higher sensitivity because energy deposited into the thin resist layer is roughly inversely proportional to the electron energy. The resist sensitivity can also be increased by coating the resist on a high atomic number sub-layer that generates more backscattered electrons to further expose the resist. For instance, resist sensitivity is increased by $\sim$2$\times$ when it is coated on a thick Au sub-layer as compared to bare silicon wafer; yet excess backscattering is unfavourable when exposing dense pattern.

For applications where throughput is most critical, highly sensitive chemically amplified resists such as SU-8, NEB-22, NEB-31 and UVN30 are typically used [6, 7]. One issue with chemically amplified resists is acid diffusion that proceeds on the length scale comparable to the feature size. As a result, high resolution writing can only be achieved with strict process control, and any deviation from optimal condition may compromise the resist performance. This is probably one important reason that those resists have not gained enough popularity for R&D. In this Letter we will show that the popular e-beam resist ZEP can achieve sub-5 μC/cm^2 sensitivity when using methyl ethyl ketone (MEK):MIBK developer and 5 keV exposure, though at the cost of reduced contrast and resolution compared to standard developers xylene, *n*-amyl acetate or hexyl acetate.

2. Experimental: As-purchased ZEP-520A was further diluted with anisole with a ratio of 1:2, which gave the film a thickness of 45 nm when spun at 2000 rpm. After spin-coating, the film was baked on a hotplate at 180°C for 10 min. Exposure was performed using a Raith 150^{TWO} tool at acceleration voltages of 20 and 5 kV. To obtain the contrast curves, we exposed arrays of 5 by 5 μm squares with exponentially increasing doses. After development, the remaining resist thickness at unexposed area and the depth of each exposed square were measured by atomic force microscope (AFM) after plane-fit of the captured image. For high-resolution study, we exposed periodic line arrays with the lines defined as single-pass lines with beam step size of 15 nm. After exposure, the samples were developed using MEK:MIBK = 40:60 for 30 s, followed by rinsing with 2-proponal and nitrogen drying.

As it was found, the resist's performance depends critically on its adhesion to the substrate (or sub-layer). We studied three substrates. The first was bare silicon wafer cleaned by solvents followed by oxygen plasma. The second was anti-reflection coating (ARC, XHRIC-16, Brewer Science) spun on a silicon wafer and baked at 180°C for 3 min on a hotplate. Finally, ARC was treated (and thus thinned) with oxygen plasma. The as-purchased ARC gave a thickness of 160 nm after spin-coating and baking. To minimise its effect on pattern transfer, we diluted it by propylene glycol monomethyl ether to obtain a film of 50 nm, which can be further thinned to sub-10 nm by oxygen reactive-ion etching (RIE) (20 W, 20 sccm O_2, 20 mTorr, etching rate 3 nm/s).

3. Results and discussion

3.1. Resist sensitivity and contrast: Fig. 1 shows the contrast curves for ZEP-520A exposed at 5 and 20 keV and developed using MEK:MIBK = 40:60 for 30 s. AFM was used to obtain the contrast curves. The resist sensitivity was found to be 9.2 and 2.6 μC/cm^2 for 20 and 5 keV exposure, respectively. The dependence of sensitivity on e-beam energy is fairly in agreement with the fact that

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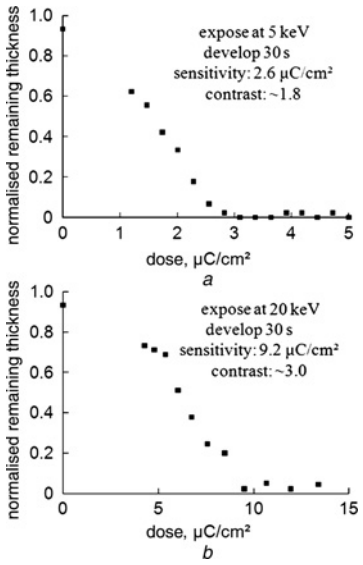

Figure 1 *Contrast curves for ZEP-520A resist exposed at 5 and 20 keV and developed by MEK:MIBK = 40:60 for 30 s at room temperature*
a 5 keV
b 20 keV
Thickness is normalised to the original film thickness. The unexposed area (dose = 0 μC/cm^2) has normalised thickness <1.0 because the developer dissolves slowly the unexposed resist

sensitivity is expected to be roughly inversely proportional to the beam energy (E) as predicted by the Bethe equation for electron energy loss (E_{loss}) in the resist: $E_{loss} \propto 1/E \cdot \log(\alpha E)$ with α being a constant. In fact, using even lower beam energy of 1 keV, sensitivity as high as 1 μC/cm^2 has been reported previously [8]. For comparison, the sensitivity for ZEP resist exposed at 25 keV and developed using hexyl acetate at room temperature was 72 μC/cm^2 [9]; and is expected to be around 58 μC/cm^2 if exposed at 20 keV, which is over 6× lower than using the current developer. As expected from Yamaguchi *et al.* [4], replacing hexyl acetate with the more common developer amyl acetate, the sensitivity is increased by about 50% (to ~30 μC/cm^2 if exposed at 20 keV), though at the cost of slightly reduced contrast [10]. Another study showed sensitivity for ZEP-520A to be 100 μC/cm^2 when exposed at 30 keV and developed using xylene at room temperature [11]. As shown in Fig. 1, the contrast of ZEP resist using the current developer is 1.8 and 3.0 for 5 and 20 keV exposure, respectively; these values are lower than the above study that demonstrated a contrast of 3.6. In addition, even the unexposed resist was found to be developed by ~4 nm within the development time of 30 s, which is due to the presence of the relatively strong solvent MEK. In principle, increasing the development time can increase resist sensitivity to an infinitely high value. However, we fixed the development time to be 30 s for the current film thickness of 45 nm, because longer development time (e.g. 2 min) was found to lead to poorer pattern definition. Similarly, more concentrated MEK would lead to higher sensitivity but lower contrast and poorer pattern definition, as demonstrated by Yamaguchi *et al.* using MEK:*n*-hexane of various ratios [4].

3.2. Resolution: To study the achievable resolution (half-pitch) of this resist, we exposed dense line arrays at 5 keV since low e-beam energy increases resist sensitivity. We first coated the ZEP resist on a bare silicon wafer that was cleaned by solvents (acetone and 2-propanol) and oxygen plasma. However, no well-defined pattern was obtained as seen in Fig. 2. Evidently once the resist was developed to the bottom at certain spots, the spots expanded quickly in an uncontrolled way possibly due to the lack of adhesion to the substrate. Note that ZEP resist coated on bare

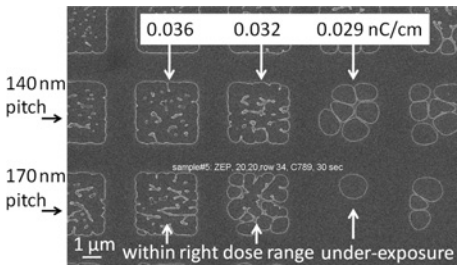

Figure 2 *Line array pattern poorly defined in ZEP-520A that was spun on bare silicon wafer*
Resist was exposed at 5 keV and developed by MEK:MIBK for 30 s. The array periods are 140 and 170 nm, which cannot be resolved due to resist's poor adhesion to the substrate

silicon can achieve high resolution when developed using standard developers such as amyl acetate. To improve the resist's adhesion to the substrate (sub-layer), we coated 50 nm ARC on silicon wafer before spinning the ZEP resist. Previously we have demonstrated that ARC can also improve the adhesion of polystyrene electron beam resist to silicon substrate for the ultra-dense patterning of 15 nm pitch dot array using EBL [12]. A thin layer of alternative materials or a self-assembled monolayer surfactant such as trichloro(phenyl)silane may also help enhance the adhesion. As seen in Fig. 3, the improvement of ARC sub-layer over bare silicon substrate was substantial, with resolvable grating pitch down to 110 nm (55 nm half pitch). It is well known that denser pattern can be obtained when proximity effect is insignificant due to small pattern area (compared to the range of backscattered electrons) or exposure on a thin membrane [13, 14]. However here the pattern area is larger than the proximity effect range for 5 keV

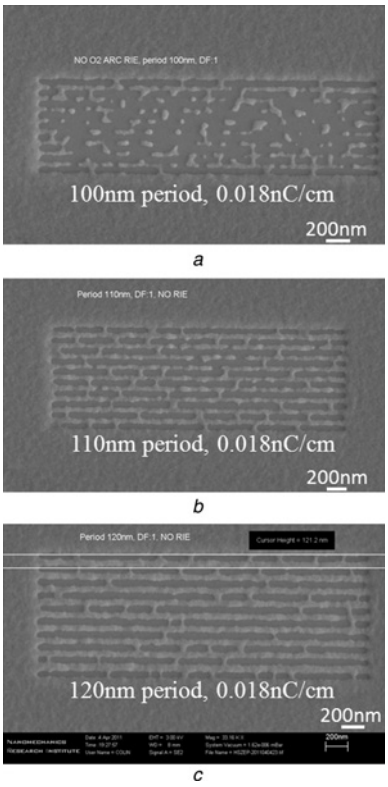

Figure 3 *Line array pattern in ZEP-520A that was spun on 50 nm ARC film*
a Array periods are 100 nm
b 110 nm
c 120 nm
Resist was exposed at 5 keV with line dose of 0.018 nC/cm and developed by MEK:MIBK for 30 s

exposure, hence similar resolution is expected when writing over large area. Although ARC coating improves resist's adhesion, it would affect pattern transfer to the substrate by either lift-off or direct etch process. To minimise this effect, we thinned the ARC layer by oxygen RIE, which modifies its surface energy and thus resist's adhesion to it. The exposure performance is shown in Fig. 4. The line array with 100 nm pitch is better defined for the same exposure dose of 0.018 nC/cm than ARC sub-layer without oxygen plasma treatment, indicating oxygen plasma treatment further improved ZEP's adhesion to ARC. For denser line array patterns, the pattern definition deteriorates as shown in Fig. 5 for ZEP resist coated on oxygen plasma treated ARC sub-layer. We claim that the current process can achieve a resolution of 40 nm half pitch. This resolution is slightly lower than SU-8 resist (34 nm half pitch) as demonstrated by Bonam *et al.* [6]. 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 addition to proximity effect that is significant since the pattern area is much larger than the backscattering range (200 nm for 5 keV), the noticeable defects for the 35 nm half-pitch pattern may be due to inadequate adhesion of the film to the substrate and agglomeration or phase separation of additives in the resist film.

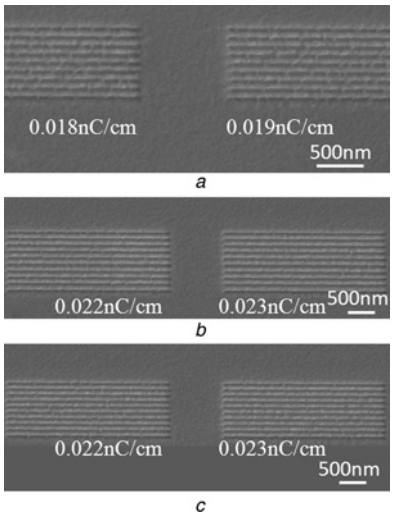

Figure 4 *Line array pattern in ZEP-520A that was spun on oxygen plasma-treated ARC film*
a Array periods are 100 nm
b 110 nm
c 120 nm
Resist was exposed at 5 keV and developed by MEK:MIBK for 30 s

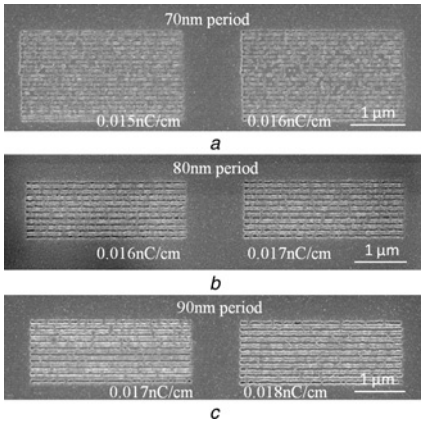

Figure 5 *Line array pattern in ZEP-520A for different periods*
a 70 nm
b 80 nm
c 90 nm
Resist was spun on oxygen plasma-treated ARC film, and exposed at 5 keV and developed by MEK:MIBK for 30 s

4. Summary and conclusions: We studied the performance of ZEP-520A resist using MEK:MIBK developer. Very high sensitivity of 2.6 μC/cm^2 was achieved at 5 keV exposure. The resist contrast was lower than that using standard high-resolution developer's xylene, *n*-amyl acetate or hexyl acetate. In addition, even the unexposed resist was dissolved by the developer at ~8 nm/min. The achievable resolution was found to depend strongly on the resist's adhesion to the substrate; and we obtained 40 nm half-pitch resolution using ZEP resist spun on a layer of anti-reflection coating that was treated by oxygen plasma.

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6 References

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