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Characterisation of a novel electron beam lithography resist, SML and its comparison to PMMA and ZEP resists

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ABSTRACT

We present study on a novel, positive-tone electron beam lithography (EBL) resist known as SLM and compare its lithographic performance to well-established positive resists such as 950 K polymethyl methacrylate (PMMA) and ZEP 520A. SML has been fabricated to have processing parameters similar to PMMA, but with enhanced functionality. Processing parameters such as film deposition, baking temperatures as well as the developers used for PMMA work well with SML resist.

Contrast curve measurements were generated for different thicknesses of SLM and exposure voltages. Two temperature variants were employed for developing the resist with 7:3 IPA:water co-solvent developer, *viz.* room temperature and 0 °C. To verify the resolution of SML resist, dense gratings of single pixel lines were compared to those fabricated using 950 K PMMA and ZEP 520A resists. Fundamental pattern transfer skills of metal lift-off and dry etching were compared with ZEP. Metal lift-off was carried out using 5–10 nm thick chromium metal and Microposit 1165 resist remover. The resilience of the SML resist to dry etching (ICP etching system with SF_6 and C_4F_8 gas mixture) was compared to ZEP and PMMA resists and then dense gratings on ZEP and SML were etched into Si.

The data obtained from the contrast curves show high contrast of the new resist. From the grating results, SML demonstrates very high resolution like ZEP and PMMA. The pattern transfer abilities of SML are also similar and in some aspects even outdo that of ZEP resist.

1. Introduction

The trend in reducing the feature size in microelectronic fabrication has been persistent since prefatory stage of semiconductor device fabrication to avail speedy functionality of devices [1]. To achieve extremely small feature sizes, nanolithography techniques like electron beam lithography (EBL), nanoimprint lithography (NIL) and focused ion beam lithography (FIB) are currently the most common choices in research and development. EBL is undoubtedly the favourite tool for lithography as it is a direct write method, more flexible as compared to NIL and non-destructive technique compared to FIB, and has a very high resolution as the electron beam can stay well focused below 10 nm beam size [2]. Continuous advances are being made to improve resolution of EBL technique and the main inclination is also towards developing ultra-high resolution resists.

Poly methyl methacrylate (PMMA) is a simple, *positive* tone and still a dominant EBL resist. However, chiefly under special conditions PMMA is able to produce extremely high resolution structures. Sub 5 nm wide lines have been reported using PMMA with EBL voltages of 80–100 keV [3,4]. Suchlike resolution is however, unobtainable with lower voltages like 10–30 keV. Another positive tone resist that has gain popularity due to its superiority over PMMA in terms of sensitivity is ZEP resist. This resist is structurally similar to PMMA except the side group which is substituted with a chlorine atom and phenyl group [5]. In addition to a superior sensitivity and resolution, ZEP resist has been reported to have higher plasma etch durability for C_2F_6 and SF_6 gases [5]. ZEP lags behind PMMA because it is more expensive than PMMA.

In this work, a new EBL resist presented by EM Resist Ltd. (Macclesfield, UK), named SML, is studied. It is a positive tone organic resist that has been produced to have similar processing

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parameters to PMMA, but with enhanced performance. In the present study, contrast curves were obtained for different thicknesses of SML and developed at room temperature and 0 °C. The resist can be developed with all the developers used for PMMA. An initial study on the resist, however, has shown that the 7:3 IPA:water co-solvent developer provides a higher contrast to sensitivity ratio as compared to other positive resist developers [6]. Hence, the developer used in the current study is 7:3 IPA:water. Existing positive resists, ZEP 520A and PMMA, were chosen to compare the sensitivity, contrast, resolution, etch resistance and lift-off proficiency of SML. This works brings to the forefront the characterisation of SML resist and compares its quality to that of ZEP and PMMA resists for semiconductor fabrication.

2. Materials and methods

The SML resists of three concentrations i.e. SML 50, 100 and 300 used in this study were provided by EM Resist Ltd. The ZEP520A resist was purchased from Nippon ZEON Corp. and 950PMMA A7 from MicroChem Corp. Bulk silicon substrates of ⟨100⟩ orientation and sized 10 mm × 10 mm were used throughout the experiments.

Three SML resists were spun on the substrates with 4000 rpm for 60 s to give films of 50, 100 and 300 nm. The substrates were then soft-baked on a hot plate at 180 °C for 180 s prior to the exposure. PMMA substrates were processed in the same fashion. ZEP resist was also spun at 4000 rpm, but soft-baked at 120 °C. All the exposures within 10–30 kV voltage range were performed on Raith e-LiNE Plus and the 50 kV exposures on JEOL JBX 6000FS. The substrates with PMMA and SML resists were developed in a 7:3 IPA:water developer. ZEP was intentionally developed with its recommended ZED-N50 developer throughout the study, since attempts with 7:3 IPA:water lowered its sensitivity up to 10 times [6]. All developments were 15 s long, followed by a 15 s IPA rinse.

For generating the contrast curves, an array of 50 μm × 100 μm rectangles were exposed on the substrates with increments in dose by a factor of 0.07. Post exposure, the substrates were developed using their appropriate developers. For cold temperature developments, all the solvents were cooled in a freezer submerged in an ice-bath until the temperature obtained was 0 °C. The step height in the resist was measured using a DEKTAK Profilometer.

Gratings of single pixel lines spaced with pitch sizes of 30, 40, 60, 80, 100 and 200 nm were exposed on SML, ZEP and PMMA having a thickness of about 50 nm. The exposures were carried out at a 30 kV voltage, with a step size of 2 nm and a 10 μm aperture size. The substrates were imaged on Raith e-line Plus and FEI Helios NanoLab 600 at 10 kV and 5 kV, respectively. Prior to imaging all the substrates were coated with Au/Pd for suave imaging.

For the metal lift-off, 5 and 10 nm thick chromium layers were deposited on SML and ZEP resists having high resolution gratings using electron beam evaporation in a Temescal FC-2000 machine. The lift-off was performed by immersing the substrates in a Microposit 1165 remover (Shipley) for 5–10 min at 60 °C. The substrates were then washed under flowing deionised (DI) water and nitrogen dried prior to scanning electron microscope (SEM) imaging the substrates.

The etching tests were carried out using Plasmalab 100 ICP etching system (Oxford Instruments) with SF_6 and C_4F_8 gas mixture [7]. In order to determine the etch rates of SML, ZEP and PMMA resists, ~300 nm thick resists were spun on Si and etched for time intervals of 1, 3, 5 and 7 min and the film thicknesses were measured by an ellipsometer (M2000-Wollam). Identical aforementioned high resolution gratings written on 50 nm thick SML and ZEP resists were etched using the same recipe for 1 min.

The line edge roughness (LER) of the gratings with 30 nm pitch size on all the three resists was determined using ImageJ software (3σ value). Process latitudes were acquired by exposing single pixel lines with 60 nm pitch size on SML and ZEP resists within specific e-beam dose range and the linewidth was measures as a function of the dose.

3. Results and discussion

Table 1 illustrates the sensitivity and contrast values of the SML resist of three different thicknesses, 50, 100 and 300 nm exposed with 10, 15, 25, 30 (the highest voltage offered by the Raith system) and 50 kV voltages (the highest voltage offered by the JEOL system) at room and low temperature (SML50). The contrast (γ) values are calculated from the dose values by using the equation $\gamma = [\log_{10}(D_1/D_0)]^{-1}$, where D_0 and D_1 represent the dose values at which the resist thickness is full and zero, respectively [8]. The dose values expressed in Table 1 equal to the dose at which the irradiated resist completely developed (D_1). Considering the sensitivity-contrast values in Table 1 in ambient development, it can be interpreted that the contrast values of all the thicknesses appear in the range of 9–10, regardless of increase in voltage or thickness. Nevertheless, it is a common establishment that rise in voltage results in the reduction of sensitivity, a trend that can be seen in Table 1 as well. Generally, with higher voltages up to 100 kV, higher contrast and lower sensitivity can be expected. Surprisingly, the contrast values observed at 50 kV are slightly lower than those at the lower voltages. This could be due to the fact that these exposures were carried out on the JEOL EBL system as well as with different minimum increment in the exposure dose. This might have affected the steepness of the curve giving contrast values slightly different than the trend.

Cold development has previously shown resolution enhancement in other positive resists like PMMA and ZEP [8,9]. In order to better understand the influence of cold temperature on the development of SML resist, contrast curves were generated at voltages of 10, 15, 20 and 25 kV using the SML 50 resist that was developed at 0 °C with the 7:3 IPA:water developer. A comparison between the contrast curves of the resist developed at different temperatures can be seen in Fig. 1a. The values in Table 1 suggest a decrease in the sensitivity by 4 times from room temperature values and a moderate increase in the contrast (by approximately 1.6 times) due to the use of low temperature developers.

Next, the contrast curves of SML 300 were compared with those of the standard positive resists ZEP and PMMA having a similar thickness and exposed at the same voltage of 10 kV (Fig. 1b). It is observed from the contrast curves that ZEP resist shows the highest sensitivity (~22 μC/cm^2) amongst all the resists. The sensitivity of PMMA (~78 μC/cm^2), as expected, lags behind ZEP resist by a factor of ~2.2 while the sensitivity of SML (~107 μC/cm^2) resist developed in 7:3 IPA:water is almost 5 times lower than that of ZEP resist. The contrast values, on the other hand, show that the SML contrast equals to that of PMMA, i.e. ~12 and is higher than that of ZEP resist. From this data it can be established that SML

Table 1
Values of clearance dose D_1 (μC/cm^2) and their corresponding contrasts values (γ) of SML resist with 50, 100 and 300 nm thickness and SML 50 developed at 0 °C.

Voltage (kV)	SML 50		SML 100		SML 300		Cold development	
	D_1	γ	D_1	γ	D_1	γ	D_1	γ
10	63	9.2	72	7.0	102	10.4	280	7.7
15	84	9.0	108	9.0	143	9.8	369	9.2
20	103	9.0	129	10.4	194	8.2	397	11.3
25	111	8.8	156	8.9	218	7.0	563	14.8
50	398	8.6	378	6.7	480	7.9	–	–

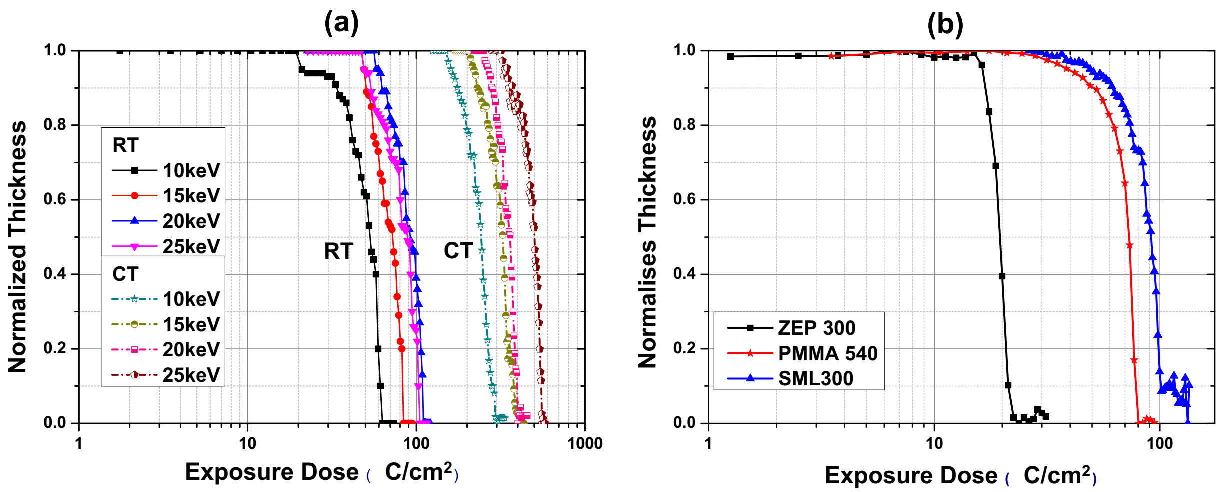

Fig. 1. Contrast curves of (a) SML 50 developed at cold temperature (0 °C) and at room temperature; (b) SML 300 compared to ZEP and PMMA resists of 300 nm thickness.

resist shows poorer sensitivity than the standard PMMA and ZEP resists. The contrast is, however, appreciably high.

In order to investigate the quality of the new resist, high resolution gratings were written on SML and ZEP resists of 50 nm film thickness. The patterned substrates were developed in their respective cold developers. Since the contrast curves values in Table 1 suggest greater contrast with high voltages and cold development, 30 kV voltage (the maximum voltage offered by the Raith e-Line Plus system) was preferred to write the high resolution gratings, together with development in cold developers.

Fig. 2 demonstrates SEM images of gratings written as single pixel lines with 30 nm pitch size in SML (Fig. 2a), ZEP (Fig. 2b) and PMMA (Fig. 2c) resists. Fig. 2d and e illustrate the micrographs of the ultrahigh resolution structures created in the SML and ZEP resists. As observed in Fig. 2a, 14–16 nm wide lines were readily written with a space of ~15 nm in SML. The arrays of lines were continuous, straight and neat throughout with very few dwellings where nano-bridging was observed. Moreover, resist clearance from the bottom of the trenches is visibly observed in Fig. 2a. Trivial widening of linewidths from 18 to 20 nm is seen in pitches greater than 30 nm. However, there was no bridging noticed in larger pitches and the gratings appeared more uniform, sharp, with clean trenches and unceasing lengths than that observed in 30 nm pitch gratings. Furthermore, it was observed that below the optimum dose the linewidth did not reduce but the resist residue remained in the trenches. Identical high resolution gratings

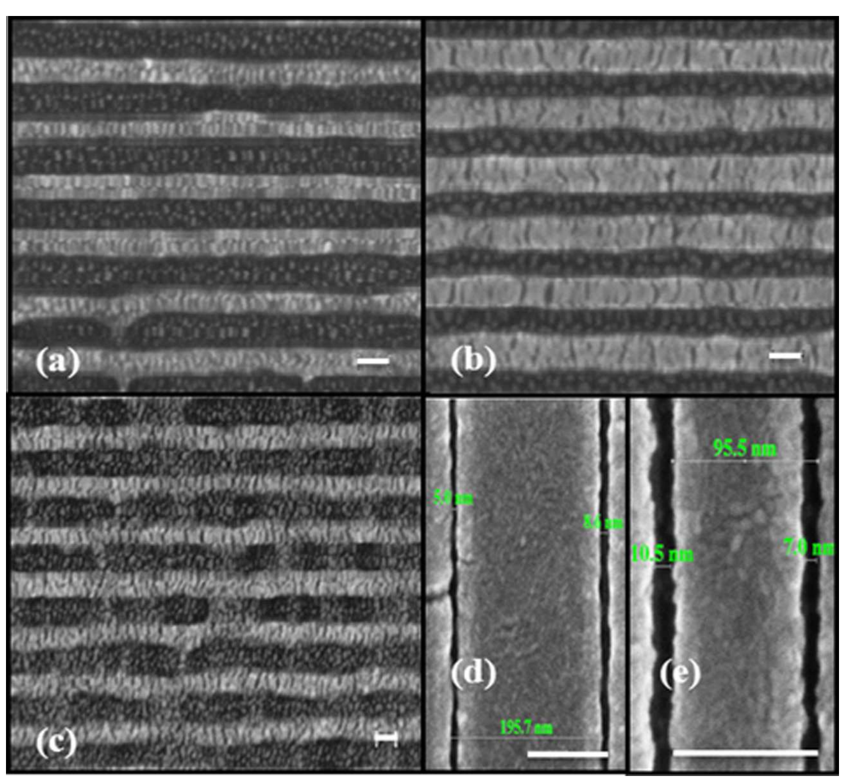

Fig. 2. High resolution gratings with 30 nm pitch size on (a) SML 50 developed in 7:3 IPA:water developer, (b) ZEP developed in ZED-N50 and (c) PMMA developed in 7:3 IPA:water (20 nm scale bar). Images (d) and (e) show the smallest linewidths achieved in SML 50 and ZEP, respectively (100 nm scale bar).

exposed on ZEP resist of similar thickness are presented in Fig. 2b. The linewidth observed throughout the gratings and in all the pitches is 15 nm on an average, without any widening or evident nano-bridging observed. Based on the Fig. 2a and b the quality of gratings in the two resists can be estimated as comparable. The line edge roughness, however, seems faintly higher in the ZEP resist. Thus, it can be established that dense and sub 20 nm lines are easily achievable with SML resist with the mild 7:3 IPA:water developer. Additionally, the line edge roughness is appreciably lower than in the standard ZEP resist. The next SEM image in Fig. 2c shows the same gratings exposed on PMMA with identical working conditions. Meagre quality of gratings is observed in this image with evidently high line edge roughness, poor resist clearance from the trenches and larger linewidths from 22 nm up to 30 nm at higher pitches (not shown). SML resist, thus, exhibits unrivalled gratings in comparison to PMMA.

Fig. 2d shows that 5 nm wide lines were obtained in SML and are the smallest lines reported to date with this resist. Sub 10 nm lines were also achieved in ZEP resist as seen in Fig. 2e. These results demonstrate that both resists are capable of very high resolution patterning.

In order to inspect the pattern transfer capabilities of the new resist, high resolution gratings on 50 nm thick SML and ZEP resists were subjected to basic etching and metal lift-off techniques. During the metal lift-off it was observed that from pitch size 80 nm and higher the metal was lifted off easily within 60 s in acetone at room temperature, whereas the results for smaller pitches were poor even after long time (>8 h) immersions in acetone as well as at an elevated temperature of 60 °C. Therefore, to completely clear off the resist from sub-80 nm pitches, the substrates were immersed overnight in the Microposit 1165 remover, which is known as a stronger solvent than acetone. Fig. 3a and b show the metal lines resolved from 5 nm thick chromium layer deposited on SML and ZEP resists, respectively. Dense lines (40 nm pitch) of ~15 nm linewidths were achieved in SML. Metal lines as small as 10 nm were obtained in ZEP resist, which is a very good achievement. The line quality improves slightly with increasing pitch size in the case of both resists.

In the case of etching, the etch rates of the three resists were compared with 300 nm thick layers and are demonstrated in Fig. 4. As seen from this figure, the amount of SML consumed initially is lower than that of ZEP and PMMA. However, as time progresses the SML consumption becomes higher than that of ZEP. It can also be observed that although ZEP resist has higher etch resistance than SML after 3 min, the difference between the etch rates in not large. In contrast, the difference in the etch rates at 1 min is quite notable, also suggesting that SML is a more suitable candidate for shallow etching. PMMA on the other hand shows the highest etch rates as compared to the other two resists at all intervals. This is in a good agreement with a number of previous works reporting poorer etch resistance of PMMA as compared to ZEP [5]. The different etch behaviour of the three resists is obviously determined by their different molecular structure. It has been suggested that ZEP demonstrates a lower etch rate than PMMA due to the phenyl ring in its structure which is not present in PMMA [10]. Unfortunately, the molecular structure of SML is not yet released by the vendor EM Resist Ltd. and its etch behaviour is difficult to comment at this stage.

The high resolution gratings were etched for 1 min using the same recipe with ZEP and SML. Fig. 3c and d illustrate the gratings having 60 nm pitch etched into silicon using SML and ZEP, respectively. The results with SML are slightly better than with ZEP resist,

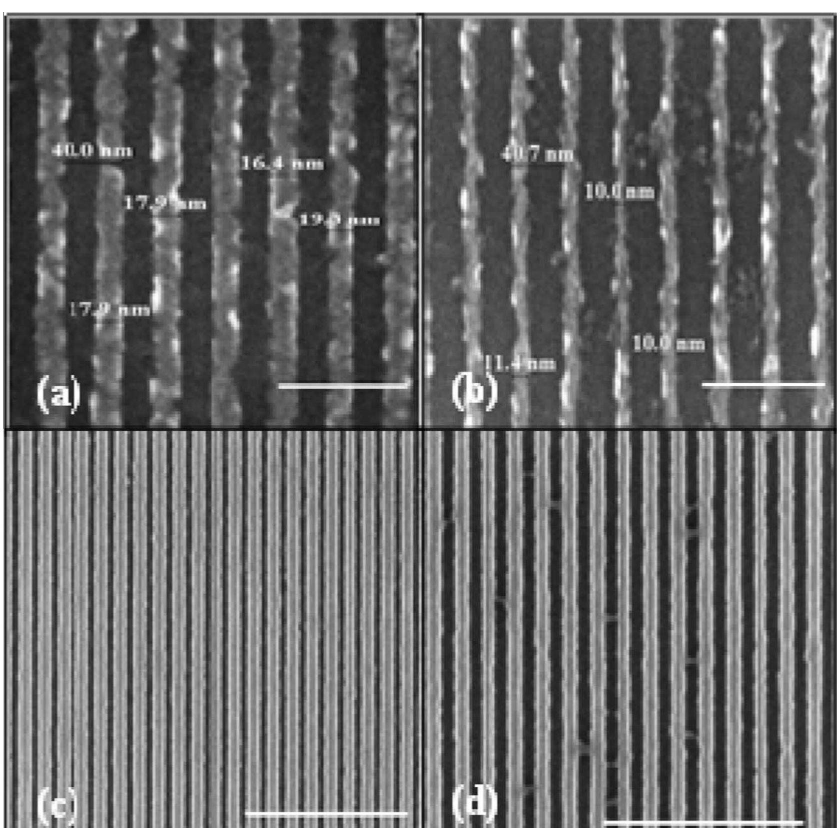

Fig. 3. 5 nm Thick chromium metal lines obtained by lift-off using Microposit 1196 for (a) SML 50 and (b) ZEP (100 nm scale bar). Gratings etched into Si via ICP etch for 1 min using (c) SML 50 and (d) ZEP resists as an etch mask (300 nm scale bar).

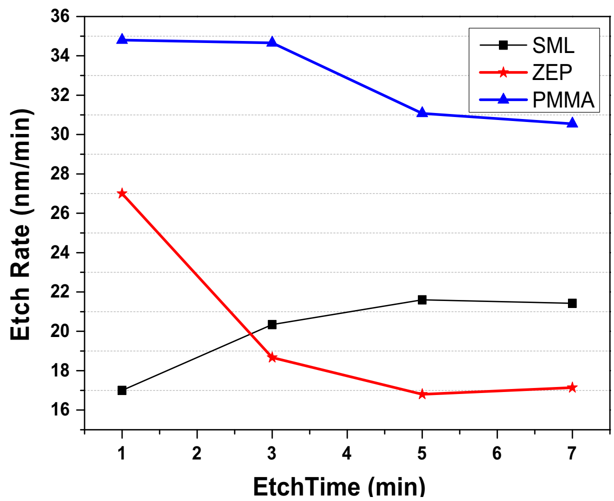

Fig. 4. Etch rates of the SML 300 (squares), ZEP (stars) and PMMA (rectangles) at time intervals of 1, 3, 5 and 7 min via ICP etch (SF_6 and C_4F_8 gas mixture).

which is usually acknowledged for its superior etch performance than most of the positive tone resists [5]. It can be seen from Fig. 3c and d that etching of dense gratings in Si is easily possible with both the resists. Nevertheless, in the case of ZEP eminent bridging between the trenches was observed throughout the gratings with 40 nm and larger pitches (not shown). This bridging effect was not evident in the case of SML. As the pitch size is increased, the quality of the etched lines enhances with both resists. However, widening of the Si trenches up to 20 nm occurred with ZEP when compared to the ~15 nm grating linewidth achieved in the resist. Moreover, bridging at few dwellings even in pitch sizes larger than 60 nm were present. These two effects were not observed in the case of SML. Therefore it can be concluded that pattern transfer via etching delivered better results with the SML resist than with ZEP.

LER calculations were done on images in Fig. 1a–c. It was found that the LER of the SML gratings is 0.245 nm whereas that for the ZEP gratings is 1.005 nm and for PMMA is 0.854 nm. Thus, the least LER of SML resist is an advantageous property over the other two resists.

The plot in Fig. 5 illustrates the dose windows for fabricating lines with 60 nm pitch size in SML and ZEP resists developed at 0 °C. It is apparent from this figure that although smaller linewidths are obtained with ZEP resist in ZED-N50 developer, the process window for SML resists with 7:3 IPA:water developer is slightly bigger than that for the ZEP resist. This means that SML offers the advantage of more relaxed requirements of maintaining the optimum exposure dose for obtaining a certain linewidth.

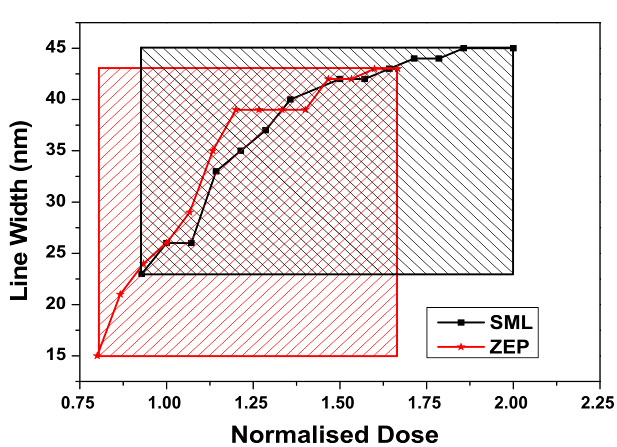

Fig. 5. Comparison of the dose windows for fabricating 60 nm pitch gratings with change in linewidth with respect to dose on SML (squares) and ZEP (circles) resists.

4. Conclusions

A detailed characterisation of SML resist was expressed in this work focusing on its sensitivity and contrast, resolution, pattern transfer abilities and process latitudes. It was established from the contrast studies that this resist bears a high contrast of about 12 with the 7:3 IPA:water developer. Additionally, comparison to ZEP and PMMA resists showed that SML's contrast equals to that of the other two but with the lowest sensitivity amongst three.

Single pixel gratings of pitches down to 30 nm exposed on SML showed outstanding quality lines with width of ~15 nm, suggesting its resolution equalling to that of the high resolution ZEP resist. Assessment of SML's etching and metal lift-off ability showed that SML is a good candidate for both the processes. Etch results showed that etching is more uniform with this resist since no feature widening and bridging was observed in contrast to ZEP. Using SML, dense (40 nm pitch) metal lines of ~15 nm linewidth are readily achievable with a basic lift-off technique. The larger process window and low LER values confirm that it is more commendable EBL patterning than ZEP and PMMA resists.

This preliminary study on SML can conclude that it is a proficient EBL resist. The resist properties are similar and in some aspects even better that those of the well-established resists ZEP and PMMA, which accounts for its superior quality as an EBL resist.

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